Final Report

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Abstract

The MARCEE Project was established to understand the problems associated with electronics recycling and to develop solutions that would allow an electronics recycling industry to emerge. While not all of the activities have been funded by MARCEE, but through private investment, they would not have occurred had the MARCEE Project not been undertaken. The problems tackled and the results obtained using MARCEE funds are discussed in detail in this report.

The most significant MARCEE accomplishments are described below:

Establishing a Recycling Industry in West Virginia

- PAZ has set up a Polymer Technology Park (PTP) on a 158 acre tract of land in Parkersburg, WV, that includes a 313,000 sq. ft. building. This building has been upgraded and forms the core of the electronics recycling project. This building is now filled and new space is being sought for expansion. A second building is now being planned.
- Amandi Services was recruited as the lead organization to establish a profitable and self-sustaining EOLE recycling industry in West Virginia. This company had experience in demanufacturing electronic products and in the recycling of glass and metal. Until the fall of 2007, they were operating successfully, demanufacturing 400K pounds/month of EoLE at the PTP. They were then acquired by another large recycling company who decided to consolidate their activities in New York State and pulled out of WV. PAZ is looking for another EOLE recycler to invest in WV.
- In 2006, NCER took the lead in organizing electronic product collection events around West Virginia for households and small businesses. Eight events were held which collected 250K pounds of product for recycling by Amandi Services. Similar events are planned for 2007.
- One of the barriers to building a recycling industry in WV has been the lack of a regular infrastructure for electronic waste collection in the state. This will change in the near future since the WV legislature passed (SB746), and the Governor signed the bill into law in April 2008. This initiative will establish a statewide recycling program. The WV bill harmonizes with the requirements in place for manufacturers in Maryland, which is expected to lead to an enhanced electronics recycling activity in WV.
- SDR Technologies has worked with IMTS to build an IT platform and tools for marketing EoLE plastics. This internet marketing tool is currently being used today and is known as *Polymer Shop*.

Finding Solutions to Outstanding Technical Problems

- SDR Technologies, with assistance from *Gaiker*, has been designing a process that will be able to identify and sort the numerous plastics from EoLE. Studies have indicated that combining new optical and x-ray identification techniques into a production line will allow recycled plastics to be obtained with purity levels >95%. The identification and sorting demonstration undertaken by SDR Technologies has shown that it is possible to

meet the purity target levels. This has the potential to open a market for recycled engineering plastics that doesn't presently exist.

- WVU faculty members have made reinforced composite materials from EOL plastics which have been made into a variety of construction materials. For instance, the West Virginia Highway Department has expressed interest in using these products, provided we can commercialize them.
- The Extrusion-Compounding Center at WVU has shown that the plastics from EoLE can be reused in wood-polymer composites for the construction industry. This work has been carried out with Star Plastics of West Virginia. A partner is being sought to explore commercialization of this R&D.

Developing an Infrastructure for an Electronics Recycling Industry

- Numerous research projects have been initiated to enhance the national infrastructure for electronics recycling. In order to make a viable, long-term recycling industry in West Virginia, there needs to be a consistent supply of EoLE material to process. The NCER has taken on this challenge through targeted research and pilot collection programs across the country. In an important initiative, NCER tracks the amounts of EoLE that is collected across the US, as well as brand information about these products. This data is available on the NCER website which is used as a resource by Federal and State Agencies. This website has become a clearinghouse for electronics recycling information in the US.
- In November 2005, WVU held an international Electronics Recycling Conference (RECCON'05) in Morgantown. The conference hosted many well known speakers; it was well attended and generated considerable publicity. Because of its influence, MARCEE has become a well known "brand" in the EoLE recycling world.

Educational Impact

- MARCEE is an R&D, planning and implementation group; consequently, it mainly employs professional personnel. These organizations employ 16.5 people directly involved in EoLE recycling research activities. It has also supported the education of 3 Ph.D. and 4 M.S. students.
- WVU has a Polymer Research which is operational. Six projects were funded under MARCEE and these are described in this report.

Table of Contents

1.0	Introduction.....	1
A.	Project Objectives	1
B.	Scope of the Project.....	2
C.	Project Highlights.....	3
2.0	Task-by-Task Breakdown of Activities	8
Task 1.1:	Development of wood-polymer composites as a means of recycling plastics from EOLE (Rakesh Gupta/WVU)	9
Task 2.1:	Natural Fiber/plastic composites research and development.....	9
2.1	Recycling Polymers from End-of-Life Electronics into Wood-Polymer Composite Materials	10
Task 1.2:	Selection of constituents and manufacturing methods for reinforced composite polymer products from recycled EOLE plastics (Hota GangaRao/WVU)	31
Task 2.2:	Manufacture of reinforced composite polymer shapes with fiber/fabrics using conventional and hybrid processing technologies	31
Task 2.2	Manufacturing and Durability Evaluation of Structural Composites with Recycled Polymers	32
Task 1.3:	Process closed loop and open loop EOLE plastics to develop high level technology designs plastics recycling train	88
Task 2.3	Demonstration of Recycling Technologies and High Level Design.....	89
MARCEE	Plastics Demonstration (PI/D. Ritchie)	89
Task 1.4:	Develop Information Technology (IT) tools, methodologies and standards for MARCEE Information Technology Platform.....	101
MARCEE	Information Technology Support (PI/J. Tucker).....	101
Task 1.5	Set goals and develop a business plan/strategy for the NCEER	109
1.5	The Role of the National Center for Electronics Recycling in the E-Waste Industry (PI/J. Linnell).....	110
Task 1.6:	WVU Polymer Research Center (Mel Croucher/WVU).....	127
Development	of a Polymer Research Center at WVU (PI/M. Croucher).....	127
3.0	New Research Activities Sponsored by the WVU Polymer Research Center	149
Polymer	Nanocomposites for CO ₂ Capture (PI/R.Gupta)	150
Polymer	Films and Thin-laminates for Renewable Energy and 'Green' Infrastructure (PI/D. Cairns).....	159
New	Functional Polymers based on Triazoles (PI/X. Shi)	171
Using	Hybrid Poplar for More Efficient Biofuels and Bio-Nanocomposites Production (PI/J. Wang).....	181
List	of Figures and Reaction Schemes	200
List	of Tables	205

1.0 Introduction

Every year it is estimated that more than 1.5B lbs of waste from end-of-life electronic devices are disposed of in the U.S. each year. Much of this obsolete equipment is stored by consumers and organizations, but a significant amount of it finds its way into landfills either in this country or overseas. It is estimated that only about 10% of e-waste is recycled and it comprises between 2-4% of municipal solid waste. However, the e-waste stream is growing three times faster than conventional waste streams in landfill sites.

In an effort to solve this problem, the MARCEE Project was formed in 1999 at the request of Representative Alan Mollohan, who had an awareness and interest in this subject. A consortium of research and business groups was assembled, which included West Virginia University (WVU) and the Polymer Alliance Zone (PAZ) of West Virginia. In Phase I of this project numerous other organizations were also involved. However, as the project has matured and tasks have been completed, new organizations were recruited or formed to continue development of the project and to meet its goals. The companies recruited for Phase II included SDR Technologies (Millwood, WV), who have undertaken the plastics recycling project, MBDC (Charlottesville, VA), who undertook tasks related to flame retardants in plastics and Gaiker (Zamudio, Spain) who undertook to understand the plastics identification and sorting task as well as estimating the economic value of “pure” recycled plastics. MARCEE also initiated the National Center for Electronics Recycling (NCER) which was set up as a not-for-profit 501(c) with the mandate to help build an electronics recycling infrastructure in both WV and the nation.

At the start of Phase II of this project in 2005 the budget outlined was approximately \$8.3M. However, this funding was cut back due to budgetary constraints to \$6.3M. Consequently, the scope of the project was reduced as requested by the Department of Energy. The research area that has been most affected by the budget changes has been the plastics recycling demonstration that has been carried out by SDR Technologies and establishing a Polymer Research Center at WVU.. At the urging of the Department of Energy, the project goals were revised to address the changes to the budget.

A. Project Objectives

The project objective is to have a viable end-of-life-electronics (EOLE) industry in Wood County, WV through

- Develop high-value uses for recycled polymers
- Demonstrate proof-of-concept recycling of plastics from EOLE
- Establish a coordinating entity and research center to promote technology transfer and research in recycling of EOLE
- Create new economic development opportunities in the recycling and polymer industries
- Develop an industry standard Information Technology platform for recycling activities, products, services and data
- Demonstrate the successful application of technology, supply chain and logistics solutions for recycling plastics from EOLE

B. Scope of the Project

The scope of this work includes a comprehensive Four-phase evaluation and development program for the management of recycled plastics and other materials derived from end-of-life electronics.

In the first phase, the Recipient shall:

- Evaluate applications for EOLE recycled plastics, including wood-polymer composites and the evaluation of additives that improve performance of EOLE polymer composites
- Select constituents and manufacturing methods for reinforced composite polymer products using plastics from EOLE
- Perform a proof-of-concept demonstration for recycling plastics from electronics back into new electronic products utilizing separation and recycling technologies developed by this project and elsewhere around the country
- Proof-of-concept demonstration of both closed loop and open loop EOLE plastics recycling will be performed, and the demonstration integrated with selected electronics recycling pilots administered around the country
- High level designs will be initiated for plastics recycling lines
- Outreach and educational services will be performed to promote EOLE recycling
- IT tools, methodologies and standards will be developed that enhance and enable electronic information services , data services, and market services to help position the MARCEE IT platform as a primary industry support tool
- The National Center for Electronics Recycling (NCER) will be initiated with leading US manufacturers of consumer electronic products to coordinate and facilitate efforts in EOLE recycling
- The WVU Polymer Research Center will be established to coordinate polymer research activities within the university and with polymer industries to further applications development for EOLE plastics

In the second phase, the Recipient shall:

- Further research in the area of wood-polymer composites
- Coordinate the on-going demonstration of recycling plastics from electronics on the commercial scale
- Manufacture reinforced composite polymer shapes with fiber/fabrics
- Continue to design and build plastic composite artifacts and EOLE recycling line demonstration
- Continue integration of IT tools
- Continue development of the NCER
- Continue development of the WVU Polymer Research Center

During the third phase, the Recipient shall:

- Expand research conducted during the first two phases through extrusion of wood-polymer composites I
- Improve on the manufacturing of the prototypes developed in Phase II
- Proof-of-concept demonstration of various scenarios of feedstock plastics to identify optimal recycling process parameters
- Continue integration of IT tools with the US
- Institutionalize the NCER
- Institutionalize the WVU Polymer Research Center

During the fourth phase, the Recipient shall:

- Expand research conducted during the first three phases through accelerated aging of wood-polymer composites and field testing of the prototypes developed in Phases II and III
- Continue to identify barriers to EOLE plastics recycling and how to overcome them
- Based on work in Phases I, II and III operate a fully sustainable industrial information exchange for the electronics recycling industry
- Finalize the activities and operation of the NCER
- WVU Polymer Research Center becomes operational

It should be recognized that the funding received for this project was significantly less than had been budgeted for given the plan that was submitted to the EPA/DOE. The scope of the project had to be changed and phase three and phase four of the plan were not carried out for most tasks.

C. Project Highlights

In 1999 West Virginia University (WVU) was asked by the Department of Energy to manage a Cooperative Agreement on electronics recycling research. Congressman Alan Mollohan (D-West Virginia) had taken an interest in the issue of electronic waste and saw an opportunity to support the development of an industry in West Virginia (WV) that would certainly grow in coming years. At that time this problem was not well understood and attracted little attention from the environmental movement or from government. In an effort to get started on understanding this problem, a consortium was formed which was called the Mid-Atlantic Research Center for End-of-Life Electronics, better known as MARCEE.

During the start-up phase of MARCEE, the Polymer Alliance Zone (PAZ) of West Virginia became involved as a consortium member to assess the scope of the electronic waste problem and to outline a research and development plan with stakeholder input. The main tenets of the plan were:

1. Develop an organization that would be involved in policy, logistics and in collecting and disseminating information about electronic waste.
2. Understand how to recycle and reuse the plastics from end-of-life electronic products.

3. Develop a strategic plan to build an electronics recycling industry for the Mid-Atlantic States which would be based in West Virginia.

All of these issues have been tackled over the past decade. The research carried out between 1999 and 2005 was documented in a report written for the Department of Energy in February 2006. The research undertaken from 2005 to 2008 is described in this report.

1. Policy, Logistics and E-Waste Information

While MARCEE has been involved in these tasks from the beginning, the National Center for Electronics Recycling (NCER) was formed in 2005 to formalize this activity. It was recognized that the internet would play an important role; consequently, IMTS (Fairmont, WV), a technology service provider, was recruited as a partner for this initiative. The NCER was initially built around three themes; information exchange, data collection and electronic commerce.

Information Exchange: A web portal www.electronicsrecycling.org was registered and created. The initial focus was the development of a centralized industry resource that could be used for sharing information related to electronics recycling. This web portal has grown to become one of the most recognized web resources on the Internet for electronics recycling information. Today the website is the portal for the National Center of Electronics Recycling and maintains a wealth of information about electronics recycling. It currently receives traffic worldwide and has become a valued industry resource.

Data Collection: The creation of an information technology infrastructure has agencies such as Environmental Protection Agency looking to MARCEE to help provide assistance in the creation of a standardized set of electronics recycling data elements and the corresponding data collection activities. This has lead to the creation of three new databases (1) the Centralized Data Repository (CDR) which holds up-to-date information on the collection and recycling of electronic waste from twenty-six states. (2) a Brand Data Management System (BDMS). The goal of the BDMS is to allow stakeholders the opportunity to view and customize brand return share reports from across the country. Implementation of electronics recycling laws in Maine and Washington have utilized these and similar data to determine manufacturer recycling obligations in those states. (3) The National Electronics Recycling Infrastructure Clearinghouse (NERIC) was started in 2006 in conjunction with the Consumer Electronics Association (CEA) and provides information on a variety of recycling systems-level issues of interest to stakeholders who are part of the recycling value chain. It is hoped that this will help ensure development of logical and efficient electronics recycling systems.

Electronic Commerce: MARCEE recognized the importance of green procurement and therefore participated in the development of the Electronic Product Environmental Assessment Tool (EPEAT). With MARCEE support, the first prototype of the online product registry and database system was developed. Today, EPEAT is a rapidly expanding system to help purchasers in the public and private sectors evaluate, compare and select desktop computers, notebooks and monitors based on their environmental attributes.

In order to showcase how e-commerce could be used within the field of electronics recycling, a prototype marketplace was developed for materials. PAZ has utilized this technology to develop the Polymer Virtual Center of Excellence, which is used to help market WV to prospective companies worldwide. Star Plastics (Millwood, WV) has developed an online component called The Polymer Shop which allows them to market materials via the internet and develop and expand markets for recycled materials.

2. Recycle and Reuse of End-of-Life Plastics from Electronic Products

Since the formation of MARCEE, a collection and recycling industry has started to evolve, with the separation of glass and metals becoming economically viable. However, the separation and reuse of plastics has not occurred. These materials are either placed in landfill sites or sold to overseas vendors for marginal value. Neither of these approaches are sustainable, consequently, alternative methods of disposing, or of recycling plastics, still need to be developed. Early in its existence, MARCEE identified this as a major problem, and both WVU faculty and SDR Technologies agreed to tackle different aspects of this task.

Identification and Separation of Commingled Plastics: Numerous companies have attempted to identify and separate the numerous plastics in electronic waste. However, these attempts to develop a high volume, continuous processing line have met with limited success. SDR Technologies (Millwood, WV) joined the MARCEE project in 2003 and has been assessing the use of both dry and wet sorting techniques in an effort to develop an economically viable separation process. The processes they have investigated include sink-float, hydrocyclone, electrostatic, near infrared (NIR) identification, various metal removal processes, x-ray and aspiration systems. During the past year, SDRT has been able to dramatically improve the effectiveness of these techniques. However, for the plastics recycling industry to flourish, additional processes such as size reduction, special material handling and decontamination/cleaning need to be demonstrated in conjunction with the identification and sorting steps at acceptable throughput rates. Collecting meaningful data on all of these issues has allowed SDR Technologies to gain valuable insights into the economics of plastics identification and purification. These results are described in detail in the body of the report.

Potential Uses for Recycled Plastics: Researchers at WVU and SDRT have been working to find applications for “pure” recycled plastics. One of the most promising applications for these materials is in wood-polymer composites (WPC’s).

In almost all discussions about WPCs it is outdoor applications that are discussed. By comparison, few studies have been directed towards indoor applications which are where the WVU team has concentrated its effort. The present generation of WPC’s has significant problems. In particular, the flexural modulus, or stiffness of current materials is significantly less than that of wood. Consequently, WPC-constructed structures tend to flex excessively. In order to improve the flexural modulus it is essential to start with a relatively stiff plastic. Preliminary work had shown that using recycled ABS, whose modulus is about twice that of polypropylene, it is possible to obtain a 35 to 50% enhancement in the stiffness as compared to a polypropylene based WPC at an equivalent wood content. Consequently, enabling the use of ABS in WPC’s

could noticeably expand the market to semi-structural applications. These applications are not possible with polyolefin based WPC's.

WVU researchers have also been developing fiber reinforced plastics (FRP's), using both pre-sorted and commingled polymers with reinforcing matted materials. The applications include highway guardrail blocks and dowel bars, signboards and signposts and more recently window frames and door frames. This research has centered on developing an understanding of the materials, and the process necessary to manufacture these composites. Developing a knowledge of what type of reinforcing agent is required, whether or not it needs to be sized (to improve adhesion to the polymer matrix) and what process conditions yield a composite with the desired properties has been the objective of these activities. While this research is applications specific, it has yielded results that have wide applicability for composite materials development. This research has been enhanced by the application of numerical modeling, which allows for rapid prototyping of a new application, thereby significantly reducing the product development timeline.

3. Development of a Recycling Industry in West Virginia

In 2000 a study was carried out by the WVU College of Business and Economics, PAZ and SAIC to address the feasibility of developing a recycling industry for electronic waste in West Virginia. These authors gathered data on variables such as:

- the supply of electronic waste for recycling
- logistics and transportation issues in obtaining electronic waste
- a proposed demanufacturing facility
- financial assessment of the proposed facility
- break-even scenarios for a proposed recycling industry

From their studies the group determined that identifying a supply stream of electronic waste for a recycling center is a critical issue as are transportation costs. The study also completed a feasibility analysis of demanufacturing and separation processes for an electronic waste recycling business. Numerous breakeven scenarios representing various economic conditions were analyzed. The study concluded that there was the potential for a successful recycling industry in West Virginia.

In 2001 PAZ engaged SAIC to write a business plan for MARCEE together with a comprehensive economic model for electronics recycling. The Business Plan was finalized in 2002 and has been periodically updated. The plan envisaged a coalition of key industry participants being formed to develop industry efficiencies, an industry environmental ethic, and the economic stimulus to make large-scale e-waste recycling viable. This plan was viewed as ambitious, but modeling studies indicated that this was the most attractive option.

In anticipating the building of a recycling industry PAZ set up a Polymer Technology Park (PTP) on a 156 acre tract of land in Parkersburg, WV, that includes a 313,000 sq. ft. building. This building has been upgraded and forms the core of the electronics recycling project. This building was acquired using private funding and is now fully occupied. A second building is now being designed in anticipation that future recycling facilities will be needed.

One of the barriers to building a regional facility has been the lack of a regular infrastructure for electronic waste collection in the state. This is expected to change in the near future since the WV legislature passed, and the Governor signed a bill into law in April 2008, that will establish a statewide recycling program. The WV bill harmonizes with the requirements in place for manufacturers in Maryland, which is expected to lead to an enhanced electronics recycling activity in WV.

2.0 Task-by-Task Breakdown of Activities

The research carried out under this contract was split into four phases, each phase corresponding to a specific budget period. Six tasks were outlined under each phase. The tasks specified under each phase were not discrete tasks but a continuation of the task outlined in detail in Phase I/Budget Period I. Only Phases I and II are described in detail in the Statement of Project Objectives (SOPO). Phases III and IV remained undefined since reduced funding reduced the scope of the research activities that were carried out. The National Energy Technology Laboratory (NETL) of the Department of Energy fully funded the Phase I/Budget Period I activities. However, the funding for Budget Periods II and III were aggregated into Budget Period II by the NETL. Funding for Budget Period IV/Phase IV studies were not received because of a suspension on the funding of Congressional Appropriations.

The topics outlined in the SOPO for each Budget Period/Phase are outlined below:

Phase I/Budget Period 1 – Polymer composite research, proof-of-concept demonstration of plastics recycling; web-based trading platform development, coordinating entity and research center initiation.

Phase II/Budget Period II- Polymer Composite R&D; EOLE recycling proof-of-concept demonstration; integration of Information Technology tools; development of coordinating entity and research center.

Phase III/Budget Period III- Polymer Composite Manufacturing Development, proof-of-concept demonstration of various feedstock plastics; continue integration of IT tools; develop coordinating entity and research center.

Phase IV/Budget Period IV- Accelerated aging and field testing of EOLE plastic composites, proof-of-concept demonstration of varied feedstock plastics; finalize IT tools; finalize the activities of and fully operate the coordinating entity and research center.

Each task for Budget Periods I-III is discussed next. A detailed description of each of the tasks is outlined as is the response by the Principal Investigator for each task.

Task 1.1: Development of wood-polymer composites as a means of recycling plastics from EOLE (Rakesh Gupta/WVU)

The Recipient shall investigate the use of plastics from EOLE to develop wood polymer composite (WPC) materials. The use of appropriate additives will be studied in order to improve composite physical properties, as well as improve manufacturing ability. Additives to be studied include, but are not limited to coupling agents, lubricants, ultraviolet stabilizers, antimicrobial compounds, foaming agents, and inorganic fillers.

The research will be divided into formulation or materials development, extrusion or processing of the chosen formulations, characterization of the structure of the manufactured shapes or extrudates, measurement of the mechanical and other properties of the products, and optimization of the entire process with respect to cost or properties of interest.

Industrial partners will participate technically in the development of WPC materials. Industrial partners will also be identified, and will participate in the research through an Industrial Advisory Board.

A structured investigation will be implemented into the fundamental causes for current poor coupling agent (CA) performance. Better understanding of the interaction of CAs with other components at the fiber-matrix interface will be used to guide research into improved fiber-matrix bonding. Parameters to be studied include additives, mixing torque, the order of additive blending, and process temperature. The goal of this task is to increase the strength of WPC materials by 60 to 70%.

The use of nanofillers in recycled plastics will be investigated in order to increase composite stiffness. Between 2 to 5 wt% of montmorillonite clay will be added to the WPC during processing with the goal of producing a nanocomposite material. Thermogravimetric analysis and scanning and transmission electronic microscopy will be used to examine the extent of clay dispersion.

Task 2.1: Natural Fiber/plastic composites research and development

The Recipient shall continue to investigate the use of plastics for Wood/Polymer Composite materials and continue commercial development activities. The goal of this task is to increase the strength of WPC materials by 60-70%.

Once the WPC parameters have been optimized, prototype WPC products for the construction industry, such as indoor trim, shall be produced and tested.

Tasks 3.1 and 4.1 were not defined for the SOPO since the funding level was reduced and the scope of the project curtailed.

2.1 Recycling Polymers from End-of-Life Electronics into Wood-Polymer Composite Materials

Abstract

Most efforts aimed at recycling post-consumer plastics into high-value applications involve separating polymers by chemical type since the collection process necessarily results in commingled plastics, and mixed plastics have poor mechanical properties. Indeed, we have shown in the past that when the impurities present in the plastic are either immiscible with it or require higher temperatures for processing, more than 99% purity is needed to prevent a very significant loss in impact strength and ductility; satisfying this extremely stringent requirement is prohibitively expensive, and alternative approaches were explored. Here, we demonstrate that reinforcing recovered ABS (acrylonitrile-butadiene-styrene) with wood particulates is a viable method of reusing ABS from end-of-life electronics. When ABS obtained from computer monitors and keyboards was extrusion compounded with an equal amount of wood flour and appropriate additives, the measured mechanical properties of the resulting wood-plastic composites (WPCs) were only slightly different from the corresponding properties of virgin ABS containing the same amount of wood reinforcement. Thus, the added reinforcement is able to properly mask the composition-dependent variation of mechanical properties of the base polymer. Having settled on this basic approach to polymer recycling, systematic studies were carried out to identify processing conditions and parameters to design successful extrusion and injection molding operations to produce ABS-based WPCs.

Various additives such as coupling agents and impact modifiers were identified to improve the mechanical properties of these WPCs and to reduce their water absorption.

Non-halogenated flame retardants, in conjunction with wood flour, were used to successfully make *eco-friendly flame retardant WPCs* which should enable the use of these ABS-WPCs in indoor applications.

Both halogenated and non-halogenated flame retardants were used to obtain desirable flame-retardant properties while maintaining mechanical properties.

ABS-based WPCs were foamed using a solid-state foaming method with the help of carbon dioxide. A significant reduction in density can be achieved by this method, and the final product is comparable to solid wood in many respects.

The rest of this report describes the above accomplishments in greater detail. Note that ABS-based WPCs are already available in the building products market, and the research done as part of this project will make it likely that these products will be made using recycled ABS in the future.

A. Wood Plastic Composites made with Virgin as well as Recycled ABS

Accomplishments and Main Conclusions

- It is feasible to use recycled ABS resins obtained from end-of-life electronics as the matrix material for wood plastic composites. ABS-based WPCs are much stronger than most present-day polyolefin-based WPCs products.
- In terms of mechanical properties, the modulus of ABS-based WPCs is about 33% higher than that of polypropylene (PP)-based WPCs at 50wt% wood content. Even without using an expensive coupling agent, the strength of ABS-WPCs is higher than that of PP-based WPCs and employing a coupling agent.
- Two different coupling agents, SMA (styrene maleic anhydride) and SEBS-g-MA (styrene-ethylene-butylene-styrene grafted maleic anhydride), were employed in this study. It was found that SMA works as an effective coupling agent for ABS-based wood plastic composites. The tensile, flexural and impact strength of ABS-based WPCs was found to increase in the presence of SMA. However, as expected, the addition of SMA did not affect the modulus of the WPCs.
- The reversed Izod impact strength of 50wt% wood/ABS WPCs is less than 80 J/m. This is because the impact strength of ABS decreases in the presence of wood flour. In the future, it may be necessary to develop a new coupling agent in to improve this property.
- The rate of water absorption of ABS-based WPCs was found to decrease by 12% in the presence of 2wt% SMA which was used as a coupling agent. A low value of moisture absorption is desirable to prevent structure breakdown as a result of freeze-thaw cycling.

Experimental Details and Key Results

Materials Used

Maple wood flour of 80-mesh size (about 177 μm) was provided by American Wood Fiber (Maple 8010). Two different ABS resins were used in the experiments, the first one was GE Cycolac MG-94 (MFI = 11.7g/10 min at 230°C / 3.8kg) while the second one was recycled ABS from end of life electronics provided by SDR plastics (MFI = 3.2g/10min at 230°C / 3.8kg). The mechanical properties of virgin and recycled ABS polymers are listed in Table 1.

Table 1: Mechanical properties of virgin and recycled ABS. Numbers in the parenthesis are standard deviation (* Partial break, ** Complete break).

	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at Break (%)	Flexural Modulus (GPa)	Flex Strength at Yield (MPa)	Notched Impact Strength (J/m)
Virgin	38.50 (0.17)	2.54 (0.05)	52.14 (14.52)	2.3 (0.07)	65.75 (0.15)	215.58 (5.84)*
Recycled	34.43 (0.13)	2.20 (0.15)	3.02 (0.3)	1.90 (0.04)	58.07 (0.25)	87.82 (2.96)**

As it can be seen from Table 1, the elongation at break and notched Izod impact strength of recycled ABS are much lower than that of virgin ABS. This is because recycled ABS usually contains impurities. These impurities act as stress concentrators and decrease both ductility and impact strength tremendously.

Styrene maleic anhydride, SMA 3000F was provided by Sartomer (number average molecular weight $M_n = 3800$, KOH/gm = 480). A lubricant package, TPW 113, obtained from Struktol, was used to reduce melt fracture of WPCs during compounding.

Sample Preparation

Wood plastic composites having different weight percentages of wood flour were prepared using a twin-screw extruder. The wood flour was dried at 100°C for 7 hours to ensure that the moisture content was less than 1wt%. In the extruder, the processing temperature of WPCs was kept between 165 to 180°C from the hopper to barrel 6. To prevent severe melt fracture, the temperatures of last three barrels were set at 200°C, while the die temperature was set at 220°C. The screw speed was set at 200 rpm, and the feeding rate was 7 kg/hr. The extruded strands were pelletized, dried and injection molded into ASTM test specimens. The tensile, flexural and impact strength and stiffness properties of these samples were measured using an Instron 5569 universal testing machine and a BLI impact tester. The tensile and flexural tests refer to ASTM D638 and D790 respectively, while the impact test refers to ASTM D256. Because WPCs generally showed relatively low impact strength in the standard Izod impact tests, the reversed notch impact test method was applied. All of the mechanical tests were conducted until the standard deviation was less than 15% of the average, except for the elongation at break. In each case, at least five samples were tested. The density of injection molded samples was determined by a Micromeritics AccuPyc 1330 helium pycnometer. The fracture surfaces of the WPCs obtained from tension tests were examined with a Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM).

Finally, the rate of water absorption of the WPCs was determined using a “blot and weigh” method. Three weighed samples were taken from each batch of WPCs to conduct this test. The typical injection-molded sample of 12.5mm x 64mm x 3.175mm was soaked in a sealed container full of distilled water, and it was periodically removed and weighed. The results of the water absorption tests were represented as the percentage of weight gained versus time of immersion.

Melt Fracture

Melt fracture is an instability that usually happens when the stress in the polymer exceed a critical value during extrusion. In our study, when the wood flour content exceeded 40wt%, melt fracture was observed. The presence of melt fracture strongly affects the appearance of the extrudate, and it makes the process of palletization difficult. Therefore, it is important to reduce the melt fracture phenomenon during extrusion.

The following methods were used to reduce the shear stress in the die land region:

- Increasing the die land temperature
- Opening up the die and land region (increasing the die gap)
- Reducing the extrusion rate
- Using a process aid (external lubricant)
- Increasing the melt temperature
- Reducing the polymer melt viscosity
- Using more shear-thinning plastic

A series of trial runs were conducted based on above methods. ABS-based wood plastic composites containing 50wt% wood were processed using a twin screw extruder. The different compositions are listed in Table 2, while the processing conditions are given in Table 3.

Table 2: Composition of ABS/wood flour composites in terms of polymer (percentage by weight), coupling agents and lubricants.

Resin	Polymer Content	Wood Content	Lubricant to matrix	SMA to wood	SEBS-g-MA to wood
Virgin	90	10			
Virgin	80	20			
Virgin	70	30			
Virgin	60	40			
Virgin	47.5	50	5		
Virgin	46.5	50	5	2	
Virgin	45.5	50	5	4	
Virgin	42.5	50	5	10	
Virgin	46.5	50	5		2
Virgin	45.5	50	5		4
Virgin	42.5	50	5		10
Recycled	47.5	50	5		
Recycled	42.5	50	5	10	

Table 3 Processing conditions of 50wt% wood-ABS wood plastic composites.

Trial	1	2	3	4	5	6	7
Feed Rate (kg/hr)	4	4	4	4	4	7	7
Screw Speed (RPM)	150	150	150	150	200	200	200
Torque (%)	78	77	77	75	63	60	62
Die Pressure (psi)	1210	1300	1080	1000	800	1300	1160
Barrel Temperature							
Barrel 1	165	165	165	165	165	165	165
Barrel 2	170	170	170	170	170	170	170
Barrel 3	175	175	175	175	175	175	175
Barrel 4	180	180	180	180	180	180	180
Barrel 5	180	180	180	180	180	180	180
Barrel 6	180	180	180	180	180	180	180
Barrel 7	180	200	200	200	200	200	200
Barrel 8	180	180	200	200	200	200	200
Barrel 9	200	180	200	200	200	200	200
Die	200	200	200	220	220	200	220
Lubricant	No	No	No	No	No	Yes	Yes
Melt Fracture	Yes	Yes	Yes	Yes	Yes	Yes	No

The loading level of lubricant was fixed at either 5wt% or 0wt% of ABS. The temperature of the extruder was kept as constant from barrel 1 to 6, while the temperature from barrel 7 to the die was changed in the different runs. Seven different trials were conducted with a view to determining conditions that reduce melt fracture. From trial 1 to 4, the rotor speed and the total feeding rate were controlled at 150 rpm and 4kg/hr respectively. In the 1st trial, the temperature of barrel 9 and the die was elevated to 200°C while that of barrel 7 and 8 was kept at 180°C to reduce the viscosity of the polymer in the die land region. In the 2nd trial, the temperature of barrel 7 and the die was controlled at 200°C while that of barrels 8 and 9 was fixed at 180°C for better venting. In the 3rd trial, the temperature from barrel 7 to die was all elevated to 200°C to further reduce the viscosity of polymer melts. In the 4th trial, the temperature of the die region was elevated again to retard melt fracture. However, melt fracture happened in all of these trials. In order to further reduce the viscosity of the polymer, the screw rotational speed was increased to 200 rpm to promote the shear thinning behavior of polymer melts. It can be seen in trial 5, when the screw speed was increased from 150 to 200 rpm, the torque experienced by the extruder decreased from 75% to 63%, and the pressure decreased from 1000 psi to 800 psi. However, melt fracture still occurred. In the 6th trial, 5wt% of lubricant was added in the matrix to reduce viscosity. The effect of lubricant turned out to be significant. To maintain a similar feeding torque, the feeding rate was increased from 4 kg/hr to 7 kg/hr when lubricant was added. After the die temperature was adjusted to 220°C, surface roughness was minimized, and the extrudates could be palletized.

Mechanical Properties

The tensile strength of ABS-based WPCs with different amounts of the two coupling agents is shown in Figure 1. It can be seen from Figure 1 that the tensile strength of WPCs increases with the loading level of SMA and goes from 41.53 MPa to 48.08 MPa. It is worthwhile to note that even with 4wt% of coupling agent, the strength of 50wt% wood PP-WPCs is only around 40 MPa. Thus, ABS-based WPCs are stronger than the commercially-available WPCs that are made with PP or HDPE. Note that the addition of SMA also improves the tensile strength of WPCs made using virgin ABS. The tensile strength increases by 16% when the loading level of SMA increases from 0wt% to 10wt% in the matrix. In order to simplify the experimental matrix, the loading level of SMA was controlled at 0 or 10wt% of wood flour in the recycled ABS-wood plastic composites. The tensile strength of WPCs made using recycled ABS is lower than that of virgin ABS-WPCs but not by a large margin. This happens because the strength of the recycled ABS is lower than that of the virgin ABS. In the presence of SMA, the strength of recycled ABS-WPCs increases, too.

Figure 1. Tensile strength of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 1 also reveals that the addition of SEBS-g-MA progressively decreases the strength of ABS-WPCs. This is because SEBS-g-MA is immiscible with ABS. The tensile moduli of 50wt% virgin or recycled ABS based WPCs are shown in Figure 2. The modulus of ABS-based WPCs is around 6.5 GPa. Adding SMA into the WPCs does not affect the modulus of the virgin ABS-WPCs much, but the modulus of recycled ABS-WPC is increased with the addition of SMA. The reason for this observation needs to be further investigated in a future study. By contrast, the modulus of WPCs decreased when SEBS-g-MA was added, especially when the content of SEBS-g-MA increased to 10wt% of the wood flour. The decrease of modulus is expected, because the modulus of any elastomer is much less than that of ABS and wood. Since the modulus of 50wt% wood-polypropylene based WPCs is around 4.2~4.5 GPa, it is clear that ABS-based WPCs possess at least 33% higher modulus than that of PP-based WPCs.

Figure 2. Tensile modulus of 50wt% wood-ABS-WPCs with different amount of SMA and SEBS-g-MA

Data for the elongation at break are shown in Figure 3. It is seen that for virgin-ABS-based WPCs the elongation-at-break is around 1.05 ~ 1.2%, while that of WPCs made with recycled polymer is around 0.8%. The elongation at break increases slightly with the loading level of SMA. This is reasonable since the modulus of WPCs does not change, but the strength increases with the addition of SMA. Unlike PP or HDPE based WPCs, the addition of SEBS-g-MA does not increase the elongation at break of ABS based WPCs. Again, the incompatibility of SEBS-g-MA and ABS may negate the beneficial effect of SEBS-g-MA. It should be pointed out that, due to the relative brittleness of ABS-based WPCs, the elongation at break and strain at ultimate stress occur are at the same point.

The flexural properties of the WPCs are shown in Figures 4 -6. The trends of the different flexural properties are similar to those of tensile properties. Flexural strength increases with SMA content, but the flex modulus remains unchanged with SMA content. As in the case of tensile properties, the flex modulus and flex strength decrease with the addition of SEBS-g-MA.

The reverse-notch Izod impact strength of ABS-WPCs is presented in Figure 7. Similar to elongation at break, the impact strength of ABS-WPCs is low, and the effect of the coupling agent is not easy to distinguish. But one can still see a trend in that the impact strength increases with SMA content. Although SEBS-g-MA is known as a good toughening agent for polyolefin-based WPCs, the impact strength of ABS-WPC samples does not increase in the presence of SEBS-g-MA. Again, this is due to the incompatibility between SEBS-g-MA and ABS. Compared to PP-based WPCs the impact strength of ABS-based WPCs is lower. Note that the reverse-notch impact strength of 50wt% wood PP-WPCs with and without coupling agent is 160 J/m and 80J/m, respectively. Therefore, it is necessary to find a good toughening agent for ABS-WPCs in the future.

Figure 3. Elongation at break of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 4. Flexural strength of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 5. Flexural modulus of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 6. Flexural strain at maximum load of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 7. Reverse-notch Izod impact strength of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Microstructure Analysis

The tensile fracture surface of 50wt% wood ABS-WPCs was observed by scanning electronic microscopy. WPC samples containing no coupling agent, 10wt% SMA and 10wt% SEBS-g-MA to wood flour were investigated. The results are displayed in Figures 8 – 10. Since ABS is hydrophilic, even without a coupling agent, the fiber wetting of ABS-WPCs is good and no gaps can be found between the fiber and the matrix. This is evident from Figure 8 (a). In addition, the wood flour tends to form aggregates since there is an abundance of hydroxyl groups on the surface of wood flour, and these form hydrogen bonds easily.

When 10wt% of SMA was added to the formulation, the morphology of the composites became different. Maleic anhydride groups from SMA reacted with the hydroxyl groups on the wood flour surface, and this reaction not only increased the strength of the material but also reduced the hydrogen bonds between the wood flour particulates. The consequence can be seen in Figure 9. Instead of agglomerates, a single fiber is visible in the matrix, and the fiber wetting is good.

The fracture surface of ABS-WPCs containing 10wt% SEBS-g-MA to wood is shown in Figure 10. There are several gaps around the fiber. This implies that the bonding between the matrix and fiber is weak. As was mentioned previously, this is because SEBS-g-MA reacted with the wood flours and remained on their surface, but SEBS-g-MA is incompatible with ABS.

As a part of this research, the reverse notch Izod impact strength test was also conducted to investigate the effect of wood flour content on impact strength. The results are given in Figure 11. As was expected, virgin ABS did not fail under the reverse notch Izod impact test. Consequently, one may consider the impact strength of virgin ABS to be infinite. The impact strength drops down significantly in the presence of wood flour. This is a critical issue for ABS-WPCs. In the future, this problem may be solved by developing a better coupling agent.

Figure 8. Tensile fracture surface of 50wt% wood ABS-WPCs samples without coupling agents

Figure 9. Tensile fracture surface of 50wt% wood ABS-WPCs samples with 10wt% SMA to wood flour

Figure 10. Tensile fracture surface of 50wt% wood ABS-WPCs samples with 10wt% SEBS-g-MA to wood flour

Water Absorption Tests

The rate of water absorption of ABS-WPCs was measured until the samples were saturated. The results of water absorption of 50wt% ABS-WPCs are displayed in Figure 12. In this figure, R-ABS indicates recycled ABS, and ABS means virgin ABS. The rate of water absorption and the equilibrium moisture content of ABS-WPCs decrease in the presence of SMA. This result indicates that SMA not only increases the strength of ABS-WPCs, but it also decreases the moisture uptake. The addition of 2wt% SMA to wood flour made the equilibrium moisture content decrease by 12%, but it did not decrease further when more SMA was added. In our results, Recycled ABS-WPCs tends to absorb more water than virgin ABS-WPCs. The reason has to be further investigated.

To compare the difference in morphology of ABS-WPC and polyolefin-based WPCs, a picture was taken for an ABS WPC sample and a polypropylene (PP)-WPC sample after 1000 hours of water absorption. These pictures are shown as Figure 13. After 1000 hours of water immersion, the color of the PP-based WPC is much darker than that of the ABS-WPC. Compared to the ABS-WPC, the surface of the PP-WPC is rough. This may be because ABS is hydrophilic and PP is hydrophobic. The ABS matrix itself absorbed water and swelled during the test but PP did not. The swelling of wood flour during the water absorption test resulted in the surface roughness of PP-WPCs.

To understand the effect of wood flour on the rate of moisture uptake, ABS and ABS-WPCs containing 10, 20, 30, 40 and 50wt% of wood flour were tested for water absorption. The results are shown in Figure 14. As was expected, the rate of water absorption increased significantly with the wood content, and all of the samples reached their equilibrium moisture content after 1200 hours of water immersion

Figure 11. Impact strength of ABS-WPCs with different amounts of wood.

Figure 12. Moisture uptake of ABS-WPCs containing 50 wt% wood as a function of SMA amount

Figure 13. Comparison of ABS WPC with PP-WPC after 1000 hours of water immersion

Figure 14. Moisture uptakes of wood ABS-WPCs of various wood content – no SMA is added

B. Flame Retardant Properties of ABS-based WPCs

Accomplishments and Main Conclusions

- Halogenated and Non-halogenated flame retardants were evaluated as FR additives for ABS-based wood plastic composites. Both virgin and recycled ABS resins were used for this purpose. Flammability properties were characterized in terms of UL-94 type flame burn tests and limiting oxygen index (LOI).
- It was found that excellent FR properties can be obtained for both virgin and recycled ABS-based WPCs using non-halogenated flame retardants.
- It was found that the most efficient non-halogenated flame retardant is AP423. A v0 rating can be attained with this additive at a low loading level. The effectiveness of other additives in decreasing order is AP423 > ADP > TBBA = AP750.
- Char formation, which is desirable for good flame retardant properties, increases both in the presence of halogenated and non-halogenated FRs.
- The presence of a coupling agent, such as SMA, increases the LOI value and also the char formation.
- It was found that adding flame retardants increases the flexural modulus but reduces the flexural strength and strain. AP423 shows the best mechanical properties as compared to other potential FRs. The combination of halogenated and non-halogenated flame retardants shows synergism in mechanical properties, especially in flexural strain.
- It is found that ABS is better than polyolefins as a matrix for WPCs in terms of flammability and mechanical properties.

Experimental Details and Results

Materials, Sample Preparation and Characterization

CYCOLAC ABS-MG94 (melt flow index = 13 g/min, 220⁰C/5.0kg), Styrene-acrylonitrile (SAN581), and elastomers (BLX338 and BLX362) were obtained from GE Plastics (now SABIC Innovative Plastics). Recycled acrylonitrile-butadiene-styrene was obtained from Star plastics of Millwood, WV. These resins were used as received. Tetrabromobisphenol A (TBBA) was provided by Dead Sea Bromine Group, and its chemical formula is C₁₅H₁₂Br₄O₂. Antimony pentoxide (Sb₂O₅) was purchased from Nyacol nano technologies, Inc., and it had a particle size of 0.04 micron. Triphenyl phosphate (TPP), a white flake solid with a melting point of 48⁰C, ammonium phosphate dibasic ((NH₄)₂HPO₄), calcium carbonate (CaCO₃), and melamine were purchased from the Sigma-Aldrich company. Ammonium polyphosphates, which are Exolit AP423 and AP750, were purchased from Clariant. Hydrous Magnesium silicate (talc) was a gift from Luzenac America Inc. Cloisite 20A (I-20A), an organically modified montmorillonite clay was purchased from Southern Clay Products Inc. Polystyrene maleic anhydride (SMA) was provided by Sartomer company. Styrene-acrylonitrile maleic anhydride (SAN-MA) was supplied by LANXESS. Cellulose was provided by CreaFill company, and maple wood flour (Maple 8010, size of 80-mesh, about 177 μm) was provided by American Wood Fiber.

The mixing and compounding of all samples was carried out using a Leistritz Micro-27 co-rotating or counter-rotating twin screw extruder ($L/D = 40$, $D=27\text{mm}$) or in a Thermo Haake internal mixer. The compounded pellets were then shaped using a Battenfeld BA 1000-CDC injection molding machine or a PHI 30-ton hot press to produce standard testing samples for further characterization. Polymer pellets, wood flour and additives such as flame retardants or coupling agents were fed to a co-rotating extruder through the hopper using K-Tron loss-in-weight feeders at a total feeding rate of 3 and 4 kg/hr. The screw speed was of 80 rpm, and the temperature was set at 60°C at the hopper, and it increased to 165 or 180°C at the die depending on the type of flame retardants used.

Limiting oxygen indexer (LOI), which measures the minimum oxygen concentration of a mixture of oxygen and nitrogen to support the candle-like flaming combustion, was measured using Dynisco limiting oxygen index tester. The sample size was $127 \times 12.7 \times 3 \text{ mm}^3$. The UL-94 tests were carried out in the vertical burning situation according to the prescribed method in the standard. Test specimens of dimensions ($127 \times 12.7 \times 3 \text{ mm}^3$) were ignited by a methane burner kept 10 mm below the sample. Mechanical testing of these samples was performed as described in the previous section.

Results

Table 4 gives results of UL-94 tests and provides LOI values of ABS/wood flour composites. Generally, UL-94 ratings and LOI values are used as indicators of fire resistance and are also used to express the relative flammability among polymeric materials. As can be seen, without wood flour, ABS itself has a LOI value of 20 and NC in UL-94. However, with the addition of wood flour, there is no change in UL-94 test, but the LOI value increases to 21 and is independent of wood content; this could be attributed to the char formation of wood. Char formation is a known strategy to protect the underlying solid polymers, and it has been successful and efficient for a long time.

Table 4. Experimental data of flammability and mechanical properties of WPCs.

Samples	Components composition (mass%)			Flammability		Flexural tests		
	ABS	Wood	SMA	UL-94	LOI (vol.%)	Strength (MPa)	Modulus (GPa)	Strain (%)
1	100	–	–	NC	20	70.90	2.28	>5
2	80	20	–	NC	21	76.41	3.61	3.00
3	60	40	–	NC	21	81.81	5.01	2.01
4	70	30	–	NC	21	77.38	3.91	2.54
5	68.6	30	1.4	NC	21	79.61	3.87	2.8
6	67.2	30	2.8	NC	21	79.97	3.71	2.89
7	65.8	30	4.2	NC	21	81.1	3.87	2.82
8	64.4	30	5.6	NC	21	81.31	3.89	2.78
9	63	30	7	NC	21	83.10	4.47	2.39

It has been found that nitrogen, phosphorus, and boron derivatives such as ammonium phosphate, ammonium halide, and boric acid can be used to improve the char formation of wood, and, as a consequence, the fire performance of wood can be increased. Therefore, the goal of

using non-halogenated flame retardants in this section was to increase the char formation of wood in ABS/wood composites. The char was expected to act as a heat and mass barrier and protect the underlying solid phase.

The effect of different types of flame retardants

From the previous discussion, the LOI of ABS-based WPCs is 21. However, the addition of different non-halogenated flame retardants into ABS-based WPCs increases the LOI values significantly to the range of 27 to 29 as shown in Table 5. This is attributed to the increasing rate of dehydration of wood flour catalyzed by phosphoric acid which increases the char formation in the case of non-halogenated flame retardants. The same phenomenon of increasing values of LOI of polyolefin based WPCs with addition of ammonium polyphosphate (APP) have been reported.

To obtain a V-0 rating on the UL-94 test employing WPCs, the needed amount of the various flame retardants is found to be different at the same wood content. By comparing samples 1, 3 and 5 (Table 5), it is clear that AP423 is the most efficient FR since it allows one to reach V-0 at a loading level of 20wt%. By contrast, AP750 needs the highest amount of 30wt%. Further comparing the LOI values among the FRs shows that high amounts of non-halogenated flame retardants can get higher values of LOI. These results suggest that AP423 is more effective for triggering char formation of wood at the beginning of combustion than other acid providers; however, after that, a solid barrier against mass transfer is proportional to the loading percentage of non-halogenated flame retardants.

Table 5. Experimental data on flammability and mechanical properties of WPCs with Virgin ABS with different FRs.

Samples	Components composition (mass%)						Flammability		Mechanical properties		
	ABS	Wood	ADP	AP423	AP750	SMA	UL-94	LOI (vol.%)	Strength (MPa)	Modulus (GPa)	Strain (%)
1	45	30	25	–	–	–	V-0	28	67.51	6.10	1.28
2	40.5	30	25	–	–	4.5	V-0	29	65.45	5.58	1.34
3	50	30	–	20	–	–	V-0	27	71.59	4.77	2.00
4	45	30	–	20	–	5	V-0	28	63.74	4.55	1.84
5	40	30	–	–	30	–	V-0	28	75.78	6.21	1.38
6	36	30	–	–	30	4	V-0	28	67.95	5.10	1.65

FR properties of WPC based on recycled ABS are shown in Table 6. ADP and AP423 were used in this study, and they are effective flame retardants for recycled ABS/wood composites. They act as acid providers to promote the dehydration of wood, and this leads to forming of char which serves as a heat and mass transfer barrier. Moreover, both of them increase the modulus of the composites.

The effect of coupling agents is mainly to improve the compatibility between the wood and the matrix and to increase the flexural strength. However, it has been found that the interaction between SMA and wood was inhibited by the presence of ADP. With the help of FTIR study, it was observed that the inhibition behavior by ADP is due to a physical interaction. Furthermore, coupling agents not only influence the mechanical properties but also have an impact on the flammability. When coupling agents (such as ADP and AD423) interact with wood, the UL-94

rating shifts from V-0 to V-1, and the LOI decreases. However, if flame retardants inhibit the reaction between coupling agents and wood by physical interference, results show that UL-94 rating remains the same, but the LOI value increases to 31 (sample 4); this is due to not only the increase of dehydration of wood but also the cross-linked network formed between coupling agents and flame retardants at high temperatures.

Table 6. Experimental for flammability (AP423 as flame retardants) for WPC with recycled ABS

Sample	Components composition (mass%)					UL-94 rating
	Re-ABS	Wood flour	AP 423	SMA	SAN	
1	65	30	5	–	–	NC
2	65	30	5	–	–	NC
3	60	30	10	–	–	V-0
4	60	30	10	–	–	V-0
5	57.5	30	10	2.5	–	V-1
6	57.5	30	10	2.5	–	V-1
7	57.5	30	10	–	2.5	V-1
8	57.5	30	10	–	2.5	V-1
9	55	30	15	–	–	V-0
10	55	30	15	–	–	V-0
11	70	30	–	–	–	NC
12	70	30	–	–	–	NC

C. Solid State Foaming of ABS-based WPCs

Accomplishments and Main Conclusions

- ABS-based WPCs were foamed using a solid state foaming technique by first saturating the samples with CO₂ and then foaming by immersing samples in a hot liquid.
- Equilibrium sorption time for the ABS/Wood composite containing 0-20% wood is in the range of 40 hours.
- ABS/Wood composite foam can be achieved at relative densities at least as low as 0.34.
- It is seen that the 100° C foaming produced lower relative density samples than the 120° C.

Experimental Details and Results

ABS-based WPC samples were prepared at WVU using extrusion and injection molding as described before. Foaming and foam characterization was carried out at the Microcellular Plastics Laboratory of Professor Vipin Kumar at the University of Washington. The materials investigated in this experiment were a blend of ABS and wood having ABS/Wood ratios of 100/0, 95/5, 90/10, 85/15, and 80/20. Solid ABS appears off white whereas the composite appears to be a chocolate brown color.

For the gas saturation step, a 63.5 mm diameter and 50.8 mm deep carbon steel pressure vessel was used. The pressure vessel is rated for use up to a maximum pressure of 10.34 MPa at 0°C. The pressure inside the vessel was regulated using an OMEGA CN8500 process controller with a resolution of ± 0.01 MPa. A Mettler-Toledo AE240 precision balance with an accuracy of 10 μg was used to measure the gas solubility in the materials prior to and after foaming. Water bath foaming was conducted in a heated circulating water bath controlled by a Techne TE-10D heater/circulator with a working temperature range of ambient +5 to 120 °C and set point accuracy of $\pm 1^\circ\text{C}$. Oil bath foaming were conducted in a HAAKE silicone oil bath (accuracy of $\pm 2^\circ\text{C}$).

Sample blends to be investigated were chosen to be 100/0 (ABS/Wood), 95/5, 90/10, and 80/20. Samples of material were cut from a $\frac{1}{2}$ " wide and $\frac{1}{8}$ " strip of material into 1" lengths. Two samples were prepared for each of the blends tested.

Initial masses of each sample were recorded to establish sample masses prior to CO₂ uptake. Samples were interweaved with a strip of paper towel and placed into a pressure vessel. The vessel was sealed and set at saturation pressure of 5 MPa. During saturation, samples were removed from the pressure vessel, massed, and returned to pressurization to obtain sorption data.

When samples appeared to all be fully saturated, samples were removed from the pressure vessel and foamed at specified temperatures via hot water bath or silicone oil bath. Density data of these foamed samples was collected and then interpreted. Each sample was fully saturated at 5 MPa with carbon dioxide gas at room temperature. Half of the samples were foamed in a hot water bath at 100°C for about 1 minute while the rest were foamed in a silicone oil bath at 120°C for roughly 1 minute.

The sorption data on CO₂ uptake can be seen in Figure 15 below.

Figure 15. Plot of Carbon Dioxide uptake over time in various ABS/Wood material blends.

It can be seen from the plot that at about 40 hours or so, the material fully saturates. This result is similar to the theoretical sorption trend of solid ABS at this particular thickness which is about 40.3 hours.

In regards to the foaming, Figures 16 and 17 below portray the relative density of the foam versus the composition of the material at 100°C and 120°C foaming temperature respectively.

Figure 16. Relative Density versus wood composition for samples foamed at 100°C.

Figure 17. Relative Density versus wood composition for samples foamed at 120°C.

It can be seen from each of the plots that the lowest relative densities achieved during this experiment occurred with the 95%/5% specimens. These produced densities of about 0.34 at both 100° and 120°C foaming. Because of the preliminary nature of this experiment, a range of different material compositions was not fully explored. The graphs suggest that the lowest achievable relative density is between 100%/0% and 85%/15% and that 95%/5% is one experimented example of this claim. In regards to the effects of temperature on foam, it is seen that the 100°C foaming produced lower relative density samples than the 120°C. However, further tests would be required to make more meaningful conclusions. Also, in order to be practically useful, a continuous foaming process needs to be developed.

Conclusions

- It has been shown that both recycled acrylonitrile-butadiene-styrene (ABS) recovered from end-of-life-electronics and virgin ABS can be used to make wood plastic composites (WPCs) with superior properties compared to conventional olefin-based wood plastic composites.
- Systematic studies were carried out to identify processing conditions and parameters to design a successful extrusion and injection molding operation to produce ABS-based WPCs.
- Various additives such as coupling agents and impact modifiers were identified to improve the mechanical properties of these WPCs and to reduce their water absorption.
- Non-halogenated flame retardants, in conjunction with wood flour, can be used to make *eco-friendly flame retardant WPCs* which should enable their use of in indoor applications.
- It was found that both halogenated and non-halogenated flame retardants can be used to obtain desirable flame-retardant properties while, maintaining desirable mechanical properties.

- ABS-based WPCs can be foamed using a solid-state foaming method with the help of carbon dioxide. A significant reduction in density can be achieved by this method.

Polymer name abbreviations: ABS (acrylonitrile-butadiene-styrene), HDPE (high density polyethylene), SAN-gMA (styrene-acrylonitrile grafted maleic anhydride), SEBS-gMA (styrene-ethylene-butylene-styrene grafted maleic anhydride), SMA (styrene maleic anhydride)

Task 1.2: Selection of constituents and manufacturing methods for reinforced composite polymer products from recycled EOLE plastics (Hota GangaRao/WVU)

The Recipient shall select composite constituents and manufacturing methods, as well as develop structural and nonstructural composite artifacts from EOLE plastics. Additives and manufacturing processing will be identified and optimized.

Collaboration with the manufacturing community will facilitate proper selection of processing parameters for different blends of recycled polymers, die design, temperature, viscosity, impurity and fiber blending, and additives, including retardants.

Results of the research efforts will be shared and discussed with potential customers and project stakeholders, including government agencies, private industries and the construction industry for future installation.

The reuse of recycled thermoplastics and/or compounding will be investigated to increase recycled plastic content for composite products. Injection molding of sign posts/boards and reinforced grids products will be accomplished at quarter scale during this phase.

Evaluation of composite materials will be performed, and thermo-mechanical properties established. Evaluation of recycled/discarded polymers will be performed in collaboration with the recyclers on different streams to establish base-line properties and material acceptability.

Task 2.2: Manufacture of reinforced composite polymer shapes with fiber/fabrics using conventional and hybrid processing technologies

The recipient shall refine the screening process and the compounding techniques to make use of EOLE materials. Composite products with hybrid processing shall be produced using recycled polymers provided by the commercial partners in this project.

The overall focus of this task shall be cost effective mass manufacturing of recycled polymer products for commercial applications.

Tasks 3.2 and 4.2 were not defined for the SOPO since the funding level was reduced and the scope of the project curtailed.

Task 2.2 Manufacturing and Durability Evaluation of Structural Composites with Recycled Polymers

Abstract

Compression molding method was used for manufacturing recycled ABS polymer composites with 0, 1, 3 and 5 layers of glass fabrics and their short-term tension, bending, compression, and impact strengths were evaluated. To evaluate their long term performance, recycled composite specimens were subjected to salt and alkaline solution aging at room and freeze thaw conditions for 1, 4, 8 and 12 months. Base test results were compared with aged specimens, and strength and stiffness variations were noted. The strength of non aged specimens with 5-layers of glass fabrics (12% fiber volume fraction) was evaluated to be 10,484 psi, 13,044 psi, 6,969 psi and 5.36 ft lbs for tension, bending, compression, and impact tests, respectively. These strength gains increase with increasing fiber volume fractions and typical fiber volume fractions in structural composites are in the range of 45% to 70%. Among salt and alkaline conditioning schemes at room temperature or with freeze thaw variations, maximum reduction in tensile and bending, strengths with up to 5 layers of glass fabrics were found to be 36% and 71%, respectively, whereas those of compression and impact strengths were in excess of 80%. These reductions are expected when glass reinforcements are subjected to high pH alkaline environment in accelerated aging studies that relate to a actual service life of 50 to 100 years in field conditions. These durability studies provide a basis for understanding degradation patterns of composites and highlight the importance of proper resin saturation.

Manufacturing of thermoplastic (TP) thermoset (TS) sandwich composites were also carried out in this research to evaluate their tension and bending properties. Hand layup method was selected for manufacturing thermoplastic and thermoset composite plates. Altogether, six types of composite plates were manufactured, i.e., i) TP/TS/TP (roughened) and (un-roughened) ii) TS/TP/TS (roughened) and (un-roughened) iii) TP/TS (roughened) and (un-roughened). The surface was roughened to provide good bond between thermoplastic and thermoset components. Poor bond and early delamination was noted for un-roughened specimens during machining. Bending strengths of TS/TP/TS composite specimens having vinyl ester on either side of roughened ABS plate increased by 13.88% compared to vinyl ester composite on only bottom side of the sandwich. Test results showed that vinyl ester composite with 2 layers of glass fabric is about 3 times stronger and 2.5 times stiffer than similarly reinforced ABS. Hence, it is advantageous to use thermoset composite as a shell and thermoplastic as a core in a sandwich specimen to maximize bending strength of products such as composite RR ties.

These research results indicate the significant potential and strength gains in recycled polymer composites with the use of continuous glass fabrics (e.g., bidirectional fabrics). These fabrics were successfully utilized in making recycled polymer composite structural components for highway, housing, and automobile applications. These products can be scaled to suit other prototype applications. One such application involving the manufacture and development of full-scale recycled railroad composite tie is being further explored. It is important to ensure proper resin coating of continuous glass fabrics in structural composites, because they are susceptible to aging related degradations (locally or globally), particularly under alkaline solution exposures.

1.1 Introduction

Thermoplastics are replacing most of the metallic materials in the modern world and technology because of recycling capability, feasibility, and suitability to various applications. Materials like aluminum and steel have very good strength and stiffness but are heavier and may corrode. Polymers are light weight and corrosion resistant. Thermoplastics have many advantages over metals and perform excellently when combined with fibers. Fibers can be made of glass, carbon, aramid and others. When polymers are combined with fibers they are called as Fiber Reinforced Polymer (FRP) or composites. Acrylonitrile-butadiene styrene (ABS) used in this research was obtained from Star Plastics Inc, Ravenswood, WV. Their recycling includes collection of the scrap from domestic, industrial, and commercial sources. Impurities are separated and then the recycling stream is provided to manufacturers. ABS is a two phase polymer blend. A continuous phase of styrene-acrylonitrile copolymer gives the materials rigidity, hardness and heat resistance. The toughness of ABS is derived from submicroscopically fine polybutadiene rubber particles uniformly distributed in the SAN matrix (BASF Plastics). In addition to strength and stiffness, attaining required shape and finish are equally important for composite products. Recycled ABS polymers are used in automobile dashboard, conduits, pipelines, cell phones, toys, electronic appliances, medical equipments (where they do not produce magnetic field), window panels, sign posts etc. Depending on its application, users prefer virgin or recycled ABS. In this research, use of continuous glass fabrics for manufacturing recycled polymer composite, their mechanical properties, and their aging behavior are investigated.

1.2 Objectives

1. To manufacture and evaluate mechanical properties (e.g. compression, bending, tension, and impact) of the recycled polymers reinforced with continuous bi-directional glass fabrics (previous research focused on short-discontinuous fibers).
2. Aging effects on recycled ABS polymer composites with different fiber volume fractions.
3. Mechanical properties of sandwich composites structures with reinforced thermoplastic and thermoset polymers.

1.3 Scope

Mechanical properties of the recycled polymer composite materials were evaluated in this study for use in civil infrastructure. Recycled ABS polymer plates and coupon specimens were manufactured with 0, 1, 3, 5 layers of bi-directional glass fabrics. Mechanical properties were evaluated for 1, 4, 8, 12 months of salt and alkaline aging at room temperature and freeze thaw conditions. A total of more than 1000 specimens were manufactured and tested to evaluate their durability.

1.4 Earlier research at CFC-WVU

Bargo (during 2000) worked on the evaluation of mechanical properties of the virgin/recycled, ABS, and PC polymers with 25% of fibers by weight and without fibers. In addition, specimens using 20%/80% blend of recycled and virgin ABS and PC with 25% fibers by weight and

without fibers were manufactured. Six types of tests, i.e., namely tension, compression, bending, impact, hardness and creep of ABS and PC plastics were carried out. Average maximum tensile strength and stiffness of ABS composite was evaluated to be 7613.38 psi and 0.649E+06 psi, respectively. Average maximum tensile strength and stiffness of PC was evaluated as 12401 psi, and 0.665E+06 psi, respectively. Average maximum bending stress for ABS and PC composite was evaluated to be 13.141 ksi and 17.4 ksi. Similarly, average maximum compression stress and stiffness of ABS composite was found to be 11.446 ksi and 0.67E+06 psi, respectively. Average maximum compression stress and stiffness of PC was found to be 1613.8 psi and 0.613E+06 psi, respectively. Corrected impact strength on ABS and PC was calculated as 0.24 ft-lbs and 1.04 ft-lbs, respectively. Average hardness without and with 626g weight on ABS was 11.15 and 25.75, respectively. Similarly, average hardness for PC with and without weight was 10.67 and 25.38, respectively.

Basto, (during 2002) carried out the evaluation of mechanical properties of polymers such as tension, bending, compression, Impact, hardness and creep of the ABS polymer. Chopped and continuous fibers specimens were used to manufacture coupon specimens and structural components. Specimens were also subject to limited chemical aging for up to 18 months. Basto worked on the manufacturing and testing of the structural components like rubber tire reinforced offset block modules for highway guard rail system, channel section, trapezoidal section, box section, flat plate made of recycled ABS were tested. Maximum tensile strength of recycled ABS without fabric was found to be 5578.85 psi and tensile stiffness was 0.333×10^6 psi. Tensile strength with 12% of fabric was found to be 8800 psi and tensile stiffness was 0.964×10^6 psi. Bending strength without fabric was 9187 psi and bending stiffness was observed to be 0.4×10^6 psi. Bending strength with 12% of fabric was found to be 16740 psi and Stiffness was 1.08×10^6 psi. Compressive strength without fabric was 8792 psi and Compressive stiffness was 0.42×10^6 psi. Compressive strength with fabric was found to be 14891 psi and stiffness was $.92 \times 10^6$ psi. Aditham carried out the manufacturing of structural products using the glass fabrics from BGF industry. Maximum tensile strength without fabric was 4413 psi and tensile stiffness was 0.317×10^6 psi. Tensile strength with fabric was found to be 4643 psi and tensile stiffness was 0.376×10^6 psi. Bending strength without fabric was 11865 psi and bending stiffness was observed to be 0.382×10^6 psi. Bending strength with of fabric was 17219 psi and Stiffness was 0.489×10^6 psi. Compressive strength without fabric was 6616 psi and Compressive stiffness was observed to be 0.167×10^6 psi. Compressive strength with fabric was found to be 8479 psi and Stiffness was 0.215×10^6 psi.

Amarnath (2006) evaluated the mechanical properties of recycled ABS with and without fibers (Table1). FEM analysis of stress and strain due to processing temperature and load was also evaluated. Based on the positive CFC-WVU results and regarding the use of recycled composite for structural applications, their long term mechanical properties were evaluated through aging studies in this research.

Table 1 Tensile strength (Amarnath 2006)

Fiber volume fraction	Tensile strength (psi)	Tensile stiffness ($\times 10^6$ psi)	Bending strength (psi)	Bending stiffness, E ($\times 10^6$ psi)	Compressive strength (psi)	Compressive stiffness, E ($\times 10^6$ psi)	Average impact strength (ft.lbs)
No Fabric	4296	0.322	9038	0.324	7724	0.233	0.49
4%	4866	0.378	9081	0.326	7266	0.232	1.54
7%	7465	0.524	11550	0.399	6837	0.224	2.85
12%	10618	0.651	13668	0.456	5945	0.23	5.51

Materials

2.1 Materials Used

Recycled Acrylonitrile Butadiene Styrene (ABS) used in this research. (chemical formula $(C_8H_8 \cdot C_4H_6 \cdot C_3H_3N)_n$) is typically manufactured from polymerization of the basic monomers acrylonitrile, butadiene and styrene using a common process adopted for ABS polymer was batch type emulsion graft polymerization process. Acrylonitrile (represented as C_3H_3N) is a pale yellow liquid in changeable state, has pungent smell, and polymerizes quickly when heated. This material is flammable when exposed to fire. Butadiene (1, 3-butadiene) can be listed under dienes (hydrocarbons which can hold two double bonds). Butadiene (represented as C_4H_6) is a monomer used for production of the rubber copolymer; its molecular formula is C_4H_6 . Styrene, (represented as C_8H_8) styrol, ethenyl benzene, vinyl benzene, and phenetylene, etc is generally a color less oily material and its molecular formula is C_8H_8 . Styrene is a volatile material which provides the materials gloss property and makes the surface impermeable.

Figure 2.1 Granulated recycled polymers

A blend of acrylonitrile and styrene provides superior mechanical properties and toughness. In addition, butadiene which is in the form of rubber has increased its application. Variation of amount of monomers in ABS polymer provides better heat and impact resistance. ABS polymers have power to resist liquid acids like concentrated hydrochloric and phosphoric acid and mineral oils. However, these get dissolved in esters and ketones. Quality of ABS resin can be controlled by maintaining the diameter of rubber material used during manufacturing process. Optimum diameter of rubber would be 0.2 micron to 0.5 micron for better shock resistance and surface luster.

Recycling process of these polymers includes collection of the materials from the various sources like scrap from factories, research laboratories, disposed auto parts, domestic wastes, wastes from hospitals etc. These materials collected are sent to industry for recycling. Work of industry begins with separation of the impurities in the collected waste materials, which can be achieved by any of separation procedures, i.e., gravity or magnetic separation. At this stage, they are added with required additives and then mixed under pressure and temperature, and then molded into required size and shape.

2.2 Grinding of pellets

Recycled ABS specimens obtained from Star Plastics Inc. were subjected to grinding operation prior to manufacturing coupon specimens of this study. Grinding of pellets into smaller particles was achieved by using a granulator. Generally, pellets that came from the manufacturer were ¼” in diameter with uneven shape. They were ground to manufacture a quarter inch thick FRP plate with 1, 3 and 5 layers of bi directional glass fibers/fabrics using compression molding machine and to ensure proper distribution of resin between two layers of fabric. Grinding of pellets resulted in lower voids and enhanced strength of composites.

Figure 2.2 Pellets grinder

2.3 Glass fiber

Glass fibers enhance strength and stiffness of the composites. Glass fibers are preferred for reinforcement because of their good strength, stiffness, heat and corrosion resistance characteristics, and feasibility for different environment, and low cost. These fabrics are available in wide variety of configuration and densities.

Their low thermal expansions make them more dimensionally stable. Glass fibers have good electrical insulation and low moisture absorption. Glass fibers are fire resistant and do not undergo physical change. For this project, bi-directional (0, 90 degrees) fabrics with a density of 12 oz/sq yard were used.

Manufacturing Process

3.1 Manufacturing methods

Compression molding method was used to manufacture the specimens. Hand layup method was selected for sandwich plate preparation consisting of thermoplastic and thermoset components.

3.2 Compression molding process

Compression molding machine has top and bottom platens with independent temperature controls. Optimum temperature needed to melt ABS polymer was 475° F. Initially, the mold was placed on an aluminum plate. Using a brush, de-molding agent was applied on the mold and on the plate. Layers of polymer and glass fibers were laid in the mold. Then the mold was closed using another plate on the top. This setup was placed between hot platens of compression molding machine and pressure was applied. As the resin started to soften, the pressure application was increased and the mold was closed gradually. A pressure of about 12-15 kips was applied to close the mold completely. After a few minutes, the mold was air cooled and when the temperature dropped from 475° F to 400° F, the cooling was changed from air cooling to water cooling. The cooling was stopped when the temperature reached to about 80° F.

Figure 3.1 Compression molding machine

Once recycling composite plate fabrication was completed, they were machined to prepare test specimens conforming to ASTM standards for material property evaluation (compression, tension, flexural and impact). A minimum of three samples were evaluated for each category of test.

Figure 3.2 Tension, bending, impact and compression specimen

3.3 Fiber Volume fraction

Fiber volume fraction was evaluated by placing recycled composite specimens (w_1 mass) in an oven. They were burnt to remove matrix and the mass of left out glass fibers was (w_2). Fiber volume fraction is calculated by using:

$$\text{Fiber Vol. Fraction} = [1 - (w_1 - w_2)/w_1] * 100$$

Durability/Aging

4.1 Aging

Continued exposure of composites to many of the common environmental elements of our planets such as sunlight, air, oxygen, water, cold, heat and micro-organisms-can cause polymers to decompose into small molecules similar to those from which they are made. This process is called aging, and it leads to brittleness and eventual failure (Wallder). Composite materials were subjected to chemical aging of salt and alkaline solution to know the long term behavior. Long term properties and thorough knowledge of composite materials become important for engineers while designing structures. Material properties help engineers to check for the limits for stresses, strains, deflections and various other parameters during design. Vijay et al (2006) has presented some of the environmental conditions that affect durability of composite materials under accelerated/natural conditions including sea water, salt, alkaline and acid solution, prolonged freezing, Thermal cycle, Elevated temperature, thermal gradient, oxidation, UV radiation, creep and relaxation, fatigue, fire and others.

4.2 Solutions used for aging

Chemical aging was done for two different types of solution namely, salt solution (with pH: 7.0) and alkaline solution (with pH: 13.0). Salt Solution was prepared by adding 3% by weight of Sodium chloride (NaCl) to the standard water and pH was measured to be 7.0. Alkaline solution was prepared by mixing 1.4% of potassium hydroxide (KOH), 1% of sodium hydroxide (NaOH) and 0.2% of calcium hydroxide ($\text{Ca}(\text{OH})_2$) salts by weight. This results in a pH of 13.0 and produces an effect of environment typical of wet Portland cement. The pH of both the salt and alkaline solutions was measured twice in a week using a digital pH meter. Specimens were conditioned under freeze thaw and room temperature. The specimens subjected to freezing and thawing was placed in a Thermotron environmental chamber.

4.3 Environmental Chamber

In an environmental chamber where temperature and humidity can be controlled by choosing different cycles programmed for specific humidity and temperature variation. Environmental chamber simulates the accelerated aging conditions. In this study minimum temperature of -29 C and a maximum of 49 C was used.

Figure 4.1 Environmental Chamber

Figure 4.2 Temperature variation

Figure 4.3 Humidity variation

Manufacturing of Composite Sandwich Thermoplastic/Thermoset (TP/TS)

5.1 Manufacturing

Virgin ABS plates with glass fabric were manufactured for sandwich specimens using compression molding process. A layer of thermoset resin with glass fabric was laid over ABS composite plate to form a sandwich of vinyl ester and ABS. Wooden mold was machined initially to manufacture the composite sandwich of ABS and vinyl ester polymer to maintain uniform thickness of both thermoplastic and thermoset. However, composites were found to contain voids and misaligned fiber. Hence, hand layup method was used for manufacturing i) Roughened ABS plates (the surface of ABS plate was roughened using a DeWALT Heavy-Duty 7"/ 9" large angle sander for better grip between thermoplastic and thermoset) and ii) Unroughened ABS plates.

Figure 5.1 DeWALT Heavy-Duty 7"/ 9" Large Angle Sander

5.2 Manufacturing procedure

5.2.1 Procedure for manufacturing thermoplastics/thermoset composite sandwich (TP/TS)

- i. Glass fabrics were placed on an aluminum foil. Vinyl ester resin (with 2% of Methyl Ethyl Ketone Peroxide curing agent) was poured on glass fabrics and was spread using 1" wide brush.
- ii. Glass fibers with resin coating were placed on ABS plate with or without surface roughening.
- iii. Proper brushing ensured removal of entrapped air in glass fibers.
- iv. Finally, the plates were cured at room temperature.

5.2.2 Procedure for manufacturing thermoplastics/thermoset/thermoplastics (TP/TS/TP)

- i. Above steps i), ii) and iii) were followed and then glass fabrics coated with vinyl ester and were placed between ABS plates.
- ii. A weight of 3-4 lbs was placed over the plate as shown in Fig 5.3(a) and 5.3(b) which squeezes out extra resin from plate.
- iii. Sandwich composite was cured it at room temperature.

Figure 5.2 (a) glass fiber sheets

Figure 5.2 (b) Pouring of vinyl ester

Figure 5.2 (c) Spreading resin using brush

Figure 5.2 (d) Vinyl ester glass fibers are ready

Figure 5.2 (e) Laying of glass fiber sheets on ABS plates

Figure 5.2 (f) Second layer of glass fiber on ABS plate

Figure 5.2 (g) Brushing for removal of air voids

Figure 5.2 (h) Plates are cured at room temperature

Figure 5.2 Manufacturing of composite sandwich

Figure 5.3 (a) Weight placed on plate to squeeze resin

Figure 5.3 (b) Trickling down extra resin

Figure 5.3 Bonding of composite sandwich components (TP/TS/TP)

5.2.3 Procedure for manufacturing thermoset/thermoplastics/thermoset (TS/TP/TS)

- i. Thermoset glass fabric layer to one side of the thermoplastic plate patch was bonded.
- ii. After curing, another layer of glass fabric was bonded to other to other side of the plate and cured at room temperature.

These plates were reinforced with extra fabrics at end zones as shown in Fig 5.4(d) to facilitate strengthening of gripping near end zones (tab area) during tension test.

5.3 Bonding between thermoplastic and thermoset (TS/TP/TS) with end tabs

Plates were machined to rectangular shape tension test specimens; however, several un-roughened specimens de-bonded because of the vibrations caused by machining as a result of poor bond between thermoplastic and thermoset composites. Following coupon specimen preparations, different tests were carried out as per applicable ASTM standards.

Figure 5.4 (a) Wetting glass fabrics with vinyl ester resin

Figure 5.4 (b) Placing of glass fiber on plate

Figure 5.4 (c) Brushing for the removal of voids

Figure 5.4 (d) Plates are ready with tabs on either side

Figure 5.4 Application of tabs for sandwich specimens

6.0 Durability Test Results and Discussion

6.1 Tension test

Tension, bending, compression and impact coupon specimens manufactured in this study were tested with and without aging. Results of coupon specimens without aging are presented in various tables and further used as a basis to compare the results of aged specimens. Table 6.1 shows tension test results of recycled composite specimens without aging for different number of glass fabric layers.

Table 6.1 shows tension test results of recycled composite specimens without aging.

Table 6.1 Tension test results

Layers	Sample #	Load	Area	Stress	Average stress
		lbs	in ²	psi	psi
0	2	736	0.19	*3873.684	4653
	5	493	0.1176	4192.177	
	6	534	0.10442	5113.963	
1	1	913	0.195	4682.051	5010
	7	601	0.11086	5421.252	
	8	565	0.11466	4927.612	
3	3	1001	0.1875	*5338.667	8563
	9	1062	0.11564	9183.673	
	10	914	0.115668	7901.926	
5	4	2007	0.19	10563.16	10484
	11	1128	0.12642	8922.639	
	12	1459	0.12192	11966.86	

*Not considered for averaging of stresses due to improper (grip) failure mode

Figure 6.1 Stress strain graph for tension test specimens

6.1.1 Tensile stresses

Average stress of the tension test coupon specimens without glass fabrics (Table 6.1) was found to be 4653 psi and the average stresses with 1, 3 and 5 layers of glass fabrics were 5010 psi, 8563 psi and 10484 psi, respectively. Stress increase of 8%, 84% and 125% was noted (Table 6.2) for tension test specimens with 1, 3 and 5 layers, respectively, having a corresponding fiber volume fraction of 4%, 7%, and 12%. This resulted in a per layer stress increase of 8%, 28%, and 25% for specimens with 1, 3 and 5 layers specimens, respectively, indicating higher strength gains with increasing reinforcement area.

Table 6.2 Stress and tensile stiffness increment

Layers	Average stress	Per layer average stress increase	% increase in stress	Per layer increase	Tensile stiffness	Per layer stiffness increase	% increase in stiffness	Per layer stiffness increase
	(psi)	(psi)			$\times 10^6$ psi	$\times 10^6$ psi		%
0	4653	-----	----	-----	0.31	----	----	-----
1	5010	357	8%	8%	0.463	0.153	49%	49%
3	8563	1296	84%	28%	0.675	0.121	117%	39%
5	10484	1166	125%	25%	0.774	.092	149%	49%

6.1.2 Tensile Modulus

Average tensile stiffness without fibers was 0.31×10^6 psi, and with 1, 3 and 5 layers the values were noted to be 0.463×10^6 psi, 0.675×10^6 psi, and 0.774×10^6 psi, respectively. Tensile stiffness increased by 49%, 117% and 149% for 1, 3 and 5 layers, respectively. This resulted in per layer tensile stiffness increment of 49%, 39%, and 49% for 1, 3 and 5 layers of glass fabrics, respectively.

6.2 Bending Test

Table 6.3 shows bending test results of recycled composite specimens without aging.

Table 6.3 Bending test results

Layers	Sample	Load	Width	Depth	Stress	Average
	#	Lbs	in.	in.	psi.	psi.
0	1	40	0.51	0.233	8668.2	8516
	2	43	0.508	0.24	8817.2	
	3	38	0.512	0.235	8063.6	
1	4	44	0.508	0.254	8055.1	8587
	5	44	0.51	0.246	8553.8	
	6	53	0.514	0.26	9152.0	
3	7	60	0.511	0.252	11093.8	11045
	8	58	0.503	0.251	10981.5	
	9	61	0.501	0.257	11060.5	
5	10	75	0.514	0.258	13152.5	13044
	11	81	0.506	0.267	13473	
	12	72	0.511	0.26	12506	

6.2.1 Bending stresses

The average bending stress without fibers was 8516 psi. Average bending stresses with 1, 3 and 5 layers of bi-directional glass fabrics were 8587 psi, 11045 psi and 13044 psi, respectively. Percentage increase in bending stress for 1, 3 and 5 layers (having 4%, 7% and 12% fiber volume fraction, respectively) with respect to specimens without fibers were 1%, 30% and 53%, respectively.

Figure 6.2 Stress strain curve for bending specimens

Table 6.4 Percentage stress and stiffness increment for bending test

Layers	Average stress	Per layer average stress increase	% increase in stress	Per layer increase	Tensile stiffness	Per layer stiffness increase	% increase in stiffness	Per layer stiffness increase
	psi	psi			$\times 10^6$ psi	$\times 10^6$ psi		
0	8516	-----	----	-----	0.304	----	----	-----
1	8587	71	1%	1%	0.447	0.143	47%	47%
3	11045	843	30%	10%	0.447	0.047	47%	16%
5	13044	905	53%	11%	0.994	0.138	227%	45%

6.2.2 Bending stiffness

Bending stiffness for specimen without fabric was 0.304×10^6 psi and the stiffness for specimens with 1, 3 and 5 layers of fabrics was 0.447×10^6 psi, 0.447×10^6 psi and 0.994×10^6 psi, respectively. Percentage increase in bending stiffness was 47% for specimens with 1 and 3 layers, and 227% increment was noted for bending specimens with 5-layers when compared to bending specimens without fiber. Per layer bending stiffness increase was 0.143×10^6 psi, 0.047×10^6 psi, and 0.138×10^6 psi was noted for 1, 3, and 5 layers of glass fabric reinforcement,

respectively. Bending stiffness increase per layer was noted to be 47%, 16% and 45% corresponding to 1, 3 and 5 layers of glass fabric.

6.3 Compression test

Table 6.5 shows compressive test results of recycled composite specimens without aging.

Table 6.5 Compression test results

Layers	Sample	Load	Area	Stress	Average stress
	#	lbs	in ²	psi	psi
	1	2013	0.250	8030.6	8278
0	2	1989	0.249	7977	
	3	2179	0.246	8827.6	
	4	2034	0.251	8087	8172
2	5	1953	0.251	7777	
	6	2221	0.256	8652	
	7	1803	0.252	7141.0	7404
6	8	1860	0.253	7332.2	
	9	1976	0.255	7738.5	
	10	1749	0.255	6849.3	6969
10	11	1724	0.252	6818.6	
	12	1827	0.252	7240.3	

6.3.1 Compressive stresses

Average stress of compression test specimens without fabric was 8278 psi and the strength decreased with the increase in number of fabrics. The average stress of 2-layers compression specimens was 8172 psi which was 1% less than the specimen without fabric. Similarly, 11% and 16% reduction was noted for 6 and 10 layers compression specimens with the average stresses of 7404 psi and 6969 psi, respectively, when compared with non fabric compression specimens (Table 6.6).

Figure 6.3 Stress vs strain curve for compression specimens

Table 6.6 Compressive stresses and stiffness

Layers	Average stress	Per layer stress decrease	Stress decrease	Per layer decrease in stress	Compressive stiffness	Per layer increase in compressive stiffness	% stiffness increase	Per layer stiffness increase
		Psi	%	%	$\times 10^6$ psi	$\times 10^6$ psi	%	%
0	8278	----	----	----	0.312	----	----	----
2	8172	52.2	1%	0.5%	0.419	0.053	34%	17%
6	7404	145	11%	2%	0.598	0.047	91%	15%
10	6969	130	16%	2%	0.678	0.036	117%	12%

6.3.2 Compressive stiffness

Average compressive stiffness for specimens without fiber was 0.312×10^6 psi, and with 2 layers of bi-directional glass fabric the stiffness increased by 34%, and average stiffness was found to be 0.676×10^6 psi. Similarly, the average compressive stiffness for 3 and 5 layers compressive specimens were 0.393×10^6 and 0.559×10^6 , respectively, and the corresponding increment in the compressive stiffness was 25% and 79%, respectively. The per layer stress decrement for compressive specimens were 52.2 psi, 145 psi and 130 psi, and per layer compressive stiffness increase was 0.053×10^6 psi, 0.047×10^6 psi and 0.036×10^6 psi for 2, 6 and 10 layers, respectively.

6.4 Impact Test

Table 6.7 shows impact test results of recycled composite specimens without aging.

Table 6.7 Impact test

Sample no.	fiber layers	Correction factor weight (2lbs) (4 lbs)	Impact strength ft.lbs	type of failure	strength after correction	strength after weight correction factor ft.lbs.	Average Strength ft.lbs.
1	0	0.045	0.31	C	0.265	0.265	0.278333
2		0.045	0.33	C	0.285	0.285	
3		0.045	0.33	C	0.285	0.285	
4	1	0.045	1.16	H	1.115	1.115	1.191667
5		0.045	1.09	C	1.045	1.045	
6		0.045	1.46	H	1.415	1.415	
7	3	0.045	1.98	P	1.935	1.935	2.211667
8		0.045(2)	1.21	H	1.165	2.33	
9		0.045(2)	1.23	H	1.185	2.37	
10	5	0.035(4)	1.31	H	1.275	5.1	5.366667
11		0.035(4)	1.49	H	1.455	5.82	
12		0.035(4)	1.33	H	1.295	5.18	

ASTM (D256-03) defines the failure modes as C-complete break, H-Hinge break, and P-Partial break.

6.4.1 Impact strength

Average impact strength of specimens without fabrics was 0.278ft.lbs. For 4%, 7% and 12% fiber volume fraction, the average impact strengths were 1.19ft.lbs, 2.21ft.lbs and 5.37ft.lbs, respectively, with a corresponding strength increment of 328%, 698% and 1828% when compared to specimens without fabric.

Figure 6.4 Impact strengths with increasing number of fabrics

Table 6.8 Impact strength increment with fiber volume fraction

Layers	Fiber volume fraction	Average strength ft.lbs.	% increase	Per layer impact strength
0	0	0.27	----	----
1	4	1.19	328%	0.912
3	7	2.22	698%	0.833
5	12	5.36	1828%	1.01

6.5 Strength variation with aging

6.5.1 Tension test strength variation with aging

Table 6.9 Strength variations for tension test specimens subjected to various aging scenario and 1, 4, 8 and 12 months

Tension		Alkaline solution room temperature							
Layers	Base test (psi)	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M stress (psi)	% change	12 M Stress (psi)	% change
0.00	4653.00	2977.85	-36.00	4602.08	-1.09	3569.93	-23.28	3632.85	-21.92
1.00	5010.00	5140.65	2.61	4621.68	-7.75	3789.81	-24.36	3891.83	-22.32
3.00	8563.00	6999.22	-18.26	6381.16	-25.48	4309.80	-49.67	3916.38	-54.26
5.00	10484.00	7623.87	-27.28	8382.42	-20.05	4106.25	-60.83	3589.42	-65.76

			Alkaline solution E chamber						
Layers	Base test (psi)	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
0.00	4653.00	3862.98	-16.98	4118.62	-11.48	3855.20	-17.15	3692.13	-20.65
1.00	5010.00	3790.19	-24.35	3683.79	-26.47	4126.17	-17.64	3349.29	-33.15
3.00	8563.00	4267.32	-50.17	3685.47	-56.96	4114.48	-51.95	3299.83	-61.46
5.00	10484.00	3321.93	-68.31	3645.47	-65.23	3642.10	-65.26	2613.55	-75.07
			Salt solution room temperature						
Layers	Base test (psi)	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
0.00	4653.00	4325.11	-7.05	4146.32	-10.89	4710.70	1.24	3019.84	-35.10
1.00	5010.00	5350.87	6.80	4657.55	-7.03	5486.70	9.51	4970.29	-0.79
3.00	8563.00	8004.34	-6.52	7731.51	-9.71	8509.40	-0.63	7349.15	-14.18
5.00	10484.00	8720.24	-16.82	10097.59	-3.69	11078.91	5.67	8954.45	-14.59
			Salt solution E chamber						
Layers	Base test (psi)	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
0.00	4653.00	3778.42	-18.80	3448.07	-25.90	3308.97	-28.89	4305.05	-7.48
1.00	5010.00	4180.45	-16.56	4500.52	-10.17	5203.90	3.87	4514.36	-9.89
3.00	8563.00	6871.48	-19.75	7169.92	-16.27	7633.64	-10.85	6914.17	-19.26
5.00	10484.00	6183.66	-41.02	10206.89	-2.64	9878.24	-5.78	8079.53	-22.93

Change in overall strength values of specimens made of recycled ABS polymers with 0, 1, 3 and 5 layers of glass fabric due to 1, 4, 8 and 12 months (1M, 4M, 8M, and 12M) of aging as compared to those without aging.

Tensile strength change for specimens with different layers of fabric for 1, 4, 8 and 12 months (1M, 4M, 8M, and 12M) of aging are

Aging scheme: strength change under **alkaline solution room temperature**

Strength change with 0-layer (1M, 4M, 8M, 12M): -36%, -1%, -23.28%, 22%

Strength change with 1-layer (1M, 4M, 8M, 12M): 2.61%, -7.75%, -24.36%, 22.32%

Strength change with 3-layers (1M, 4M, 8M, 12M): -18.26%, -25.48%, -49.67%, -54.26%

Strength change with 5-layers (1M, 4M, 8M, 12M): -27.28%, -20%, -60.86%, -65.76%

Aging scheme: strength change under **alkaline solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): -16.98%, -11.48%, -17.15%, -20.65%

Strength change with 1-layer (1M, 4M, 8M, 12M): -24.35%, -26.47%, -17.64%, -33.15%

Strength change with 3-layers (1M, 4M, 8M, 12M): -50.17%, -56.96%, -51.95%, -61.46%

Strength change with 5-layers (1M, 4M, 8M, 12M): -68.31%, -65.23%, -65.26%, -75.07%

Aging scheme: strength change under **salt solution room temperature**

Strength change with 0-layer (1M, 4M, 8M, 12M): -7.05%, -10.89%, 1.24%, -35.10%

Strength change with 1-layer (1M, 4M, 8M, 12M): 6.80%, -7.03%, 9.51%, -1%

Strength change with 3-layers (1M, 4M, 8M, 12M) : -6.52%, -9.71%, -1%, -14.18%

Strength change with 5-layers (1M, 4M, 8M, 12M): -16.82%, -3.69%, 5.67%, -14.59%

Aging scheme: strength change under **salt solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): -18.8%, -25.9%, -28.89%, -7.48%

Strength change with 1-layer (1M, 4M, 8M, 12M): -16.56%, -10.17%, 3.87%, -9.89%

Strength change with 3-layers (1M, 4M, 8M, 12M): -19.75%, -16.27%, -10.85%, -19.26%

Strength change with 5-layers (1M, 4M, 8M, 12M): -41.02%, -2.64%, -5.78%, -22.93%

Figure 6.5 Stress strain curves for specimens aged in alkaline solution E chamber aged for one month

Figure 6.6 Stress strain curves for specimens aged in salt solution E chamber aged for one month

Maximum change gain in tensile stiffness for tension specimens placed in alkaline solution with freeze thaw variation (in an environmental chamber) for up to one month were 10% and 23% without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.10). Maximum change gain in tensile stiffness for tension specimens placed in salt solution with freeze thaw variation (in an environmental chamber) for up to one month were 12% and 1.5% without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.10).

Figure 6.7 Stress strain graph for eight month tension specimens placed alkaline solution E chamber

Figure 6.8 Stress strain curve for salt soln E chamber aged tension specimens

Maximum change gain in tensile stiffness for tension specimens placed in alkaline solution with freeze thaw variation (in an environmental chamber) for up to eight months were 16% and 28% without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.10). Maximum change gain in tensile stiffness for tension specimens placed in salt solution with freeze thaw variation (in an environmental chamber) for up to eight months were 15% and 37% without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.10).

Table 6.10 Stiffness variations for one and eight months aged tension specimens

No of layers	Stiffness Base	Alkaline Solution				Salt Solution			
		1M aged tensile stiffness	% change	8M aged tensile stiffness	% change	1M aged tensile stiffness	% change	8M aged tensile stiffness	% Change
	X 10 ⁶ psi	X 10 ⁶ psi	%	X 10 ⁶ psi	%	X 10 ⁶ psi	%	X 10 ⁶ psi	%
No fibers	0.312	0.342	10%	0.361	16%	0.348	12%	0.359	15%
5-layers	0.678	0.834	23%	0.871	28%	0.687	1.5%	0.927	37%

6.5.2 Bar Graph for strength variation of aged specimens

Stress variation in tension test specimens due to aging are represented in the form of bar graph-chart in following sections

Figure 6.9 Tension test specimens placed in alkaline solution in room Temperature

The variation in tensile strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at room temperature after 12 months were -22%, -22.32%, -54.26% and -65.76%, respectively.

Figure 6.10 strength reduction graphs for aged compression specimens placed in alkaline solution E chamber

The variation in tensile strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at environmental chamber after 12 months were -20.65%, -33.15%, -61.46%, and -75.07%, respectively.

Figure 6.11 Summary for tension test specimens placed in salt solution room temperature

The variation in tensile strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at room temperature after 12 months were -35%, -1%, -14% and -15%, respectively.

Figure 6.12 Strength variation summaries for tension test specimens placed in salt solution E chamber.

The variation in tensile strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at environmental chamber after 12 months were -7.48%, -9.89%, -19.26%, and -22.93%, respectively.

6.5.3 Bending strength variation with aging

Table 6.11 Strength variation for bending test specimens subjected to various aging scenario and different months

Bending		Alkaline solution room temperature							
Layers	Base test	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
No fiber	8516.00	8752.75	2.78	7950.10	-6.65	10907.94	28.09	8616.65	1.18
1-layer	8587.00	9029.76	5.16	7999.43	-6.84	9977.20	16.19	8068.38	-6.04
3-layers	11045.00	10109.32	-8.47	8434.57	-23.63	9514.97	-13.85	7714.59	-30.15
5-layers	13044.00	11238.64	-13.84	10971.73	-15.89	9046.07	-30.65	7442.62	-42.94
		Alkaline solution E chamber							
Layers	Base test	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
No fiber	8516.00	9295.44	9.15	7719.55	-9.35	9956.78	16.92	8661.99	1.71
1-layer	8587.00	8612.01	0.29	8450.12	-1.59	9258.95	7.83	7403.61	-13.78
3-layers	11045.00	8061.03	-27.02	7819.48	-29.20	8991.51	-18.59	7585.03	-31.33
5-layers	13044.00	6824.08	-47.68	7436.31	-42.99	7973.37	-38.87	6230.83	-52.23

Salt solution room temperature									
Layers	Base test	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
No fiber	8516.00	7694.56	-9.65	8644.37	1.51	10298.19	20.93	8677.52	1.90
1-layer	8587.00	7969.22	-7.19	8465.08	-1.42	11189.69	30.31	8110.86	-5.54
3-layers	11045.00	12355.51	11.87	10814.90	-2.08	13287.18	20.30	11193.21	1.34
5-layers	13044.00	13023.90	-0.15	10618.20	-18.60	14435.80	10.67	11786.07	-9.64
Salt solution E chamber									
Layers	Base test	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
No fiber	8516.00	9161.89	7.58	8298.37	-2.56	8110.16	-4.77	7382.51	-13.31
1-layer	8587.00	9042.77	5.31	7932.13	-7.63	9801.56	14.14	8224.47	-4.22
3-layers	11045.00	12101.83	9.57	10494.39	-4.99	13855.38	25.44	10493.59	-4.99
5-layers	13044.00	12636.56	-3.12	11980.67	-8.15	13591.71	4.20	11501.25	-11.83

Change in overall strength values of specimens made of recycled ABS polymers with 0, 1, 3 and 5 layers of glass fabric due to 1, 4, 8 and months of aging as compared to those without aging. Bending strength change for specimens with different layers of fabric for 1, 4, 8 and 12 months (1M, 4M, 8M, and 12M) of aging are

Aging scheme: strength change under **alkaline solution room temperature**

Strength change with 0-layer (1M, 4M, 8M, 12M): 2.78%, -6.65%, 28.09%, 1.18%

Strength change with 1-layer (1M, 4M, 8M, 12M): 5.16%, -6.84%, 16.19%, -6.04%

Strength change with 3-layers (1M, 4M, 8M, 12M): -8.47%, -23.63%, -13.85%, -30.15%

Strength change with 5-layers (1M, 4M, 8M, 12M): -13.84%, -15.89%, -30.65%, -42.94%

Aging scheme: strength change under **alkaline solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): 9.15%, -9.35%, 16.92%, 1.71%

Strength change with 1-layer (1M, 4M, 8M, 12M): 0.29%, -1.59%, 7.83%, -13.78%

Strength change with 3-layers (1M, 4M, 8M, 12M): -27.02%, -29.2%, -18.59%, -31.33%

Strength change with 5-layers (1M, 4M, 8M, 12M): -47.68%, -42.99%, -38.87%, -52.23%

Aging scheme: strength change under **salt solution room temperature**

Strength change with 0-layer (1M, 4M, 8M, 12M): -9.65%, 1.51%, 20.93%, 1.9%

Strength change with 1-layer (1M, 4M, 8M, 12M): -7.19%, -1.42%, 30.31%, -5.54%

Strength change with 3-layers (1M, 4M, 8M, 12M): 11.87%, -2.08%, 20.30%, 1.34%

Strength change with 5-layers (1M, 4M, 8M, 12M): -0.15%, -18.6%, 10.67%, -9.64%

Aging scheme: strength change under **salt solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): 7.57%, -2.56%, -4.77%, -13.31%

Strength change with 1-layer (1M, 4M, 8M, 12M): 5.31%, -7.63%, 14.14%, -4.22%

Strength change with 3-layers (1M, 4M, 8M, 12M): 9.57%, -4.99%, 25.44%, -4.99%

Strength change with 5-layers (1M, 4M, 8M, 12M): -3.12%, -8.15%, 4.2%, -11.83%

Figure 6.13 Stress strain graph for one month bending test alkaline solution E chamber specimens

Figure 6.14 Stress strain graph for one month bending test salt solution E chamber specimens

Maximum change in bending stiffness for bending specimens placed in alkaline solution with freeze thaw variation (in an environmental chamber) for up to one month were 69% and -60% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.12). Maximum change in bending stiffness for bending specimens placed in salt solution with freeze thaw variation (in an environmental chamber) for up to one month were 64% and -63% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.12).

Figure 6.15 Stress strain curve for bending specimens placed alkaline solution E chamber for eight months

Figure 6.16 Stress strain curve for bending specimens placed salt solution E chamber for eight months

Maximum change in bending stiffness for bending specimens placed in alkaline solution with freeze thaw variation (in an environmental chamber) for up to eight months were 115% and -65% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.12).

Maximum change in bending stiffness for bending specimens placed in salt solution with freeze thaw variation (in an environmental chamber) for up to eight months were 53% and -62% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.12).

Table 6.12 Stiffness variations for one and eight months aged compression specimens

No of layers	Stiffness for non aged	Alkaline Solution				Salt Solution			
		1M aged Bending stiffness	% change	8M aged Bending stiffness	% change	1M aged Bending stiffness	% change	8M aged Bending stiffness	% change
	X 10 ⁶ psi	X 10 ⁶ psi	%	X 10 ⁶ psi	%	X 10 ⁶ psi	%	X 10 ⁶ psi	%
No fibers	0.304	0.513	69%	0.654	115%	0.499	64%	0.464	53%
5-layers	0.994	0.398	-60%	0.343	-65%	0.371	-63%	0.368	-62%

6.5.4 Bar graph for bending strength variation for aged specimens

Stress variation in bending test specimens due to aging are represented in the form of bar graph-chart in following sections

Figure 6.17 Stresses for bending test specimens placed in alkaline solution room temperature

The variation in bending strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at room temperature after 12 months were 1.18%, -6.04%, -30.15% and -42.94%, respectively.

Figure 6.18 Bending strength variations for specimens placed in alkaline solution E chamber

The variation in bending strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at environmental chamber after 12 months were 1.71%, -13.78%, -31.33% and -52.23%, respectively.

Figure 6.19 Stress variations for bending test specimens placed in salt solution room temperature

The variation in bending strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at room temperature after 12 months were 2%, -6%, 1.34% and -9.64%, respectively.

Figure 6.20 Graphs for aged bending specimens placed in salt solution E chamber

The variation in bending strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at environmental chamber after 12 months were -13.31%, -4.22%, -4.99% and -11.83%, respectively.

6.5.5 Compression strength variation with aging

Table 6.13 Strength variation for compression test specimens subjected to various aging scenario and different months

Comp		Alkaline solution room temp							
Layers	Base test	1 M Stress (psi)	% change	4 M stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
0.00	8278.40	8778.34	6.04	7824.27	-5.49	8572.13	3.55	8031.72	-2.98
2.00	8172.30	7955.05	-2.66	7426.46	-9.13	7984.62	-2.30	7202.60	-11.87
6.00	7404.00	7604.35	2.71	6970.08	-5.86	7161.07	-3.28	6708.29	-9.40
10.00	6969.50	6963.04	-0.09	5662.40	-18.75	6086.33	-12.67	5552.70	-20.33
Alkaline solution E chamber									
Layers	Base test	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
0.00	8278.40	8781.46	6.08	8245.76	-0.39	7299.48	-11.82	8250.61	-0.34
2.00	8172.30	8337.65	2.02	6565.23	-19.66	6153.93	-24.70	5720.84	-30.00
6.00	7404.00	7503.12	1.34	5824.71	-21.33	6305.01	-14.84	5224.49	-29.44
10.00	6969.50	5454.23	-21.74	4680.18	-32.85	4607.78	-33.89	3780.78	-45.75

Salt solution room temp									
Layers	Base test	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
0.00	8278.40	8778.34	6.04	8121.83	-1.89	8332.53	0.65	8115.95	-1.96
2.00	8172.30	8540.26	4.50	7468.32	-8.61	8553.17	4.66	7416.63	-9.25
6.00	7404.00	8039.01	8.58	7088.92	-4.26	7443.77	0.54	7229.77	-2.35
10.00	6969.50	6012.70	-13.73	5887.66	-15.52	6226.47	-10.66	6034.97	-13.41
Salt solution E chamber									
Layers	Base test	1 M Stress (psi)	% change	4 M Stress (psi)	% change	8 M Stress (psi)	% change	12 M Stress (psi)	% change
0.00	8278.40	8555.91	3.35	7976.02	-3.65	7878.50	-4.83	7836.85	-5.33
2.00	8172.30	8360.60	2.30	7508.90	-8.12	7986.15	-2.28	7541.12	-7.72
6.00	7404.00	7623.49	2.96	7379.93	-0.33	7707.05	4.09	7290.50	-1.53
10.00	6969.50	6301.11	-9.59	5822.36	-16.46	5689.89	-18.36	5821.45	-16.47

Change in overall strength values of specimens made of recycled ABS polymers with 0, 1, 3 and 5 layers of glass fabric due to 1, 4, 8 and months of aging as compared to those without aging.

Compressive strength change for specimens with different layers of fabric for 1, 4, 8 and 12 months (1M, 4M, 8M, and 12M) of aging are

Aging scheme: strength change under **alkaline solution room temperature**

Strength change with 0-layer(1M, 4M, 8M, 12M): 6.04%, -5.49%, 3.55%, -2.98%

Strength change with 2-layers(1M, 4M, 8M, 12M): -2.66%, -9.13%, -2.3%, -11.87%

Strength change with 6-layers(1M, 4M, 8M, 12M): 3.71%, -5.86%, -3.28%, -9.4%

Strength change with 10-layers(1M, 4M, 8M, 12M): -0.1%, -18.75%, -12.67%, -20.33%

Aging scheme: strength change under **alkaline solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): 6.08%, -0.4%, -11.82%, -0.34%

Strength change with 2-layers(1M, 4M, 8M, 12M): 2%, -19.66%, -24.7%, -30%

Strength change with 6-layers(1M, 4M, 8M, 12M): 1.34%, -21.33%, -14.84%, -29.44%

Strength change with 10-layers(1M, 4M, 8M, 12M): -21.74%, -32.85%, -33.89%, -45.75%

Aging scheme: strength change under **salt solution room temperature**

Strength change with 0-layer (1M, 4M, 8M, 12M): 6.04%, -1.89%, 0.65%, -1.96%

Strength change with 2-layers (1M, 4M, 8M, 12M): 4.5%, -8.61%, 4.66%, -9.25%

Strength change with 6-layers (1M, 4M, 8M, 12M): 8.58%, -4.26%, 0.54%, -2.35%

Strength change with 10-layers (1M, 4M, 8M, 12M): -13.73%, -15.52%, -10.66%, -13.41%

Aging scheme: strength change under **salt solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): 3.35%, -3.36%, -4.83%, -5.33%

Strength change with 2-layers (1M, 4M, 8M, 12M): 2.3%, -8.12%, -2.28%, -7.72%

Strength change with 6-layers (1M, 4M, 8M, 12M): 2.96%, -0.33%, 4.09%, -1.53%

Strength change with 10-layers (1M, 4M, 8M, 12M): -9.59%, -16.46%, -18.36%, -16.47%

Figure 6.21 Stress strain graph for compression specimens placed in alkaline solution E chamber for one month

Figure 6.22 Stress strain graph for compression specimens placed in salt solution E chamber

Maximum change in compressive stiffness for compression specimens placed in alkaline solution with freeze thaw variation (in an environmental chamber) for up to one month were 262% and 50% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.14).

Maximum change in compressive stiffness for compression specimens placed in salt solution with freeze thaw variation (in an environmental chamber) for up to one month were 5% and -64% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.14).

Figure 6.23 Stress strain curve for salt soln e chamber eight months aged compression specimens

Figure 6.24 Stress strain curve for alkaline soln E chamber eight months aged compression specimens

Maximum change in compressive stiffness for compression specimens placed in alkaline solution with freeze thaw variation (in an environmental chamber) for up to eight months were 185% and 24% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.14).

Maximum change in compressive stiffness for compression specimens placed in salt solution with freeze thaw variation (in an environmental chamber) for up to eight months were 38% and -

50% for without fibers and 5-layers of fabric (12% fiber volume fraction), respectively (Table 6.14).

Table 6.14 Stiffness variations for one and eight months aged compression specimens

No of layers	Stiffness for non aged	Alkaline Solution				Salt Solution			
		1M aged comp stiffness	% change	8M aged comp stiffness	% change	1M aged comp stiffness	% change	8M aged comp stiffness	% change
	X 10 ⁶ psi	X 10 ⁶ psi	%	X 10 ⁶ psi	%	X 10 ⁶ psi	%	X 10 ⁶ psi	%
No fibers	0.312	1.13	262%	0.89	185%	0.327	5%	0.43	38%
10-layers	0.678	1.02	50%	0.84	24%	0.245	-64%	0.341	-50%

6.5.6 Bar graph for compressive strength variation for aged specimens

Stress variation in compression test specimens due to aging are represented in the form of bar graph-chart in following sections

Figure 6.25 Aged compression specimens placed in alkaline solution room temperature

The variation in compressive strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at room temperature after 12 months were -2.98%, -11.87%, -9.4% and -20.33%, respectively.

Figure 6.26 Strength reduction compression specimens placed in alkaline solution E chamber

The variation in compressive strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at environmental chamber after 12 months were -1%, -30%, -29.4% and -45.75%, respectively

Figure 6.27 Strength variation summary for salt solution room temperature aged specimens.

The variation in compressive strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at room temperature after 12 months were -2%, -9.25%, -2.35% and -13.41%, respectively.

Figure 6.28 Graphs for strength variation for aged specimens placed in salt solution E chamber

The variation in compressive strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at environmental chamber after 12 months were -5.33%, -7.72%, -2% and -16.4%, respectively.

6.5.7 Impact strength variation with aging

Table 6.15 Impact strength under different aging condition

Impact	Alkaline solution room temp								
Layers	Base test	1 M strength ft.lbs	% change	4 M strength ft.lbs	% change	8 M strength ft.lbs	% change	12 M strength ft.lbs	% change
0.00	0.28	0.30	6.71	0.49	76.26	0.46	64.27	0.25	-8.87
1.00	1.19	1.08	-9.52	0.80	-32.49	0.40	-66.11	0.41	-65.27
3.00	2.21	1.68	-24.02	1.76	-20.40	0.60	-73.01	0.60	-72.71
5.00	5.37	4.24	-21.05	2.10	-60.86	0.38	-92.86	0.37	-93.17
Alkaline solution E chamber									
Layers	Base test	1 M strength ft.lbs	% change	4 M strength ft.lbs	% change	8 M strength ft.lbs	% change	12 M strength ft.lbs	% change
0.00	0.28	0.30	7.91	0.47	70.26	0.50	79.86	0.50	79.86
1.00	1.19	0.33	-71.99	0.35	-70.87	0.35	-70.59	0.37	-68.63
3.00	2.21	0.47	-78.97	0.79	-64.12	0.37	-83.42	0.42	-81.15
5.00	5.37	0.36	-93.29	0.89	-83.48	0.37	-93.04	0.37	-93.17
Salt solution room temp									
Layers	Base test	1 M strength ft.lbs	% change	4 M strength ft.lbs	% change	8 M strength ft.lbs	% change	12 M strength ft.lbs	% change
0.00	0.28	0.31	12.71	0.44	57.07	0.44	59.47	0.50	81.06

1.00	1.19	1.77	48.74	1.19	-0.28	1.04	-12.32	1.16	-2.24
3.00	2.21	2.48	12.17	2.36	6.89	2.57	16.39	2.53	14.43
5.00	5.37	4.49	-16.39	2.94	-45.21	2.95	-44.96	2.93	-45.33
Salt solution E chamber									
Layers	Base test	1 M strength ft.lbs	% change	4 M strength ft.lbs	% change	8 M strength ft.lbs	% change	12 M strength ft.lbs	% change
0.00	0.28	0.36	28.30	0.47	67.87	0.42	49.88	0.48	71.46
1.00	1.19	0.91	-23.53	0.85	-28.57	0.77	-35.29	1.03	-13.17
3.00	2.21	2.47	11.71	2.16	-2.31	2.20	-0.35	2.27	2.52
5.00	5.37	3.92	-27.04	2.81	-47.63	2.29	-57.39	2.55	-52.54

Change in overall strength values of specimens made of recycled ABS polymers with 0, 1, 3 and 5 layers of glass fabric due to 1, 4, 8 and months of aging as compared to those without aging. Impact strength change for specimens with different layers of fabric for 1, 4, 8, and 12 months (1M, 4M, 8M, and 12M) of aging are

Aging scheme: strength change under **alkaline solution room temperature**

Strength change with 0-layer (1M, 4M, 8M, 12M): 6.71%, 0.49%, 0.46%, -8.87%

Strength change with 1-layer (1M, 4M, 8M, 12M): -9.52%, -32.49%, -66.11%, -65.27%

Strength change with 3-layers (1M, 4M, 8M, 12M): -24.02%, 1.76%, 0.6%, -72.71%

Strength change with 5-layers (1M, 4M, 8M, 12M): -21.05%, -60.86%, -92.86%, -93.17%

Aging scheme: strength change under **alkaline solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): 7.91%, 70.26%, 79.86%, 79.86%

Strength change with 1-layer (1M, 4M, 8M, 12M): 71.99%, -70.87.66%, -70.59%, -68.63%

Strength change with 3-layers (1M, 4M, 8M, 12M): 78.97%, -64.12%, -83.42%, -81.15%

Strength change with 5-layers (1M, 4M, 8M, 12M): -93.29%, -83.48%, -93.04%, -93.17%

Aging scheme: strength change under **salt solution room temperature**

Strength change with 0-layer (1M, 4M, 8M, 12M): 12.71%, 57.07%, 59.47%, 81.06%

Strength change with 1-layer (1M, 4M, 8M, 12M): 48.74%, -0.28%, -12.32%, -2.24%

Strength change with 3-layers (1M, 4M, 8M, 12M): 12.17%, 6.89%, 16.39%, 14.43%

Strength change with 5-layers (1M, 4M, 8M, 12M): -16.39%, -45.21%, -44.96%, -45.33%

Aging scheme: strength change under **salt solution E chamber**

Strength change with 0-layer (1M, 4M, 8M, 12M): 28.3%, 67.87%, 49.88%, 71.46%

Strength change with 1-layer (1M, 4M, 8M, 12M): -23.53%, -28.57%, -35.29%, -13.17%

Strength change with 3-layers (1M, 4M, 8M, 12M): 11.71%, -2.31%, -0.35%, 2.52%

Strength change with 5-layers (1M, 4M, 8M, 12M): -27.29%, -47.63%, -57.39%, -52.54%

6.5.8 Bar graph for impact strength variation for aged specimens

Strength variation in impact test specimens due to aging are represented in the form of bar graph-chart in following sections

Figure 6.29 Impact strengths for specimens placed in alkaline solution room temperature

The variation in impact strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at room temperature after 12 months were -8.87%, -65.27%, -72.17% and -93.17%, respectively.

Figure 6.30 Impact strength variation for specimens subjected to alkaline solution E chamber aging

The variation in impact strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in alkaline solution at environmental chamber after 12 months were 80%, -69%, -81% and -93%, respectively.

Figure 6.31 Impact strength summaries for specimens subjected to salt solution room temperature

The variation in impact strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at room temperature after 12 months were +81%, -2.24%, +14.43%, and -45.33%, respectively.

Figure 6.32 Summary for impact specimens subjected to aging under salt solution E chamber

The variation in impact strength of specimens with 0, 1, 3 and 5 layers of glass fabric aged in salt solution at environmental chamber after 12 months were +71.4%, -13.17%, +2.52% and -52.54%, respectively.

Table 6.16 Maximum strength reductions for tension, bending comp and impact specimens

	Maximum property change in 12 months				
No of layers	Conditioning scheme	Tension	Bending	Compression	Impact
No fabric	A-RT	-36%	-6.65%	-5.49%	-8.87%
	A-EC	-20.65%	-9.35%	-11.82%	+7.91%
	S-RT	-35.1%	-9.65%	-1.96%	+12.71%
	S-EC	-28.89%	-13.31	-5.33%	+28.3%
1-layer	A-RT	-24.36%	-6.84%	-11.87%	-66.11%
	A-EC	-33.15%	-13.78%	-24.7%	-70.87%
	S-RT	-7.03%	-7.19%	-9.25%	-12.32%
	S-EC	-16.56%	7.63%	-8.12%	-35.29%
3-layers	A-RT	-54.26%	-30.15%	-9.4%	-72.71%
	A-EC	-61.46%	-31.33%	-29.44%	-83.42%
	S-RT	-14.18%	-2.08%	-4.26%	+6.89%
	S-EC	-19.75	-4.99%	-1.53%	-2.31%
5-layers	A-RT	-65.76%	42.94%	-20.33%	-93.17%
	A-EC	-75.07%	-52.23%	-45.75%	-93.29%
	S-RT	-16.82%	-9.64%	-15.52%	-45.33%
	S-EC	-41.02%	-11.83%	-18.36%	-57.39%

From Table 6.16, maximum reduction in tensile, bending, compression, and impact strengths were (-36%, -13.31%, -11.82%, -8.87%), (-33.15%, -13.78%, -24.7%, -70.87%), (-61.46%, -31.33%, -29.44%, -83.42%), and (-75.07%, -52.23%, -45.75%, -93.29%), respectively, for corresponding 0, 1, 3, and 5 layers of glass fabric reinforcement.

7.0 Thermoplastic Thermoset Sandwich Specimens

7.1 Introduction

Thermoset and thermoplastic sandwich specimens are useful in structural application such as rail road (RR) ties; guardrail offset blocks, and others. We can optimize their mechanical properties by combining thermoset and recycled thermoplastics and minimize the costs. For example, thermoset shell can be used on a thermoplastic core in a railroad tie. In this research, thermoplastic and thermoset sandwich specimens were manufactured to evaluate their tensile and bending strength. These specimens were prepared such that their interface were either smooth (no surface roughening-NSR) or roughened (surface roughening - SR). Altogether six combinations of thermoplastic and thermoset sandwich composite specimens were manufactured:

- i) Thermoplastic/thermoset/thermoplastic (TP/TS/TP) (roughened)
- ii) Thermoplastic/thermoset/thermoplastic (TP/TS/TP) (un-roughened)
- iii) Thermoset/thermoplastic/thermoset (TS/TP/TS) (roughened)
- iv) Thermoset/thermoplastic/thermoset (TS/TP/TS) (un-roughened)
- v) Thermoset/thermoplastic (TP/TS) (roughened)
- vi) Thermoset/thermoplastic (TP/TS) (un-roughened)

7.2 Tension test results

Table 7.1 shows tension test results of sandwich specimens with a double interface between thermoplastic, thermoset and thermoplastic surfaces, with or without surface roughening.

Note: TP-thermoplastic, TS-thermoset, TP/TS/TP –thermoplastic/thermoset/thermoplastic, N/SR- No Surface Roughening, SR- Surface Roughening

Table 7.1 Thermoplastic thermoset (TP/TS/TP) tension test result

Composite sandwich	Specimen #	Average area	Stress	Average	% increase
		sq.in.	(psi)	(psi)	
TP/TS/TP	1	0.444	8533.339	8470.641	5.8872 %
N/SR	2	0.462	7837.385		
	3	0.457	8914.47		
	4	0.428	8771.568		
	5, S	0.427	8296.446		
TP/TS/TP	6	0.416	9217.087	8969.333	
SR	7	0.408	9569.446		
	8	0.422	8532.566		
	9	0.431	8931.17		
	10, S	0.420	8596.398		

The Modulus of elasticity of TP/TS/TP roughened and un-roughened specimens were evaluated to be 0.546×10^6 psi and 0.573×10^6 psi, respectively. The tensile stresses of un-roughened and roughened TP/TS/TP sandwich composite were found to be 8470.6 psi and 8969.3 psi, respectively. The tensile stress of sandwich specimens prepared with surface roughening was 5.88% more than un-roughened specimens.

Figure 7.1 Thermoplastic/Thermoset/Thermoplastic tension test

Figure 7.2 Stress strain graph for TP/TS/TP roughened tension test specimen

Figure 7.3 Stress strain graph for TP/TS/TP roughened specimen

Table 7.2 shows sandwich composites with a single interface between thermoplastic and thermoset components.

Table 7.2 Thermoplastic thermoset (TP/TS) tension test results

Specimen type	Specimen #	Average area	Stress	Average	% increase
		sq.in.	(psi)	(psi)	
TP/TS	21	0.161	9088.438	9088.438	
N/SR					
TP/TS	11	0.159	9031.591	9174	
SR	12	0.168	*7658.28		5.88%
	13	0.160	9362.081		
	14, S	0.160	9128.131		

*values are not considered for averaging due to improper grip failure

Figure 7.4 Stress strain graph for TS/TP roughened tension test specimen

Strain gages were applied on both thermoset and thermoplastic (roughened) component of the sandwich tension test specimen and tensile modulus was evaluated to be identical on both components, i.e., 0.571×10^6 psi and 0.576×10^6 psi, respectively (Fig 8.4). The maximum recorded strain for thermoset and thermoplastic specimens were 15869 and 15327 strains, respectively. Average tensile stress of TP/TS roughened and un-roughened specimens was evaluated to be 9174 psi and 9088 psi, respectively. Tensile stresses are not compared with TP/TS sandwich specimens without roughening, because only one specimen survived the vibrations without any delamination/separation during machining.

Table 7.3 Thermoplastic thermoset (TS/TP/TS) tension test results

Specimen type	Specimen	Average Area	Max load	Stress	Average
TS/TP/TS	#	sq.in.	(lbs)	(psi)	(psi)
SR	15	0.19184	2200	11467.91	11371.16
	16, S	0.192826	2174	11274.41	
	sample1	0.22	1958.5	*8902.273	

*not considered for averaging due to improper grip failure

Figure 7.5 Stress strain graph for TS/TP/TS roughened tension test specimen

The modulus of elasticity for TS/TP/TS roughened sandwich specimens from Fig 7.5 was evaluated to be 0.72×10^6 psi. Specimens with roughened thermoplastic center and thermoset on either side carried highest average stress (11371 psi) amongst the entire tension test specimens (Table 7.3). Similar type of specimens without surface roughening delaminated during machining operation due to poor bond.

Table 7.4 Thermoplastic thermoset (ABS and vinyl ester) tension test results

Specimen type	Specimen #	Average area sq.in.	Stress (psi)	Average (psi)
Plain ABS	17	0.194	6646.812	6709.968
TP	18	0.193	6242.976	
	19	0.192	7251.072	
	20, S	0.196	6699.012	
Plain VE	22, S	0.073	18042.85	19864.34
TS	23	0.069	19030.07	
	24	0.069	22300.74	
	25	0.070	19795.06	
	26	0.062	20152.98

Figure 7.6 Stress strain curve for plain vinyl ester and virgin ABS tension test specimen

The tensile modulus of elasticity for plain vinyl ester and plain ABS specimens were calculated to be 1.14×10^6 psi and 0.45×10^6 psi (Fig 7.6). The tensile modulus for vinyl ester was 153.33% more than plain ABS specimen. Tensile stresses for plain vinyl ester ABS plates were calculated to be 19864.3 psi and 6710 psi, respectively.

7.2 Bending Test Results

Table 7.5 Thermoplastic thermoset bending test results

Specimen type	Specimen	Average area	Stress	Average	% increase
	#	b x d.	(psi)	(psi)	
TP/TS/TP	27	0.592	4115.969	4164.241	45.70%
N/SR	28	0.600	3915.919		
	29	0.584	4460.836		
TP/TS/TP	30	0.568	6832.867	6066.988	
SR	31	0.561	5780.159		
	32	0.573	5587.938		

The bending stresses for TP/TS/TP sandwich specimens were calculated to be 4164 psi and 6067 psi for un-roughened and roughened specimens, respectively. Roughening of ABS plates to grip

vinyl ester resin was efficient for TP/TS/TP specimens, which improved the bending stresses by 45.7% when compared with TP/TS/TP un-roughened specimens.

Figure 7.7 (a) Bending test setup

Figure 7.7 (b) Delamination of TP/TS/TP bending specimen

Figure 7.7 (c) Delamination of TP/TS ABS bottom bending specimen

Figure 7.7 (d) Delamination of TS/TP/TS ABS bottom bending specimen

Figure 7.7 Delamination of thermoplastic and thermoset sandwich composite

Delamination/separation was observed in every thermoplastic and thermoset sandwich composite bending and tension test specimens during the tests. Prior to delamination, buckling of compression side components were observed in the sandwich specimen.

Table 7.6 Thermoplastic thermoset (TP/TS) bending test results

Specimen Type	Specimen #	Average area b x d	Max load (lbs)	Stress (psi)	Average (psi)	% increase
TS/TP (SR)	37	0.233	62	7531.05	8064.109	
ABS bot	38	0.239	69	7969.058		
	39	0.233	69	8692.22		
TS/TP (SR)	40	0.230	71	8980.017	9092.338	12.70%
VE bot	41	0.224	62.69	8303.22		
	42	0.225	74.6	9763.288		
	43	0.232	74	9322.826		
TS/TP/TS	44	0.277	116.75	10558.28	10354.65	13.88%
SR	45	0.280	108.89	9557.521		
	46	0.275	143.34	12721.9		
	47	0.280	96.98	8580.892		

Bending stresses for TP/TS composite specimens tested with thermoplastic on bottom side was calculated to be 8064 psi. Bending stress increase was 12.7% when the TP/TS specimens were tested with vinyl ester side faced bottom with stress of 9092.3 psi. Bending strength of TP/TS composite specimens having vinyl ester on either side of roughened ABS plate was increased by 13.88% compared to vinyl ester bottom facing specimens, when tested for bending strength.

7.4 Summary

Test results show that vinyl ester composite with 2 layers of glass fabric is about 3 times stronger and 2.5 times stiffer than similarly reinforced ABS. Hence, in a sandwich specimen it is advantageous to use thermoset composite as a shell and thermoplastic as a core to maximize bending strength of products as composite RR ties.

8.1 Conclusions for Durability

8.1.1 Tension

- For testing rectangular specimens, ventilated metal tabs were developed and used. They worked very well and ensured perfect failure of specimens away from the grip location.
- Average stress of the tension test coupon specimen without glass fabrics (from Table 6.1) was found to be 4653 psi and the average stresses of 1, 3 and 5 layer tension test coupon samples were found to be 5010.3, 8543 and 10484.2 psi, respectively, with a corresponding stress increase of 8%, 60% and 125%.

- Maximum tensile strength loss was noted for specimens placed in alkaline solution and environmental chamber (Table 6.9).
- Maximum tensile strength reduction was 36% for non fabric specimens aged in alkaline solution at room temperature, whereas, the tensile strength reduction was 33.15%, 61.46%, and 75.07% for specimens with 1, 3 and 5-layers, respectively, aged in alkaline solution environmental chamber when compared to corresponding non aged specimens.
- Average tensile stiffness without fibers was 0.31×10^6 psi, and with 1, 3 and 5 layers the values were noted to be 0.463×10^6 psi, 0.675×10^6 psi, and 0.774×10^6 psi, respectively. Each per layer tensile layer stiffness increase was 49%, 39% and 49% for 1, 3 and 5 layered specimens, respectively.

8.1.2 Bending

- Bending stress without fibers was 8516.35 psi. Bending stresses for specimens with 1, 3 and 5 layers of bi directional glass fabrics increased to 8587 psi, 11092.8 psi and 13043.82 psi, respectively. Percentage increase in bending stress for 1, 3 and 5 layers specimens (4%, 7% and 12% fiber volume fraction, respectively) without fibers was 1%, 30% and 53%, respectively.
- Maximum bending strength reduction was noted to be 13.31% for non fabric specimens placed in salt solution at E chamber. However, maximum bending strength reduction for specimens with 1, 3, and 5 layer specimens were 13.78%, 31.33% and 52.33%, respectively, when compared to corresponding non aged specimens.
- Bending stiffness for specimens without fiber was 0.304×10^6 psi and the stiffness for specimens with 1, 3 and 5 layers were noted to be 0.447×10^6 psi, 0.447×10^6 psi and 0.994×10^6 psi, respectively. Percentage increase in bending stiffness was 47% for 1 and 3 layer specimens, and 164% for 5-layer specimens.
- Maximum strength reduction of 1.71%, -13.78%, -31.33% and -52.23%, was noted for all 12 months aged 0, 1, 3 and 5 layers bending specimens placed in alkaline solution at environmental.

8.1.3 Compression

- Compression stress for specimens without fibers was 8278 psi and the strength decreased with the increase in number of fiber layers. Average stress of 2-layer compression specimens was 8172 psi which was 1.28% less than the specimen without fabric. Similarly, 10.56% and 15.81% reduction was noted for 6 and 10 layers compression specimens with the average stress values of 7403 psi and 6969 psi, respectively.
- Reduction in strength and increase in stiffness was noted for fiber reinforced compressive specimens when compared to specimens without fibers. The maximum compressive strength reduction for specimens with 0, 1, 3, and 5 layers were 11.82%,

24%, 29.4% and 45.75%, respectively, aged in alkaline environmental chamber when compared to corresponding non aged specimens.

- Debonding (splitting) between polymer and fibers layers was observed for some of compression test specimens with 6 and 10 layers of glass fibers aged in alkaline solution.

8.1.4 Impact

- Average impact strength for specimens without fibers was 0.278 ft-lb's and the strength increment was noted with fiber addition. For 4%, 7% and 12% fiber volume fraction, the average impact strengths were 1.19 ft.lbs, 2.21 ft.lbs, and 5.37 ft.lbs, with a compressive strength increment of 328%, 698% and 1828% strength increment were noted, respectively.
- The maximum impact strength reduction for non fabric specimens was 8.87% aged in alkaline solution at room temperature. The impact strength reduction for specimens aged in alkaline solution E chamber were 70.87%, 83.42% and 93.29% for specimens with 1, 3 and 5 layers, respectively.
- Complete breakage of fiber layers with type C failure was observed for specimens placed in alkaline solutions only. Hinge formation was observed for specimens with 3 and 5 layers of fibers aged in salt solution.

8.2 Conclusions for thermoplastic and thermoset blend

8.2.1 Sandwich Composite Tension

- Tensile strength increased by 6% by roughening the surface of thermoplastic at the interface of the sandwich.
- Tensile stiffness of roughened and un-roughened (TP/TS/TP) specimens were evaluated to be almost identical, i.e., 0.546×10^6 psi and 0.573×10^6 psi, respectively.
- Tensile stiffness from single thermoplastic/thermoset roughened tension test specimen was evaluated to be 0.576×10^6 psi and 0.571×10^6 psi for thermoplastics and thermoset composite component, respectively.

8.2.2 Sandwich Composite Bending

- Roughened thermoplastic/thermoset/thermoplastic bending test specimens carried 45.7% higher stress than un-roughened bending specimens. However, every bending specimen delaminated first and then failed.
- Roughened thermoplastic/thermoset sandwich specimens with vinyl-ester on tension side carried 12.7% more stress, when compared with specimens with ABS polymer on tension side.

- Bending strength of specimens with vinyl ester on either side of roughened ABS plate was increased by 13.88%, when compared to vinyl ester on only bottom surface of the specimens.

8.3 Summary

Among salt and alkaline conditioning schemes at room temperature or with freeze thaw variations, maximum reduction in tensile and bending, strengths with up to 5 layers of glass fabrics were found to be 36% and 71%, respectively, whereas those of compression and impact strengths were in excess of 80%. These reductions are expected when glass reinforcements are subjected to high pH alkaline environment in accelerated aging studies that relate to a actual service life of 50 to 100 years in field conditions. These durability studies provide a basis for understanding degradation patterns of composites and highlight the importance of proper resin saturation.

These research results indicate the significant potential and strength gains in recycled polymer composites with the use of continuous glass fabrics (e.g., bidirectional fabrics). These fabrics were successfully utilized in making recycled polymer composite structural components for highway, housing, and automobile applications. These products can be scaled to suit other prototype applications. One such application involving the manufacture and development of full-scale recycled railroad composite tie is being further explored. It is important to ensure proper resin coating of continuous glass fabrics in structural composites, because they are susceptible to aging related degradations (locally or globally), particularly under alkaline solution exposures.

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17. <http://www.humiditycontrol.com/>

Task 1.3: Process closed loop and open loop EOLE plastics to develop high level technology designs plastics recycling train

The Recipient shall submit a Phase I Plastics Recycling Demonstration Plan to the DOE which delineates the location of demonstration facilities, subcontracted effort, equipment to be used and tested, and experimental parameters to be studied. The DOE will review the Plan with 30 days of receipt, and provide the Recipient with concurrence or recommended changes. The Recipient shall not proceed with demonstration activities without prior approval by the DOE.

The Recipient shall identify the best available technologies for recycling of plastics from end-of-life electronics and similar products. This will include evaluation of demonstration technologies with assessments of the capabilities of the various plastics separation and processing technologies existing around the United States. After identifying the criteria for determining the best technologies, evaluations of technologies tested through this effort will be used to determine which plastics recycling processes or combination of processes should be developed at the PTP for future plastics processing.

This approach includes proof-of-concept demonstration activities utilizing EOLE plastics for closed loop and open loop applications. The estimated cost of each step will be determined and the advantages/disadvantages and issues/concerns will be documented. When appropriate, recommendations for further research, identification of processes that need further development and other ways to reduce cost, improve efficiency and reduce material handling will be defined. High level technology designs will be initiated.

Subtask 1.3.1 Closed Loop Demonstration

The Recipient shall process EOLE plastics with specific feedstock compositions from OEMs, with the goal of recovering recycled plastics with sufficient quality to be utilized by the OEM for electronic products. Product quality and yield will be evaluated to determine feasibility of utilizing the recycled plastic for OEM re-use, high-value applications, and low-value applications.

Subtask 1.3.2 Electronics Recycling Pilots/Plastics Demonstration Integration

The Recipient shall process “open loop” EOLE plastics with mixed feedstock compositions with the goal of recovering recycled plastics with sufficient quality for high value applications. Product quality and yield will be evaluated to determine the feasibility of utilizing the recycled plastics for OEM re-use, high-value applications, and low-value applications. Other EOLE collections programs will be supported for better generation and management of plastic output.

Subtask 1.3.4 MARCEE Project Outreach and Education

The Recipient shall develop and provide outreach and education services to promote EOLE recycling and the need for electronics recycling infrastructure improvements among public and private sector interested in working cooperatively with the MARCEE project. This will involve dissemination of project information at tradeshow and conferences. This will take the form of

PowerPoint presentations, newsletters, and participating on panels specifically targeted at recycling end-of-life electronics.

Task 2.3 Demonstration of Recycling Technologies and High Level Design

The Recipient will continue to assess and refine the capabilities of the various plastic separation and processing technologies including their cost structure. The Recipient will design, develop and implement a semi-automated identification and sorting system for commingled plastics from EOLE.

Tasks 3.1 and 4.1 were not defined for the SOPO since the funding level was reduced and the scope of the project curtailed.

Only Tasks and Sub-tasks under 1.3 (with the exception of 1.3.4) and 2.3 have been addressed with the reduced funding available to this project.

MARCEE Plastics Demonstration (PI/D. Ritchie)

Introduction

A 1999 Department of Energy (DOE) and Environmental Protection Agency (EPA) congressional appropriation enabled the Mid-Atlantic Recycling Center for End-of-Life Electronics (MARCEE) to be formed. MARCEE's objective is to lay the foundation for building a viable recycling industry in West Virginia for End-of-Life Electronic (EoLE) products. It is estimated that only 10% of EoLE is recycled, but it's one of the fastest growing segments of the nation's waste stream comprising between 3-5% of municipal solid waste. This is expected to continue increasing for the foreseeable future.

The separation of glass and metals from EoLE is now being practiced and is becoming an economically viable industry. However, the separation and reuse of plastics has not occurred. Plastics are either being placed in landfill sites or sold to overseas vendors for marginal value. Neither of these approaches is sustainable and alternative methods of disposing and recycling these materials need to be developed. If plastics recycling and reuse is to become a reality, the problem of identifying and sorting these materials cost-effectively needs to be demonstrated. In 2003, SDR Technologies (SDRT) agreed to take on this task within the MARCEE project.

In 2000 the Department of Defense (DOD), through Concurrent Technologies Corporation, built a pilot plant facility to demanufacture EoLE equipment. Its mandate was to identify, explore and validate processes to recover and recycle EoLE that are environmentally friendly. A description of the equipment, known as DEER 2, and some preliminary data, is given in a DOD report entitled "*Pilot Electronic Equipment Demanufacturing, Recycling and Reuse Systems*". This process was put together under Contract Number DAAE30-98-C-1050 awarded by the DOD. This plant is no longer being used.

In September 2006 the MARCEE Project requested that the DOE/NETL relocate the DEER 2 Equipment to West Virginia (WV). This request was granted in September 2006 and title to this equipment passed from the DOD to the DOE. It was thought that SDRT needed access to this equipment because it contained all the process elements necessary for a recycling demonstration. However, over the past two years, SDRT had been investigating commercially available plastics recycling equipment in various equipment manufacturers' laboratories. They came to the conclusion that wet process methods, such as sedimentation and hydrocyclone separation, are too inefficient for a high volume process. This makes them economically unattractive. The efficiency of separation of chemically different polymers using this technique is also unacceptably low for a commercial operation. In the DEER 2 facility, they also use an electrostatic technique to separate different types of plastics. SDRT has experimentally determined that this is not an effective or economically attractive method to use.

Since 2006-2007, SDRT has been assessing the use of an optical separation technique in place of the wet processes outlined above. In this method a near infrared (NIR) spectrometer scans a conveyor belt. It identifies the chemical nature of the plastic which is redirected pneumatically into an appropriate collection bin. During the past few months, SDRT has seen the effectiveness of this technique improve dramatically with excellent separation efficiencies being observed. Besides NIR, x-ray techniques have also been modified for use in identifying mixed and additive containing plastics. For example, it is possible using x-ray identification, to separate flame retardant containing plastics from non-flame retardant plastics even when the plastic is from the same chemical class. This level of separation should greatly enhance the value of these materials.

A plan was developed for the plastics separation demonstration, which is to insert NIR and x-ray equipment with pneumatic separation methods into an automated recycling line. Implementation of this approach will allow us to demonstrate a highly efficient, scalable, recycling system for the recovery of plastics from EoLE equipment.

In this report we outline the objectives of the plastics recycling demonstration. The equipment to be used and its potential configuration in identification and sorting are described as are preliminary results.

Objectives of the Plastics Recycling Demonstration

During the past few years, the subject of EOLE recycling has attracted a lot of interest. There are now numerous conferences devoted to this subject, the best known being E-Scrap. In 2006, E-Scrap attracted close to four hundred attendees. Prior to ~2004, attendance was confined to policy and engineering research personnel. It is now attended by new entrants to electronics recycling as well as policy and research personnel.

The recycling of EOLE is now becoming a viable and fast emerging business. Profits are generated in numerous ways; by selling printer cartridges to third party vendors for refurbishment, by remanufacturing working devices and selling circuit boards for their metals content. However, a secondary market for the plastics from EoLE has not been generated. The main reason for this is that mixed plastics, or plastics with low levels of other contaminants exhibit properties that are greatly inferior compared to virgin material. As a result, the objectives of the plastics demonstration project are:

- To effectively separate mixed plastics with high purity.
- To demonstrate operations such as size reduction, metal removal and decontamination/cleaning procedures in conjunction with identification and sorting processes for the plastics from EOLE.
- Understand what the throughput limitations of the equipment are and how to circumvent throughput bottlenecks i.e. what is the optimum plant layout for a given sort volume.
- Develop an understanding of the costs involved in processing mixed plastics. The economics will dictate whether reuse of these plastics is viable, rather than reprocessing them into chemical or energy feedstock.

Collecting meaningful data on these issues should allow MARCEE to gain valuable insights into the economics of plastics identification and purification. This understanding is essential before deciding whether recycling EOLE plastics can be a viable business.

In undertaking this task Gaiker (Zamudio, Spain) and MBDC (Charlottesville, VA) were asked to recommend equipment that could be used to identify and sort plastics into individual chemical classes. These recommendations guided the demonstration project of SDR Technologies (Millwood, WV).

Description of the Plastics Identification/Separation Process

A significant amount of thinking and development work regarding plastics identification and sorting has been carried out by Gaiker and by MBDC. The results of these activities together with the lessons learned from the DEER 2 development program provides the starting point for the SDRT development activities.

General Overview

The process is divided into five sections, each of which is described below:

Plastics Preparation.

In the first step, EoLE plastics, obtained as baled, nested or loose parts will be shredded and screened to create uniform size plastic pieces. Uniform part size is critical for the successful separation of plastics by chemical class. This step also involves the detection and removal of any metals that are present in the plastic.

Plastics Identification/Separation Step 1

This process could utilize one or more NIR detectors. The first NIR unit is intended to recover a specific type of plastic. The second unit is needed to maximize the purity of the material recovered from the first NIR unit. For demonstration purposes, this section of the process will be set up to allow for the discarded plastics to be introduced back into the system. This will allow

for several “passes”, therefore the same equipment can be utilized to identify and separate several different classes of plastic. This section of the process could be enhanced by installing additional NIR units. However, the use of two NIR units is both efficient and essential for the demonstration. However, we have only utilized one unit in our experiments to date. Both the NIR and material handling equipment will need to be purchased. In this report, a comparison of the performance of the two NIR units presently on the market is discussed. A recommendation as to which brand of unit to purchase is made.

Plastics Identification/Separation Step 2

In this step we use an x-ray spectrometer to identify and separate plastics according to whether they contain a fire retardant (FR) or are FR-free. This is a new application for identifying additives in plastics which has become available during the past year. Identification of FR's in plastics is important in the present environment. The majority of FR's for plastics contain bromine, many of which are now considered to be hazardous. Consequently, separating FR from non-FR plastic enhances both their values. Following this separation, the plastic will be granulated which will reduce the particle size and will help to clean the product. Because x-ray identification separates the plastic into two streams, two granulators, two aspirators and two air classifiers will need to be purchased together with an x-ray spectrometer

Plastics Purification Process

This process is designed to remove any remaining non-metallic contamination. Using a wash and dry process, contamination such as labels, paper, foam and dirt will be removed. Removal of foreign material will improve the properties and increase the value of the plastic. It will allow recycled plastics to be used in a wider range of applications. A wash tank and a dryer will need to be purchased.

Purification/Plastics Modification

Final cleaning of the material is achieved using a melt filtration process which removes any remaining residual contaminants. This process also allows for modifiers to be incorporated into the recycled plastic. This step could be used to obtain a material for a customer which has specific requirements, or to eliminate lot-to-lot variances in the recycled plastic. An extruder with a continuous screen changer will need to be purchased.

Discussion of Materials Flow

The main plastics found in EoLE products are polycarbonates (PC), acrylonitrile-butadiene-styrene (ABS), high impact polystyrene (HIPS) and polycarbonate-acrylonitrile-butadiene-styrene (PC-ABS). The SDRT demonstration will start with demanufactured plastic rather than shredded plastic. The objective of the demonstration is to identify the various commingled plastics in real time and separate them to a high purity level. In order to explain the process, we assume, for example, that we initially need to obtain PC from this plastics mixture. The PC obtained should be at least 95% pure in order to preserve its desired physical properties. The PC

also needs to be separated into FR and non-FR containing material. There are two methods of carrying out this task. Each method is discussed below.

Manual Reclamation of Plastics

In order to process large quantities of recycled plastic, the first priority was to procure an accurate and robust plastics identification technology. This is of extreme importance since plastics procured from electronics de-manufacturing operations typically only segregate plastics into two categories: light and dark. Such plastics would increase substantially in value if separated by resin type to meet the demand of processors for producing higher valued materials. Therefore, research was carried out to discover the most desirable plastics identification and sorting technology available and evaluate its utility for meeting the goals of this project. Accordingly, a considerable amount of relevant information was generated from the literature, technical contacts, university visits, and from our MARCEE partners, Gaiker and MBDC. It was learned that in 2005 there were several commercial choices for making manual resin identifications and that auto identification and sorting equipment was under test and targeted to reach the marketplace in 2006.

The technology selected for making manual resin identifications was the mIRoSpark from IoSys in Ratingen, Germany. This “method of choice” for manual identification was used in collaborative work with the Amandi Services operation in the Polymer Technology Park. Large quantities (baled form) of EOLE plastics were identified (e.g., ABS, PS, PC/ABS, and PC) and sorted using mIRoSpark identification technology. The mIRoSpark from IoSys uses two dissimilar technologies housed within the same unit to identify various polymer materials. The first technology mIRo uses near infra-red (NIR) optical light to identify polymers. Polymers (non-black) when exposed to NIR light reflect a specific signature wavelength that in turn, can be identified via the mIRo’s multi-channel spectrometer. The analyzed light wave is then transmitted to a signal that displays the identity of the polymer on a 6.5” flat screen display. Black or opaque colored polymers cannot be analyzed by this technique as the NIR light is absorbed into the black or opaque colored material and not be reflected back for analysis.

The second technology, Slide- Spark or “Spark”, induces a brief electrical discharge across two metal electrodes which are separated from one another by distance of a few millimeters. By placing a polymer material across the two electrodes within the electrical discharger area, a small region of the surface of the polymer is vaporized, emitting a characteristic light radiation or optical emission spectrum. The optical emission spectrum is then analyzed for the composition of the polymer leading to its identification as well as the identification of elements such as bromine, chlorine and phosphorus within the polymer composition. This added level of identification allows the separation of flame retardant plastics from non-flame retardant plastics. Additionally, black and opaque polymers can often be identified with the mIRoSpark equipment from the developed vapor pattern. Relative to the mIRo mode for polymer identification, the Slide-Spark mode is less reliable but still quite useful in the manual reclamation of plastic material. With a two person operation, using equipment as shown in the Figure 1, the rate of plastics recovery was about 150-200 pounds per hour.

It was of interest to learn if manual reclamation could be an economically acceptable alternative to auto procedures (yet to be completely developed) which can provide “cleaned up plastics with good mechanical properties” at a cost that is not prohibitive.

This study targeted three types of materials to retain from the stream of commingled EOLE plastic parts; ABS, PC/ABS, and HIPS. Parts were identified for their plastic type by the use of mIRoSpark and accordingly segregated. The pressure sensitive labels were removed by scraping with a chisel or cutting off the plastic sections with a Dremel tool, nuts and bolts were removed with the use of an electric screw driver and the acoustic foams were removed by cutting off the plastic section with the use of the Dremel tool. The “cleaned parts” were then granulated and pelletized. The pellets were then molded into test specimens for determination of their notched Izod impact strength, melt flow and heat distortion temperature. The notched Izod impact strength was in the acceptable range for HIPS and PC/ABS, whereas it was low for the ABS resin. The heat distortion temperature was comparable to prime resins for all the three resins. Melt flow of ABS and HIPS was in the acceptable range; however, the melt flow of PC/ABS was on the high side. The manual “cleaning process” needs to be improved to be more cost competitive. It is believed that with some modification to the process and the addition of supplementary reclamation equipment items the conversion cost can be decreased to approximately \$0.26/pound. (which includes the \$0.15/ pound purchase cost for the commingled EOLE).

Figure 1: Two-Man Manual Identification Layout

Automated Reclamation of Plastics

By early 2006, several manufacturers were distributing literature, exhibiting at trade shows, and making customer contacts related to the development of a combined means of automation for identifying and sorting commingled shredded EOLE plastics. It was concluded that companies at the forefront of this technology development were TiTech (Koblenz, Germany), MSS (Nashville, TN), NRT (Nashville, TN) and S+S Sorting (Schonberg, Germany). In all cases, optical sorting technology was used for the identification of the plastic types and air ejection methods for the sorting of EOLE plastics. This combined technology had been used for a number of years in the sorting and separations of plastic bottles but not until 2006 had it become commercially available for the sorting of EOLE plastics. As an “add-on” technology, TiTech thru its subsidiary

(CommoDas) was marketing Atomic Density Technology (X-Tract separator) equipment. The X-Tract was advertised as useful for separating flame retardant (FR) from non-flame retardant (NFR) plastic materials. For preliminary testing, TiTech and MSS were selected for collaborative studies with SDRT.

The preliminary testing was to be conducted at the equipment manufacturer's site in 4Q-2006. The mIRoSpark equipment, purchased earlier by SDRT, was of invaluable benefit in the preparation of test specimens to be used in the evaluation of the vendor's equipment. The mIRoSpark allowed for SDR Technologies to accurately develop a synthetic "control" group of plastic materials from otherwise unknown plastics sourced from EOLE. The controls, once identified, were assigned a specific color code identifier to each specific polymer type. By using this color code system for the individual polymer types, it was possible to immediately track, measure, and compare the effectiveness of the automatic sorting technology from various manufacturers. This also allowed for SDR Technologies to verify claims made by the manufacturers as well as identify limitations with their technology. By taking these steps SDR Technologies was able to procure the most effective automated sorting technology on the market. Furthermore, these controls also allowed for the manufactures to further refine and enhance their identification technology.

In the 4Q of 2006 preliminary testing at TiTech and MSS was carried out with encouraging results being obtained. These results left no doubt that the combination of optical sensor (for ID determination) and air ejection for separation was a very effective route (validation) for automatically processing mixed stream plastics. TiTech's Polysort unit outperformed the MSS E-Sort unit. Concomitantly, the X-Tract Separator was evaluated for separation of flame retarded (FR) plastics from non-flame retarded (NFR) plastics and found to be highly effective. TiTech's Metal Finder technology was also demonstrated. While the Metal Finder was very efficient, it was quite expensive. In 2007 comparative "metal removal" testing of a similar unit from S+S showed it to be as effective but less expensive, leading to the purchase of the S+S equipment.

During the first half of 2007 trials continued in order to identify the optimum automated identification and sorting technology. SDRT conducted additional in-depth testing at TiTech (Polysort) and at MSS (E-Sort). Comparison performance data of the NIR units from TiTech and MSS are given in Table 1. Such results justified the purchase of the TiTech equipment. The technology at both companies was superior to all others.

In the second half of 2007, the design of a pilot scale facility was developed as shown in Figure 2. The design included intermixing peripheral conveying systems for bringing shredded EOLE plastics to the sorting technologies. The selection of the vibratory feeding unit to presort EOLE plastics in a uniform manner will allow the separation technology to operate effectively. The design of workstation platform units allows technicians to oversee the operation of all the combined technologies.

Figure 2: Design of Pilot Scale Facility

Table 1: Comparison Performance Data of the Optical Sorting Equipment from TiTech and MSS

Polymer Materials	MSS		TiTech	
	Purity (%)	Recovery (%)	Purity (%)	Recovery (%)
ABS	<80%	<70%	>93%	>98%
PS	<85%	<80%	>92%	>98%
PCABS	<85%	<90%	>91%	>97%

It can be seen from Table 1 that the TiTech unit performs more effectively, with both higher recovery and purity levels of the recycled polymer being obtained. The results from TiTech are also more consistent than from the MSS equipment. We therefore purchased the TiTech Polysort Unit over the MSS E-Sort equipment. However, we continue to interact with MSS in order to help them improve the performance of their NIR spectrometer.

The x-ray spectrometer currently offered for use for plastics recycling is made by CommoDas. A new x-ray spectrometer from S+S Separation and Sorting Technology GmbH will soon be available in the US. While we know the CommoDas equipment works well, we will test the S+S equipment as it becomes available.

While the process described in this document appears to be a linear process, in reality numerous activities are taking place simultaneously. For instance, once the plastic of interest has been obtained e.g. the PC in our example, the remaining commingled plastic that was discarded can be re-run through the process. This allows another plastic (e.g. ABS), to be purified. In this way, all of the chemically important plastics can be separated to a purity level that will potentially make them useful for resale.

In many of the recycling processes that already exist; the recycler has configured each process into one continuous line. While this has many advantages, it lacks flexibility. Initially, the five distinct steps described above will be utilized. Once data has been collected and analyzed, the line configuration will be assessed. This will be carried out on a continuous basis in order to optimize the efficiency of the process. While we have worked diligently towards this end, we have not collected enough data to design an optimum identification and sorting line that will meet our throughput goals.

Throughput Rates for the Proposed Process

The equipment chosen for the plastics separation demonstration has been sized to allow for the processing of 1M pounds of EoLE plastic. In the planning process we have outlined five distinct steps. The initial studies will be to test and understand the capabilities of the equipment. Once this has been achieved we should be able to configure an efficient plastic recycling line. This demonstration facility should be able to sort 1M pounds of EoLE per year; however, we don't know what the upper limit on the throughput will be for any given configuration.

The equipment chosen has the capability of processing at least 4,000 pounds per hour. However, for the process to work efficiently, it may be necessary to process material in larger quantities in some of these steps. This will be determined experimentally. The throughput specifications for this equipment are given in Table 2.

Table 2: Materials Throughput for the Plastics Demonstration Equipment

Equipment	Throughput (lbs/hr)	Comment
1. Plastics Preparation (a) loading equipment (b) metal removal	4,000+ 4,000	This equipment is readily available and used in many industrial applications.
2. Identification/Separation 1 (a) NIR (b) NIR	4,000 4,000	The NIR from TiTech is presently state-of-the-art and the equipment of choice.
3. Identification/Separation 2 (a) x-ray	4,000	This is made by CommoDaS specifically for plastics recycling.
4. Plastics Purification (a) wash tank (b) dryer	4,000+ 4,000+	This equipment is widely available and is not specific to the recycling industry.
5. Purification/Modification (a) melt filtration	4,000+	This equipment is widely used by plastics processors.

Each of the pieces of equipment needed for the plastics sorting demonstration has been sized to be able to process at least 4,000 pound/hour. At present it is difficult to be more precise in calculating total plastic throughput rates. However, we believe that when the sorting line is up and running, major efficiencies will be found that will increase throughput rates while reducing the systems cost. The other major problem in calculating throughput is that the final mix of product materials and the detailed purity levels are at present unknown.

Potential Uses for Recycled Plastic

SDR Technologies secondary role was to develop target applications for EOLE material that would compete favorably with virgin material counter parts or as a drop-in alternative. In undertaking the materials development task SDRT compounded and injection molded selected plastic material (e.g., FR and NFR versions of HIPS, ABS, PC, PC/ABS) to gauge how well they processed and to evaluate the effect of different impact modifiers. It was learned that ABS-FR

could be reformulated for extrusion applications and that a blowing agent could be incorporated to reduce density to give a melt index of 1.6 and a notched izod of 3.0. SDRT has worked with Vinyl Tech International (North Jackson, OH) to demonstrate that an actual functioning part (a gutter downspout) made from recycled ABS could be produced that met all construction requirements. This recycled ABS could be an alternative to the PVC currently in use for gutter downspouts. Numerous other similar applications have been identified. However, further development work is required to see whether these potential applications can be realized.

Task 1.4: Develop Information Technology (IT) tools, methodologies and standards for MARCEE Information Technology Platform.

The Recipient shall develop IT tools, methodologies and standards that enhance and enable electronic information services, data services, and market services to help position MARCEE Information Technology Platform as primary industry support tool. A comprehensive MARCEE Information Technology Platform will be developed under the GreenOnline suite of core technologies. The process of developing industry standards and integrating information technology tools in support of industry activities will include the following tasks:

Subtask 1.4.1 Development of an integrated information exchange for the electronics recycling industry.

The Recipient shall build upon the Electronics Recycling Data Standards to develop an integrated information exchange. The information exchange will be built around the electronicsrecycling.org web portal and will provide the ability for all interested stakeholders to collaborate and exchange information.

Subtask 1.4.2 Develop a system for interactive data management within the field of electronics recycling utilizing the GreenOnline platform.

The Recipient shall develop a system for interactive data management, collection and sharing that supports simulation and modeling activities and enables stakeholders to analyze results of pilot projects at a regional or national level. The system will integrate data collection standards and increase data sharing between industry stakeholders, OEM's, and government entities.

Subtask 1.4.3 Develop an electronics marketplace/exchange to facilitate sourcing, shipping and high value applications for plastics from EOLE.

The Recipient shall develop an electronics marketplace/exchange to facilitate sourcing, shipping and high value applications for plastics from EOLE. The exchange will provide the basis for the marketing and logistics system used to identify, buy, sell and schedule shipments of plastic scrap. The exchange effort will coordinate closely with activities described in Task 1.3.

Due to reduced funding this project was only carried out on an as need basis to support the NCER and Task 1.5.

MARCEE Information Technology Support (PI/J. Tucker)

Overview

The use of information technology and the Internet have changed the way business is done in the global marketplace. The rapid changes now underway in the electronics recycling industry require flexible business processes in order to develop a robust supply chain for the recovery of end-of-life electronics. In order to reduce complexity and gain economies of scale within a supply chain, stakeholders in other industries are looking at the benefits of information technology. By utilizing information technology tools industry partners can communicate

quicker and the quality and flow of information can be increased dramatically. The use of proprietary data systems are quickly disappearing and are being replaced by more open architecture-based systems which allow for easier data integration. The Mid-Atlantic Recycling Center for End of Life Electronics (MARCEE) project helped develop the information technology infrastructure necessary to support an end-of-life electronics recovery system within the United States.

This framework was designed to provide flexibility as well as a broad range of services that could be utilized by different aspects of the electronics recycling industry. The framework includes the following areas:

MARCEE Information Technology Framework

- Information Exchange
- Data Collection
- Data Sharing
- Electronic Commerce

Information Exchange

The proliferation of the Internet has allowed for the creation of web sites full of information relating to specific topic areas. The major drawback especially for fragmented industries like electronics recycling is that the information is scattered all over the web and it takes time to really find what you are looking for. When the MARCEE project first got established one of the common themes we heard from industry stakeholders and project participants was the lack of a centralized information resource for the electronics recycling industry. Therefore, the first aspect of information technology support was the creation of an industry web portal.

The MARCEE project set forth in the creation of the Electronic Recycling web portal and registered the domain <http://www.electronicrecycling.org>. The initial focus was in the development of a centralized industry resource that could be used for sharing of information relating to electronics recycling. This web portal has grown to become one of the most recognized web resources on the Internet for electronics recycling information. Today the website is the portal for the National Center of Electronics Recycling and maintains a wealth of information regarding the electronics recycling industry. It currently receives traffic from all over the world and has become a valued industry resource.

Data Collection

The creation of information technology infrastructure support by the MARCEE project has also initiated other agencies such as EPA to look towards the MARCEE project to help provide assistance in industry related activities. One such activity is in the creation of a standardized set of electronics recycling data elements and corresponding data collection forms.

The MARCEE project took the lead in the development of these data elements by organizing a series of conference calls designed to flush out ideas and thoughts relating to electronics

recycling data collected from take-back and pilot programs. This was a first-of-its-kind series of conference calls where over 45 individual electronics recycling related stakeholders participated. As a result, an initial set of data elements were generated and are currently being used by several pilot projects in VA, NJ, WA, and FL. In addition national retailers such as Staples, OfficeMax, and Best Buy utilized these data elements and forms in support of the Plug-In To eCycling program.

This data collection infrastructure allowed for a more robust way of analyzing the data that was being collected so that it could be used to help increase the amount of pilot projects that were being developed throughout the United States. These tools were web-based data collection tools that were created as part of the MARCEE project and allowed for a more streamlined and cost effective way of collecting data.

The outcome of collecting all of this data was the creation of different online data repositories that were created by the MARCEE efforts to help centralize the results of the data collection programs. Through the efforts of the MARCEE project and the National Center for Electronics Recycling (NCER) the creation of 3 new online databases were developed. These include:

CDR – Centralized Data Repository

The Centralized Data Repository (CDR) is an open, collaborative public/private data sharing project which is addressing the need for up-to-date information on the collection and recycling of electronic waste. Currently, the repository holds data from over 26 U.S. states.

BDMS – Brand Data Management System

The Brand Data Management System (BDMS) was developed by the National Center for Electronics Recycling (NCER) as part of the MARCEE Project, and the National Electronics Recycling Infrastructure Clearinghouse – a joint project with the Consumer Electronics Association (CEA). The goal of the BDMS is to allow all stakeholders interested in emerging electronics recycling systems in the U.S. the opportunity to view and customize brand return share reports from across the country. With this database, the NCER has compiled the known electronics brand count studies (referred to on this site as “data sources”), and will be adding more as they become available. Implementation of electronics recycling laws in Maine and Washington utilizes these and similar data to determine manufacturer recycling obligations in those states.

The BDMS allows for the management and sorting of the hundreds of different brands reported by recent brand return studies in order to gain a more detailed comparison of trends such as variations in brand return share in different regions, brand ranking trended over time (including changes of top brands collected), and the number of officially designated orphan brands. Currently the BDMS includes monitors, TVs, desktop computers and laptop computers in its scope of products.

NERIC – National Electronics Recycling Infrastructure Clearinghouse

The National Electronics Recycling Infrastructure Clearinghouse (NERIC) was begun in early 2006 to conduct research and education on electronics recycling systems. Since then NERIC research has focused on several key elements of electronics recycling systems, including analyses of private sector-led, multi-state systems as an alternative to creation of new government bureaucracies. This Clearinghouse continues to serve as an industry-backed resource on a variety of recycling systems-level issues of interest to a broad range of stakeholders, including local, state and national government officials, manufacturers, recyclers, and environmental advocacy groups.

Underlying the Clearinghouse is the assumption that cross-state harmonization and joint implementation offer an efficient alternative to independently regulated and administered state-specific systems. As more individual states develop mandatory electronics recycling programs, stakeholders from across the spectrum seem to agree on the need for industry-led collective action to help ensure development of logical and efficient electronics recycling systems.

Data Sharing

Early on in the creation of an information technology infrastructure, the MARCEE project selected the Extensible Markup Language (XML) as a standard that could be used to help standardize the data sharing throughout the electronics recycling industry.

To understand how XML standards can integrate within an industry we first must look at the three types of standards that currently exist within the area of XML.

- Infrastructure Standards for the Web
- Interoperability Standards
- Industry / Business Specific Standards

The first area primarily deals with the development of standards that impact how the Internet functions and is currently being handled by the W3C. The W3C has several working groups that concentrate on infrastructure, Internet resources, and software development. The second area is focused on how XML standards can be used to aid in interoperability between systems. The OASIS group is one example of a standards body working on topics such as a replacement for EDI transactions between electronic systems. The third area is the one that relates to the electronics recycling industry and leads to the development of XML standards for a specific industry. In order for the electronics recycling industry to utilize information technology tools efficiently such as online marketplaces or supply chain management tools, a commonly accepted terminology must be developed. This common terminology will ease the integration of data with existing systems and help increase the use of electronic tools, E-business platforms and other applications of evolving information technology solutions.

The electronics recycling industry is a prime example of an industry that could benefit from the use of information technology and an integrated supply chain management approach. Given the

industry's historically low margins and developing status, the opportunity for cost reduction is attractive.

To demonstrate the need for a common terminology the MARCEE effort has supported several pilot or demonstration projects that have required multiple stakeholders or industry partners to communicate through the use of electronic systems. The MARCEE project was instrumental in developing and demonstrating how the use of such standards could be used to help create a more streamlined and cost effective solution for sharing of data from disparate systems. Through demonstrations at international conferences such as IEEE and RECCON the MARCEE project was able to take a leadership position in helping drive the electronics recycling industry towards a more robust data sharing model. This is also evident in 3 IEEE papers regarding the efforts of MARCEE initiatives. These include:

“Development of XML industry standards for information exchange and commerce”

Summary: Information sharing via a common language is the basis upon which successful industries and supply chains are built. The rapid changes now underway in the electronics recycling industry require concurrent changes in the common language of industry commerce. Today's economy and business climate also depends on cross-border industry collaboration - yet another challenge to developing and implementing common industry terminology - brought about in large measure through the increased use of IT tools. A set of common document interfaces that would allow industry partners the ability to not only view data but also integrate the data with backend ERP or database systems is a compelling vision. The problem to be addressed is how to use the Internet and a flexible XML schema to reduce costs and ultimately help generate new market opportunities for today's businesses.

“Information Architecture for an Electronics Recycling National Coordinating Entity”

Summary: A central recommendation of the National Electronic Product Stewardship Initiative (NEPSI) process is the creation of an organization to facilitate development of the nation's electronics recycling infrastructure prior to enactment of federal legislation. This organization was tentatively called the National Coordinating Entity, or NCE. As currently envisioned, a major function of this new organization is that of an information clearinghouse of electronics recycling data and knowledge. Given this emphasis on information exchange, this paper explores the recommended design option for the overall information architecture of the NCE.

“Understanding and Examining the Impacts of Orphan Products and White Box Products on Emerging Electronics Recycling Systems”

Summary: This paper explored the data and methodology for improved identification of orphan products that are collected in electronics recycling programs, and reviewed and recommended options for better identification and incorporation of products from "white box" manufacturers covered by various existing and proposed electronics recycling systems

Electronic Commerce

The MARCEE project identified early within the initial phases of the project the need to get Federal Support for recycling efforts. This started out as a series of meetings and led to the creation of the Federal Electronics Challenge. The Federal Electronics Challenge then led to discussions of an online product assessment tool for the Federal procurement employees. Since MARCEE was already working in the field of online data exchange and was working on the development of a series of data standards, MARCEE was asked to participate on the development and design teams. The MARCEE project stakeholders were instrumental in getting the prototype of the EPEAT tool developed and online.

Today, EPEAT is a system to help purchasers in the public and private sectors evaluate, compare and select desktop computers, notebooks and monitors based on their environmental attributes. EPEAT also provides a clear and consistent set of performance criteria for the design of products, and provides an opportunity for manufacturers to secure market recognition for efforts to reduce the environmental impact of its products.

The rapid adoption of the use of this tool by OEM providers prompted the creation of a Presidential Executive Order. Executive Order 13423, *Strengthening Federal Environmental, Energy, and Transportation Management*, requires that federal agencies “when acquiring an electronic product to meet [agency] requirements, meets at least 95 percent of those requirements with an Electronic Product Environmental Assessment Tool (EPEAT)-registered electronic product.” A copy of the complete text of the executive order is available on the White House website at <http://www.whitehouse.gov/news/releases/2007/01/20070124-2.html>.

The MARCEE project also identified during the early startup phases of MARCEE the need to have the ability to create online marketplaces and allow for E-Commerce capabilities. GreenOnline which is owned by the Polymer Alliance Zone of West Virginia was utilized to help jump start the development of E-Commerce activities for organizations within the field of recycling. The GreenOnline Digital Services includes an integrated suite of Internet-based commerce and communication tools for environmental commerce. They were developed to allow industry participants to benefit from various E-business initiatives. GreenOnline Services are customized to expedite information awareness and deal negotiation and closure in individual markets. They provide the platform for development and implementation of industry-specific online commerce standards.

In order to showcase how E-Commerce could be used within the field of electronics recycling several prototype marketplaces were setup to allow for the creation of online marketplaces for materials. The Polymer Alliance Zone utilized the technology to develop the Polymer Virtual Center of Excellence, which was used to help market the area to perspective companies throughout the U.S. and abroad. Star Plastics also developed online components which allowed them to market materials via the Internet and develop and expand markets for recycled materials. SDR Technologies also used the online technologies to help develop their very first online marketplace.

MARCEE Project Achievements – Information Technology

Throughout the MARCEE project there were a number of goals or milestones that were achieved in regards to the MARCEE Information Technology Framework. This section identifies the various goals and a brief summary of the achievement.

1. Project Goal: Development of an integrated information exchange for the electronics recycling industry.

Project Achievement: The MARCEE Project developed an Internet-based integrated information exchange that increases buy-in and participation by OEMs and federal agencies. The MARCEE project used information technology to enhance the focus on National electronics recycling efforts. The MARCEE project leveraged the information exchange in order to increase buy-in from OEM's and Federal Programs.

The MARCEE project utilized state-of-the-art web technologies to build an information exchange around the nationally recognized MARCEE project's electronicsrecycling.org web portal which provides the ability for all interested stakeholders to collaborate and exchange information. This web portal is now home of the National Center for Electronics Recycling (NCER).

2. Project Goal: Develop a system for interactive data management within the field of electronics recycling.

Project Achievement: The MARCEE project developed a system for interactive data management, collection, and sharing that supports simulation and modeling activities and enables stakeholders to analyze results of pilot projects at a regional, national or international level. The MARCEE project was successful at integrating data collection standards and increased data sharing between industry stakeholders, OEM's, and government entities. This activity led to the creation of the Centralized Data Repository, Brand Data Management System (BDMS) and NERIC.

3. Project Goal: Provide integration standards between MARCEE Information Platform and other industry related sites. Development of XML standards for information exchange will be developed and utilized.

Project Achievement: The MARCEE Project positioned itself so that as the industry started to develop and recycling efforts got underway on a national scale, the MARCEE Information Technology platform would be positioned to become the industry standard for information sharing relating to the electronics recycling industry. The MARCEE project was successful at developing the initial prototypes for systems like EPEAT and NCER.

4. Project Goal: Creation of a series of information technology integration support mechanisms for industry collaboration of interactive data management within a national data repository and a national R&D coordination system.

Project Achievement: The MARCEE project combined information technology efforts along with efforts of the NCER in order to create a national data repository and R&D coordination system.

5. Project Goal: Perform information technology integration support for the interfacing of MARCEE supported electronic marketplaces with programs such as EPEAT and other Federal Electronics Challenge supported purchasing programs.

Project Achievement: The MARCEE project was successful at leveraging early information technology efforts led by MARCEE in the areas of data collection, data standards, and web-based systems to help jump start the creation of the EPEAT tool.

6. Project Goal: Development of a MARCEE Information Technology Platform transition plan in order to provide a self-sustainability model for the MARCEE Information Technology Platform.

Project Achievement: The MARCEE project understood early on that in order for the activities and initiatives that were started under MARCEE to survive they would need a path to sustainability. Therefore, the National Center for Electronics Recycling (NCER) has taken on the responsibilities for the Electronicsrecycling.org web portal.

7. Project Goal: Identification of private-sector support in order to help fund MARCEE Information Technology activities relating to the national data repository and national R&D coordination systems.

Project Achievement: The MARCEE project understood early on that in order for the activities and initiatives that were started under MARCEE to survive they would need a path to sustainability. Therefore, the National Center for Electronics Recycling (NCER) has taken on the responsibilities for the online data repositories for CDR, BDMS, and NERIC.

8. Project Goal: Identification of industry and private-sector support for MARCEE electronics recycling related electronics marketplaces.

Project Achievement: The MARCEE project understood early on that in order for the activities and initiatives that were started under MARCEE to survive they would need a path to sustainability. Therefore, the Polymer Alliance Zone has taken on the responsibilities for the GreenOnline.com suite of electronic commerce tools and the additional industry websites have been transitioned over to Star Plastics and SDR Technologies.

Task 1.5 Set goals and develop a business plan/strategy for the NCEER

The Recipient shall establish the goals and develop a business plan/strategy for the National Coordination Entity for Electronics Recycling (NCEER) under the direction of an Industry Steering Committee comprised primarily of OEM, recycling and state/local representatives. The Industry Steering Committee will be formed at an NCEER organization meeting.

Subtask 1.5.1 Identify and Verify Baseline Information on Electronics Recycling Costs, Volumes and Goals

The Recipient shall assemble and analyze data developed by public and private sector entities which encompass electronics recycling costs, actual volumes of EOLE and accessible EOLE volumes. The analysis will include recycling goals.

For EOLE volume data, a baseline of quantities of EOLE collected and recycled will be developed, as well as list of volumes reported collected and recycled in other product programs.

Development of national baseline of electronics recycling-related costs will include estimates of required collection incentives payments in cents/lb. on a national, regional and local and local basis to meet theoretical collection goals. Electronics recycling cost data collection will be used to identify appropriate recycling costs for specific areas.

Under the direction of the NCEER Industry Steering Committee, development of national performance goals for electronics will be accomplished. Goals for specific material recovery percentages will also be identified, including a goal for EOLE plastics recycling. These efforts will built upon discussion held in the Federal Electronics Challenge and legislative initiatives at the state and local levels.

Subtask 1.5.2 Coordinate Better Information Flow and Outreach

The Recipient shall develop consumer informational materials to encourage the collection and recycling of EOLE. Development and promotion of standards for customer information for use by participating manufacturers and retailers for use on websites, in product packaging and on labels will be accomplished. Content for a clearinghouse of documents will be created and added for electronicsrecycling.net website.

Subtask 1.5.3 Address Industry-Wide Standards and Material Certifications

The Recipient shall develop methodologies for defining product classes for recycling program purposes, tracking current market share, tracking current returns by brand (if needed), and tracking recent multi-year sales by brand.

Subtask 1.5.4 Coordinate Pilot/R&D Initiatives Conducted Around the Country

The Recipient shall develop a National Electronics Pilots/R&D Coordination System. Activities will include support for pilots centered in other location around the country, in coordination with Environmental Protection Agency officials.

This task will also include support as needed for implementation of the Federal Electronics Challenge and the use, promotion and management of the Electronic Product Environmental Assessment Tool (EPEAT). EPEAT is designed in part to increase demand for recycled plastics from EOLE and other sources.

Subtask 1.5.5: Promoting a Marketplace for Recycled Polymers through Sustainability Protocols and Policies.

The Recipient shall identify a material selection method that helps manufacturers to analyze and determine the ecological appropriateness of their materials. An analysis tool will be used to maximize the quality of specification decisions in the context of a product's environmental and social attributes. Product and process attributes related to product life cycle, materials, characteristics, material value recapture and organizational policy will be analyzed, and a comparative report will be developed.

In order to address the Tasks and Subtasks in 1.5 PAZ and WVU set up the **National Center for Electronics Recycling** better known as the **NCER**. From its inception in 2005 it has filled an important role in collecting and disseminating data to the E-Waste community including the Environmental Agency (EPA).

1.5 The Role of the National Center for Electronics Recycling in the E-Waste Industry (PI/J. Linnell)

Introduction

Initially referred to as the National Coordinating Entity for Electronics Recycling, the National Center for Electronics Recycling (NCER) was formed with seed funding from the MARCEE project in 2005 in order to build on the recommendations by a national group of stakeholders. The national group saw a need for an organization to coordinate the numerous initiatives on electronics recycling and to advance the national infrastructure. MARCEE jumped at the chance to locate this strategic organization in West Virginia to provide jobs, visibility, and overall economic development opportunities. Due to the commitment of funding from MARCEE, representatives from MARCEE were able to recruit and hire a former staff director of Environmental Affairs from an electronics trade association in the Washington, DC area to relocate to West Virginia and create this new organization. Shortly thereafter, the NCER incorporated as non-profit in West Virginia, applied for and received 501(c)(3) status from IRS, and established Board of Directors with four outside individuals with years of electronics and recycling industry experience, all without using project funds.

Another MARCEE partner, the Polymer Alliance Zone, had acquired a building in Davisville, WV and an initial office space for the NCER was leased in this building known as the Polymer Technology Park. The first two years of the NCER under MARCEE project involved establishing a manufacturer-based NCER Advisory Committee to provide initial input on projects and developing key research and information to establish NCER as a credible and vital research organization. The NCER launched several research projects to enhance the national infrastructure for electronics recycling across the US, with implementation from multi-stakeholder project committees, including the creation of two new online databases of collection amounts and brand information that are now widely known and referenced across the country.

The following report provides highlights on the major accomplishments of the NCER under the MARCEE project. The report is organized under three main focus areas – 1) Data Collection; 2) State Program Coordination; and 3) Analysis under the National Electronics Recycling Infrastructure Clearinghouse. Finally, the report describes major publications and conferences attended to distribute the findings of the MARCEE data and analysis.

Focus Area 1: Data Collection

At the outset of the MARCEE project and the NCER's formation, data collection was identified as a major need in the field of electronics recycling. Key data were missing on collection volumes, levels of baseline activity, and return share percentages. Throughout the MARCEE project, NCER accomplished the following projects in the area of data collection:

1. Created a national database of electronics recycling activity (Centralized Data Repository) and provided technical support for national baseline

Building upon a joint initiative began in 2004 between the [Polymer Alliance Zone](#) and [EPA's Plug-in to eCycling](#), the NCER expanded, promoted, and redesigned update of the [Centralized Data Repository](#) (CDR). The CDR is a national clearinghouse for electronics recycling data. It is an open, collaborative data sharing project developed to aid in the sharing of data from various U.S. electronics recycling efforts. Documents developed around this project can be found at: <http://www.electronicsrecycling.org/cdr/>

In developing the CDR, the NCER hoped to answer questions such as:

1. How much historic product is available for recycling?
2. How much historic product is being recycled now?
3. How much is being disposed?
4. How much is being stored?
5. How much is being re-used?
6. How much is being incinerated?
7. How much is being exported?
8. How much would a truly national system cost?

Following a June 8, 2005 NCER Data conference call, the NCER finalized the work plan for the electronics recycling **Centralized Data Repository (CDR)**, an online data repository that would

house electronics recycling data from various programs across the United States. One of the major goals of the centralized data repository was to help establish a new national electronics recycling baseline.

After a work plan was finalized, the NCER began development of the CDR. In 2006; the NCER obtained a large database of local government collectors and private recyclers from a major recycling trade publication. Database contacts were sent information on how to register and submit their recycling data to the NCER's Centralized Data Repository. After some of these contacts registered their data with the NCER, another request for data was sent to a list of over 700 local collectors. Since these initial data requests, NCER staff has assembled electronics recycling information from 58 collection programs in their database – this information includes items such as pounds and units collected by program, price per pound to recycle and number of program participants. NCER staff also formulated a redesign of the CDR site that included changes to the visual appeal as well as organizational and reporting changes. Additional “Call for Data” emails have periodically been sent to site registrants asking for program data updates, and additional information continues to be collected and entered by NCER staff. The site is in a continuous state of update and improvement and can be found by going to <http://www.electronicrecycling.org/cdr>. A visual of the Centralized Data Repository homepage is shown in Figure 1:

Figure 1: CDR Website

Currently there are seven varying reports that can be run in the CDR including volume collected by year and volume collected by state. Reports can also be run on two of the mandatory state programs with available data – Maine and California. There is a section on the CDR site

dedicated solely to cell phone collection data – this section of the site has room for as little data has been collected at this time on cell phones.

Data from the NCER was also used in providing technical support to the U.S. EPA in 2006 and 2007 for an updated baseline report of recycling activity. EPA requested NCER support and hosted several meetings with the NCER and EPA's consultants to devise a strategy and provide feedback on early drafts and findings from the research. The result was a study published in 2008 by EPA titled "Electronic Waste Management in the U.S." with key findings at <http://www.epa.gov/epawaste/conserva/materials/ecycling/manage.htm>.

2. Tested feasibility of a multi-state third party organization to run electronics recycling systems

The NCER established a 2006/2007 electronics recycling pilot program with the hope of bringing more attention to this growing issue and eventually achieving a state-wide infrastructure for electronics recycling. Using separate funds under a competitive grant awarded by the West Virginia High Technology Consortium Founding (WVHTC) in 2006, the NCER hosted a series of 9 electronics recycling collection events at various urban and rural locations throughout the state and one school pickup. Although the costs for the events and administration of the program were covered by the separate grant, the NCER used the collection events to further MARCEE research on brand data described below. The 2006 events prevented 203,520 lbs of electronic equipment from entering state landfills. In 2007, the NCER was awarded a separate grant by the West Virginia Department of Environmental Protection's Rehabilitation Environmental Action Plan (REAP) to hold seven one-day collection events in the following West Virginia counties: Cabell, Putnam (twice), Berkeley, Raleigh, Ritchie, and Wood, and two limited duration programs held in Wood and Greenbrier Counties, respectively. Through NCER and partner efforts, a total of 275,981 pounds of electronic waste was diverted from the state landfills in 2007.

The 2007 grant was more limited, and covered all collection and recycling costs as well as costs for media advertisements. As part of the MARCEE project, the NCER administered the events and conducted data analysis to further the feasibility study of the use of a private, third-party organization to manage statewide electronics recycling efforts. The results of this multi-year project demonstrated that the use of a private TPO to coordinate a statewide electronics recycling program is feasible and offers many advantages over other types of system management. The TPO concept could be expanded to incorporate additional states in order to take advantage of management efficiencies and prevent duplication of state-specific efforts. The NCER gained valuable experience on how a statewide program could operate on a long-term basis. Experience in other industries has shown that privately run recycling organizations can operate effectively and reduce the use of government resources. Although private systems for each product stream cannot completely replace government waste collection systems, nor can they operate without government oversight and involvement, they can offer a way to reduce the burden of government resources and offer citizens convenient recycling options. Specific insights gained from this project include:

- **A private management entity can offer advantages over government management:**
As a private entity, the NCER was more flexible in creating contracting arrangements,

choosing personnel, and paying invoices for services from the recyclers than a government agency would be.

- **A privately run program still requires much coordination with government:** The program would not have been successful without the active involvement of several government agencies. State government agencies knew the appropriate contacts in each county to work with in establishing suitable locations and times for each event. Local government Solid Waste Authorities had the expertise in promoting local events in order to maximize turnout. Without the involvement of these government entities, the NCER would have required much more staff resources and time in order to plan all the of necessary details for each event.
- **The program run in West Virginia could be replicated across state lines:** Although limited to one state under this program, the events and overall program could be expanded to incorporate one or more states. While more events in other states would require additional funding sources, such coordination could take advantage of administrative efficiencies and possibly reduce recycling costs over time due to the greater volumes of material being processed.

The findings on the TPO research were widely disseminate within the national electronics recycling community via two comprehensive reports published by the NCER and posted on the electronicsrecycling.org portal. The project also gained valuable insights into the recycling of plastics derived from used electronics. These plastics have traditionally been difficult to recycle due in large part to the variety of plastic resins and additives used in the original manufacturing process, and the testing performed under this project showed which types of plastics hold better potential for use recycled plastics. Overall, the project demonstrated that recycling options for used electronics is in strong demand throughout the state, and the type of system demonstrated in this project holds promise for providing a long-term solution.

Finally, although separate from the MARCEE work, a related achievement was the signing of SB746. On Thursday, March 27, 2008, Governor Joe Manchin III of West Virginia signed into law an electronics recycling bill entitled “**Establishing a Takeback Program for Certain Electronics**”. This bill was sponsored by Senator Karen Facemyer, came on the heels of the NCER’s second successful year of electronics recycling, an effort which was forced into the limelight due to NCER’s marketing and advertising efforts as well as state-wide educational efforts.

The West Virginia bill establishes a statewide take-back program for the most commonly returned electronic items – desktop computers, laptop computers, computer monitors, and televisions. Manufacturers of these covered devices need to register on an annual basis with the WV Department of Environmental Protection beginning in January 2009. Manufacturers choosing to implement a take-back program would pay a nominal annual fee, while those without a program pay a much larger fee which will support grants for local recycling efforts. The WV bill harmonizes with the requirements already in place for manufacturers in Maryland and will lead to a more sustainable and regular collection

program beginning in 2009. With luck, it may also attract more electronics recycling business to the state and possibly to the Polymer Technology Park.

- **Gather data on manufacturer in the return stream and create new Brand Data Management System**

At the outset of the NCER, there were only two states that had passed mandatory electronics recycling laws in California and Maine. The Maine law was the most recent and it presented a number of new challenges. As part of the survey conducted of the Manufacturer Advisory Committee, the NCER determined that there was significant interest in studying the effects of orphan brands and white box/no name brands under a producer responsibility system like Maine's. These two categories of products describe devices that will be returned but have no current manufacturer to assign financial responsibility to. The NCER's initial task was to research and categorize these products, look at how many might be in the waste stream, and document steps to reduce any negative consequences to stakeholders operating under systems like Maine's. Working with data and insight provided by the Maine Department of Environmental Protection and an NCER multi-stakeholder project committee, the NCER produced lists of potential orphans and a methodology for tracking and designating them. The findings were published in research paper at the 2006 International Symposium on Electronics and the Environment.

The initial orphan and white box research led pointed to the need for a permanent, open, and accessible data of brands of electronics in the waste stream. The NCER took on this task under the MARCEE project to develop the Brand Data Management System. Initially, this involved in <http://www.electronicsrecycling.org/NCER/UserDocuments/PID145092.pdf><http://www.electronicsrecycling.com/NCER/UserDocuments/Desktop Brand Sorts 5-27-05.pdf> segregating data from brand studies conducted around the United States for a national snapshot of brand returns for TVs, monitors, desktops and laptops. The goal of the BDMS is to allow stakeholders interested in emerging electronics recycling systems in the US the opportunity to view and customize brand return share reports from across the country. An additional goal was the improved identification of orphan products that are collected in electronics recycling programs, and better identification of products from "white box" manufacturers. The BDMS is available at: <http://www.electronicsrecycling.org/bdms/> and the front page is shown in Figure 2.

Figure 2: Webpage of BMDS

The site is divided into several sections. The home page shows the top five brands, by units, for the four product categories the BDMS covers - TVs, monitors, laptops, and desktops - and the total number of brands for each category. The ranking on the homepage is based on the total return share by combining the Data Sources we have compiled. The "General Brand List" shows a complete list of all the brands (and their "aliases") we have information on, and clicking on each brand brings up a "brand detail" page showing its weight/quantity in each of the data sources, and whether it has been claimed/registered in any of the states, and the name of claiming manufacturer. The "Reports" section allows users to sort and categorize the data using different scenarios. You can view information for one product category by units, or you could view a report for all product categories combined, by weight. It also allows you to view the brand rankings for each data source. This page also shows an alternative calculation for return share that may result in differences for particular brands. The "Average Reported Return Share" reports calculate return share by averaging the percentages for a particular brand in each study.

As the BDMS expanded it started to encompass the state registration lists from the now twenty states with electronics recycling laws. This added layer of data is a key component to identifying which brands have a current manufacturer, and who is registering that brand in which states. The data can be cross referenced by manufacturer or by product category. States are continually updated these lists, and the NCER has maintained monthly updates to the BDMS based on changes submitted to the state registration lists.

Finally, the BDMS development led to looking more broadly at a practical question under producer responsibility requirements – who is the manufacturer? The research on orphans led to the recognition that many different types of entities could be considered the “manufacturer” for purposes of implementing producer responsibility programs. The NCER described the various types of brand owner and licensee arrangements, as well as other circumstances for brands that have been on the market for several decades. The findings were published in a research paper presented at the 2007 International Symposium on Electronics and the Environment.

- **E-Newsletter**

As part of the another data need identified for work under the MARCEE project, the NCER began compiling and distributing bi-weekly electronic News Summaries (or eNewsletters) containing breaking news and information on electronics recycling policy to MARCEE participants and more than 250 other interested stakeholders. The newsletter broke news stories on electronics recycling into several different topical categories and highlighted the major developments over the past two week period. The newsletter was made publicly available and interested stakeholders were encouraged to sign up. The News Summary had the added benefit of being a platform to distribute information on MARCEE publications and research to a targeted audience. The NCER E-newsletter archive can be found at: <http://www.electronicrecycling.org/public/ContentPage.aspx?pageid=81> and is shown in Figure 3.

Figure 3: NCER Electronic Newsletter Webpage

Focus Area 2: Coordinating State Mandated Programs

In early 2007, the NCER began a quarterly conference call with all states with mandatory electronics recycling laws. At the time, there were only four states with these programs and many of them were only communicating infrequently at industry conferences. These calls were responded to so well that “meetings” were increased in frequency to bi-monthly. The calls have given each of the states an opportunity to share and compare information. In 2008, the NCER developed the content and hosted a workshop at the E-Scrap Conference on State Harmonization

projects. The workshop was a result of the initial findings in the State Programs group and featured a wide-ranging discussion from all stakeholders on the types of harmonization projects that could be pursued. NCER developed and devoted a portion of our website to information pertinent to these calls - www.electronicrecycling.org/stateprograms. This section of the website contains several resources for call participants such as conference call notes, contact lists for each state and interesting documents that NCER has compiled such as a document highlighting the varying definitions by state. Other key resources documents that were compiled as part of this work and updated continually include:

- State agency contact list
- Product Scope and covered entities comparison chart
- List of digital picture frame manufacture
- Notes from calls
- Bankruptcy list
- Manufacturers/Brand Differences Worksheet
- Short Definitions of Key Terms in State Laws
- State Manufacturers and New Consolidated Manufacturer Contact list
- Noncompliant/do not sell list
- Data Destruction and Sanitization Liability Chart
- Comparison chart of Washington sampling data and Oregon return shares
- Comparison chart of IL return share percentages and RI return shares

The NCER also provided some targeted assistance for specific projects under individual state laws. For example, the NCER identified a need and developed documentation forms for collectors and recyclers to use under the Minnesota recycling law. This also led to the development of a solution for the communication problem among collectors, recyclers, and manufacturers under the law known as the Minnesota Clearinghouse. The Clearinghouse provides a method for posting and browsing listings for available recycled pounds of Minnesota household covered electronic devices. Manufacturers may log-in to this web site to view the offerings and identify supply to meet requirements of the new Minnesota e-waste law.

In addition to the conference calls and resource documents on the website, the NCER undertook two major initiatives to help states address specific needs in the implementation of their laws. The first involved researching market share needs and developing a method for states to acquire and analyze data from national market research firms. The second was the development and refinement of a prototype manufacturer registration online system. The NCER gathered and compiled a breakdown of the elements of each state's manufacturer registration form. Currently, every covered manufacturer must register separately in each state, and each state asks for slightly different information. The prototype allows state administrators and manufacturers to input information online and get updated on key upcoming deadline. The prototype will be refined and incorporated into the work under the Electronics Recycling Coordination Clearinghouse described below.

Although the State Programs Group was started under MARCEE funding, we are in the process of developing into our own self-sustaining group called the Electronics Recycling Coordination Clearinghouse (ERCC), administered by the Northeast Recycling Council (NERC) and managed

by the National Center for Electronics Recycling (NCER). The ERCC will provide a platform for state agencies and impacted stakeholders to work together on cross-cutting issues and projects that will provide efficiencies and cost savings. Membership in the ERCC will provide numerous benefits. First, there will be regular meetings and conference calls for member states and stakeholders impacted by these electronics recycling laws. A governance body consisting of voting state members will determine the direction and projects for the ERCC. Second, the ERCC will serve as a central clearinghouse of vital data needed in virtually every state implementing these laws.

The launch of the ERCC is one of several tangible successes that have come as a result of NCER's involvement in the MARCEE project.

Focus Area 3: National Electronics Recycling Infrastructure Clearinghouse (NERIC)

The NCER has explored the feasibility of organizing and running a private multi-state third party organization (TPO) to support and facilitate local electronics recycling efforts. In 2006, as an extension of the Pacific NW TPO project, the NCER entered into a joint work partnership with the Consumer Electronics Association. Out of this partnership, the formation of the National Electronics Recycling Infrastructure Clearinghouse (NERIC) was developed. Discussions with manufacturer representatives regarding NERIC initial projects were held. From here, the NCER helped to develop and revise a survey of local and state government representatives on priority electronics recycling system needs, served as an information clearinghouse by updating stakeholders on electronics recycling system policy developments through media and legislation research, formed a NERIC Advisory Committee, finalized a NERIC work program and developed content for a website. The NERIC project has explored how a multi-state TPO could be formed and could function to assume responsibilities ranging from the development of a data clearinghouse to contracting for recycling services, even across state lines. Some of the projects developed under NERIC are as follows:

1. Per Capita Collection Index

The NCER utilized information from the CDR to develop their "Per Capita Collection Index" or "PCCI". The PCCI was designed to measure changes in the amount of used electronic equipment, such as computers, televisions and monitors collected in representative programs across the United States. The goal of the PCCI was to have a simple annual calculation of the levels of electronics recycling activity. The index formula is as follows:

$$IPC = \frac{[P1+P2+P3+P4+P5+P6]}{6}$$

P1 through P6 are the pounds per capita values of the six collection programs noted below. The index is stated as pounds collected per capita and is re-calculated by NCER each year. Although the numeric value of the index is noteworthy, the percentage increase from year to year is more indicative of changes in collection volumes. The index is comprised of comprehensive collection programs collecting larger used consumer electronics such as televisions, monitors and

computers. Per capita values are **not** adjusted to account variations of products across different collection programs. The index is based on reported collection amounts from six programs:

- State-wide programs in California, Maine and Delaware
- A large municipal collection program (Hennepin County)
- Two smaller municipal collection programs (Branford, CT and Frederick County, VA)

The per capita collection rate for each of these jurisdictions is averaged on an unweighted basis to calculate the national NCER Per Capita Collection Index. Specific calculations are included in Table 1 below.

Table 1: Per Capita Collection Rate by State

Program	collection total	population of area served	LBs Per Capita 2008	LBs Per Capita 2007	LBs Per Capita 2006
California	216,064,581	36,756,666	5.9	5.0	3.5
Maine	5,274,304	1,316,456	4.0	3.5	3.0
Delaware	3,560,000	873,092	4.1	3.7	3.3
Hennepin County	5,310,000	1,140,988	4.7	4.8	4.0
Branford, CT	144,780	28,984	5.0	4.4	4.8
Frederick County, VA	411,000	114,253	3.6	3.8	3.5
	230,764,665	40,230,439	4.5	4.2	3.7

The chart above indicates a 7% increase in the NCER's per capita collection index over 2007 numbers. A rising per capita index indicates an increase in the collection of e-waste across the programs included in the index and suggests a similar trend nation-wide.

2. Summary of 2007 WEEE Directive Studies

In 2006 the European Commission initiated a comprehensive review of the Directive 2002/96 on Waste Electrical and Electronic Equipment, known as the WEEE Directive. This review involved two major independent study team efforts led respectively by UN University and Oekopol. These studies analyzed the impact and implementation of the WEEE Directive and potential changes that might be required. NERIC analyzed the key points in each study. This analysis can be found on the NERIC website at:

<http://www.ecyclingresource.org/ContentPage.aspx?Pageid=29&ParentID=35>

3. State Patchwork Study

In 2006, the NCER conducted a study of the state-by-state e-waste patchwork and analyzed its economic and other effects on industry, government and consumers. We discovered that having an evolving patchwork of differing state-level electronics recycling mandates results in several

quantifiable costs to public and private sector entities that would not exist with the introduction of a national electronics recycling program. Drawing from cost estimates provided by principal public and private sector entities in state electronics recycling programs, this study identified and quantified estimates of these “dead weight” costs. A copy of this study can be found on the NERIC website at:

<http://www.ecyclingresource.org/ContentPage.aspx?Pageid=18&ParentID=35>

4. Manufacturer E-waste Compliance Costs Study

NERIC took a look at projected costs to the electronics manufacturing industry to comply with state and local electronics recycling mandates in 2010. This study identified and estimated all manufacturer compliance costs resulting from e-waste legislation adopted in the following 19 jurisdictions: California, Maine, Maryland, Washington, Minnesota, Oregon, Connecticut, North Carolina, Texas, New Jersey, Virginia, West Virginia, Oklahoma, Rhode Island, Missouri, Hawaii, Illinois, Michigan and New York City. A copy of this study can be found on the NERIC website at:

<http://www.ecyclingresource.org/ContentPage.aspx?Pageid=34&ParentID=0>

5. Summary of State E-Waste Registration Fees

NERIC developed a table showing the fees assessed to manufacturers in each of the varying states with electronics recycling legislation. The majority of states enacting mandatory electronics recycling programs have included some type of registration fee assessed to manufacturers to help pay for state program administrative costs. While a handful of states exclude very small electronics manufacturers from the fee, or have a sliding scale that places the burden on larger manufacturers, most states have enacted a flat fee to be paid by manufacturers of covered products (varies by state) regardless of business size. A copy of this table can be found on the NERIC site:

<http://www.ecyclingresource.org/ContentPage.aspx?Pageid=36&ParentID=0>

6. Summary of Maine Program - Annual

The Maine program offers a wealth of data that were not previously available. The Maine DEP publishes some of the high level pound totals, but does not have the resources to calculate and publish important pieces of other information in their data on collections of televisions, monitors and laptops. Through the NERIC project, the NCER puts together an annual table of these results that includes the weight and number of units collected and a summary of products by brand status (e.g., claimed, unclaimed, orphan, etc.). The most recent summary can be found on the NERIC site at:

http://www.electronicrecycling.org/public/UserDocuments/ME%20ewaste%20collection%20overview%20chart%201_1_08%20to%2012_31_08.xls

7. Implementation of State Electronics Recycling Programs

NERIC has developed a page on their website to keep electronics recycling stakeholders apprised of the status of mandated electronics recycling programs in the US. This page can be found on the NERIC website at: <http://www.ecyclingresource.org/ContentPage.aspx?PageId=23>

8. DTV Study

There is a lot of speculation about how the digital television transition might affect the rate at which TVs are dropped off by the public for recycling. NERIC gathered data from ten collection programs nation-wide to see what how TV drop-offs were impacted before and after the transition. Results of this study are being tabulated now and will be released to the public in the coming months.

9. Compliance Calendar Web Page

Because the states have developed a confusing patchwork of requirements on electronics recycling, manufacturers and other impacted retailers need to search many different sources to find important deadlines. To address this need, NERIC maintains a compliance calendar that highlights registration and reporting deadlines, among others at:

<http://www.ecyclingresource.org/ComplianceCalendar/index.aspx>

The Compliance Calendar is frequently cited as a key resource for manufacturers and will be a lasting impact project from the MARCEE work performed by NCER.

10. Washington State Recycling Law

NCER contracted with the state of WA to create a sampling methodology for determining manufacturer return share under the Washington state recycling law. The NCER held multiple discussions with Washington Department of Ecology, and manufacturers on scope and timelines for the project. We also selected and traveled to Washington to meet with professional statisticians to assist with completion of the project. The methodology development included draft universe characterization document detailing projected collection volumes, likely product scope splits, and current brand return share rankings from the BDMS. Finally the first draft of the sampling methodology and sent to Washington Electronic Product Recycling Law Advisory Committee for review along with Desk Manual and QA/QC plan. The methodology was ultimately incorporate into Washington regulations implementing their law, and is used as the basis for the methodology in Oregon now as well.

Publications and Conferences

NCER staff has written the following papers/studies/articles:

- “Information Architecture for an Electronics Recycling National Coordinating Entity” at 2005 International Symposium on Electronics and the Environment (IEEE).
- “Understanding and Examining the Impacts of Orphan Products and ‘White Box’ Products on Emerging Electronics Recycling Systems” presented at 2006 International Symposium on Electronics and the Environment (IEEE).

- “The Role of Brand Information in State Electronics Recycling Financing Systems in the United States” presented at 2007 International Symposium on Electronics and the Environment (IEEE).
- Produced a Brand Recording Best Management Practices published on NCER website
- Recycling sections of 2009 iNEMI Environmental Conscious Electronics Roadmap 2007
- Prepared articles on electronics recycling and NCER activities for publication in Resource Recycling, E-Scrap News, Cargo Magazine, Popular Science, Waste Age, Waste Management World and WV Executive.
- State Patchwork Study published at E-Scrap 2006
- Published “Who’s Responsible under Manufacturer Responsibility” paper on NCER research to present at ICM Electronics and Battery Recycling conference in June 2008

Conferences and Trade Shows Attended

NCER attended and presented research at numerous conferences and trade shows since the outset of MARCEE. By doing this, the NCER proved its dedication to improving the national infrastructure for electronics recycling through working closely with other stakeholders as well as educating both national and international audiences.

A description of the conferences attended, accomplishments and results are as follows:

2005

- Attended and presented MARCEE and NCER presentations at IOF-WV Symposium in Charleston and RECCON 05 Conference in Morgantown.
- Worked on design team and helped prepare and host discussions at EPA’s 2005 National meeting on electronics recycling. Several initial NCER projects initiated at this meeting
- Made presentation on MARCEE-supported NCER projects and met with administrators of local and state recycling programs to discuss electronics recycling data and issues at the Metropolitan Washington Council of Governments Environment Committee meeting on July 21.
- Continued to provide support for EPEAT implementation, including preparation and participating in an EPEAT demo on July 7 and participation in EPEAT Implementation Team conference calls. Participated in EPEAT beta test organized by DN American

2006

- Participated in webcast workshop on new requirements for participation in the California electronics recycling program.
- Presentation at ISEE regarding the NCER’s data collection efforts and trends
- Prepared presentation on electronics recycling program implementation status and policy efforts for International Electronics Recyclers Institute.

- Prepared and delivered presentation at ISEE regarding the Northwest TPO project
- Presentation delivered via conference call on NCER activities, electronic recycling programs and policies to the Missouri E-Scrap Stakeholders Committee
- Prepared and Delivered presentation on TPOs in general and the NCER Multi-state TPO project and its relationship to the NWTPO Project at the Product Stewardship Institute Forum
- Prepared and delivered presentation to meeting of electronics recycling officials from EPA Region 3 States
- Prepared and delivered presentation at E-Scrap 2006 conference on state of the US infrastructure for recycling used electronics.
- Attended EPA Stakeholder Collaboration workshop immediately following E-Scrap 2006 conference and hosted working group to develop new NCER project called the “Infrastructure Inventory”
- Developed and hosted workshop on brand data return share issues for stakeholders prior to E-Scrap conference.
- Prepared and delivered a presentation on US electronics recycling developments at the International Conference on Electrical and Electronic Products (ICEEP) on December 11.

2007

- Prepared and presented preliminary tasks and cost estimates for the Washington Materials Management and Financing Authority. Held meeting with WA Department of Ecology and manufacturers to discuss and modify findings.
- Held meeting with Reuse Industries in Albany, OH and toured facility to discuss coordination on reusing computers collection in 2007 WV program.
- Met with Solid Waste Management Board Round-table Meeting in Charleston - put together statistics, photos and talking points, and put together packets of material to hand out to the Board
- Prepared and delivered presentation on NCER and MARCEE activities to WV Senate Committee on Infrastructure and Transportation
- Traveled to Minnesota for reporting workshop to describe and educate about NCER MN documentation forms
- At request of EPA, prepared and participated in recording of podcast of electronics recycling trends with EPA OSW Director and J Powell. Podcasts were made available to the public.
- Participated in INSEAD workshop on individual producer responsibility in Paris via phone and provided an update brand sampling and recording in the US.
- Participated in several working group calls of the CT Regulatory working group. Provided NCER data on brand, market share and manufacturer issues for consideration.

- Coordinated planning and presentation for meeting with a delegation from Japan (Toshiba, Hitachi, and Minebea).
- Prepared NCER overview presentation, attended WV Solid Waste Authorities Conference and educated local government representatives on electronics recycling and NCER efforts.
- Presented update NERIC activities to CEA Environmental Policy Committee on
- Finalized presentation and held NERIC Workshop on state electronics recycling requirements at 2007 Consumer Electronics Show on January 10. Also moderated a panel of electronics recycling experts.
- Set up booth and attended IOF-WV Capitol Day on January 22nd. Developed a presentation for the IOF-WV show.
- Prepared and delivered presentation on NCER and electronics recycling systems at the 2007 Solid Waste Association of North America conference “Thinking Outside the Blue Box”
- Prepared and delivered a presentation on state recycling requirements for manufacturers and retailers at the CEA Washington Forum on March 26th in DC. Meeting was attended by 150-200 participants from industry and government.
- Prepared and delivered two presentations for E-Scrap 2007 in Atlanta. First presentation summarized requirements for recyclers under state laws and the second gave an overview of the implementation of state programs.

2008

- Prepared and hosted workshop overview session on state recycling laws at 2008 International CES
- Prepared and delivered presentations on Oregon program for E-Scrap 2008 in Atlanta. Hosted and moderated workshop on State Harmonization efforts.
- Hosted workshop for International Electronics Recyclers Institute (IERI) on state electronics recycling laws at E-Scrap 2008
- Prepare and delivered presentation at Waste Expo on state electronics recycling laws
- Prepare and delivered presentation at National Recycling Coalition Congress on state electronics recycling laws
- Presented and delivered presentation on electronics recycling trends at “It’s Not Easy Being Green: New Laws, New Materials and a New Way of Doing Business” an IPC Symposium on Electronics and the Environment”

2009

- Presented on panel of recycling industry experts at 2009 International CES
- Hosted State Program’s group meeting and registration prototype demonstration at EPA’s Resource Conservation Challenge meeting

- Moderated discussion panel of state program representatives at ISRI's Electronics Recycling Summit
- Prepared and delivered presentation at Waste Expo on state electronics recycling laws
- Prepared and delivered presentation at the Reuse Conference

Conclusions

The major achievements are as follows:

- Have helped educate stakeholders, government and consumers about electronics recycling issues
- Have enabled NCER to make contacts within state governments which has led to government contracts and consequently organization growth and stability
- Have helped NCER obtain funding from WV Solid Waste Authorities which enabled us to expand our WV E-cycling events throughout the state

Task 1.6: WVU Polymer Research Center (Mel Croucher/WVU)

The Recipient shall coordinate all polymer related research at West Virginia University and develop an industry, university, government coalition to support advancement and growth of the polymer industry. The coalition will evolve into a membership organization with a fee structure for participation in setting the research agenda and benefiting from results of the Center's programs. A variety of sources of support for the Center's research agenda will be developed.

Subtask 1.6.1 Electronics Recycling Conference

The Recipient shall plan and co-sponsor the RECONF '05 Conference to be held in Morgantown, West Virginia in October 2005.

Task 2.6 WVU Polymer Research Center

The Recipient shall work with various constituencies to develop a long term vision and strategic business plan for the WVU Polymer Research Center. The Center shall concentrate its accomplishments in science and technology that contribute to the next generation of polymer industry growth in the state. A long-term goal of the Center shall be to develop its technical and scientific credentials to the point that the Center becomes a self-sufficient profit Center.

Subtask 2.6.1 Electronics Recycling Conference

The Recipient shall complete planning and execution of the RECONF '05 Conference in Morgantown, West Virginia in October 2005.

Subtask 2.6.2 Coordination of MARCEE Activities

The Recipient shall assume the overall coordination of MARCEE Activities aiming at integration of all R&D and operational activities.

Tasks 3.6 and 4.6 were not defined for the SOPO since the funding level was reduced and the scope of the project curtailed. However, the WVU Polymer Research Center is now operational and applying for competitive awards.

Development of a Polymer Research Center at WVU (PI/M. Croucher)

In July, 2005 the WVU Research Corporation officially formed a Polymer Research Center (PRC) with a dual mission. A major objective of the Center is to stimulate and coordinate interdisciplinary polymer research across the WVU campus and to expand partnerships with the polymer industry since West Virginia is a major polymer producing state. It was expected that innovative polymer research on the WVU campus could lead to further economic activity, as well as produce graduates with research experience in polymer science and engineering.

A second reason for forming a PRC is WVU's participation in, and coordination of the Mid-Atlantic Research Center for End-of-Life Electronics (MARCEE). WVU's research role in this partnership was to find value added applications for the polymers that are recovered from

discarded computers, printers and other electronic devices. The research tasks carried out by WVU faculty members on recycled polymers is ably described in Tasks 1.2 and 1.3 and will not be repeated here. However, the electronics recycling industry is growing rapidly, since EoLE are viewed as an environmental problem. The industry is calling for federal government support for research in this area.

MARCEE Activities

Published Research on EOLE

In the years from 1998-2007 five hundred and eighty-eight papers were published [4] on electronics recycling and end-of-life product management. Of these 67% were contributions from academic institutions. The breakout by year is shown below.

Figure 1: Number of EoLE Recycling Papers Published by Year [4]

The figure shows that the number of papers published each year over the last decade has remained relatively constant and modest in number. When these papers are grouped by subject six major research areas emerge. They are:

- Design for Recycling/Design for the Environment
- Process Technologies for Recycling
- Materials Issues Associated with Recycling
- EoLE Operations Management and Strategy
- Secondary Markets
- Policy and Regulation

While six categories have been identified, some studies fall under more than one activity since they are not mutually exclusive. The number of papers published by category is shown in Fig. 2.

Figure 2. Number of papers published by category

The graph shows that Design for Recycling, EOL Operations Management (including Logistics) and Policy Issues dominate the publication list. The area where WVU has been active has been in the area of plastics reuse (Materials). WVU is the only university, through the work of Professors GangaRao and Gupta in the College of Engineering, with a consistent publication record in this subject.

In order to understand what types of research are included in each category, we briefly describe some of the published work. It should be stressed that this is not a definitive review of published work but more a roadmap of activities in the EoLE industry. We have also ignored the publications on secondary markets since the volume of published work is negligible.

Design for Recycling/Design for the Environment. Most product engineers have to balance a variety of factors such as new technology, energy efficiency, product safety, manufacturability and cost when designing a new product. Rarely does the engineering community give much thought to what happens to the product at the end of its useful life. However, this is beginning to change as the need to recycle becomes part of the cultural mindset. A good example of this change in thinking is described on the Toshiba website [5]. The recycling issues that product engineers need to address as part of the product development process include:

- Reducing the number of different recyclable material in the product
- Reduction or elimination of hazardous constituents

- Increased yield of the products recyclables
- Design that allows for easy disassembly for recycling

In 2006, the Institute of Scrap Recycling Industries (ISRI) announced its first Design for Recycling Award [6]. HP was the first recipient in recognition of the improvements they have made in their new products that enable more efficient recycling. These include:

- Use of modular design for ease of replacement and upgrading the product
- Eliminating adhesives by using snap-in features
- Marking plastic parts weighing more than 25g according to ISO 11469 to allow for materials identification. They also use only single plastic polymers
- Reduction in the number and types of materials used
- Using molded-in colors and finishes instead of paint or plating

While many of these activities can only be carried by larger companies, one area where the academic has played an important role is in finding benign substitutes for many of the hazardous chemicals found in these products. For instance, circuit boards are soldered using a tin-lead solder. The European Union (EU) Restriction of Hazardous Substances (RoHS) Act prohibited the use of lead as of July 1, 2006. Numerous universities [7] have looked at alternatives to lead that would be as effective as presently used solders and which are cost competitive. New solders composed of tin-silver-copper and tin-copper mixtures have been developed from these studies. While these materials do not have the same functionality as lead based solders, improvements to these materials can be expected to occur.

In most electronic devices some of the plastic components contain bromine containing flame retardants, most of which have now been banned. Unfortunately, many of the non-bromine containing flame retardants have not proved as effective as brominated flame-retardants [8]. Professor R. Gupta at WVU has developed an effective and inexpensive flame retardant for styrene based polymers. This is presently being patented and is likely to be commercialized by a major plastics company [9].

Process Technology for Recycling. Recycling plants presently come in one of two configurations.

- Shredding Technologies
- Manual Disassembly

In recycling plants configured for shredding the product to be recycled is put through a shredder and reduced to smaller units of commingled materials which are then sorted. The sorting technologies used are well known [10, 11, 12] and utilized in other industries. For instance, ferrous metals are separated magnetically while non-ferrous metals such as aluminum and copper are separated using an eddy current separator. Materials such as glass and plastic can be separated using an air table separator. In this process separation depends upon a difference in the specific gravity of these materials.

In the second configuration the product is disassembled manually. This is very labor intensive and only useful when a small product volume is being recycled. If disassembly could be made into a high volume process this might be the economically preferred route. Consequently, some universities are seeking to improve the productivity of such plants by using technological solutions where appropriate. For instance, the New Jersey Institute of Technology (NJIT) has demonstrated a computer controlled system that uses a water jet to cut the leaded glass from a CRT [13]. They have demonstrated a processing time of 15 seconds in the laboratory which is much faster than manual disassembly. It is this type of thinking that will ultimately produce a more automated and productive disassembly facility.

The recycling processes presently used to reclaim the component materials from EoLE products are presently low-tech systems. These have emerged because recycling operations are extremely cost sensitive and presently lack economies of scale. The number of different products and the large number of manufacturers making these products make it difficult to put together an automated facility with present recycling volumes. Since recycling of these products will become commonplace in the next decade, recycling processes will need to change to make the demanufacturing process efficient and cost-effective. This will mean that more automated processing will be required. Although many demanufacturers believe automation is one way to proceed, there are presently very few ongoing R&D activities addressing this issue.

One subject that has received attention recently is the identification and sorting of EoL plastics. At present, almost all the plastic obtained from electronic products is either placed in landfill sites or sold to overseas vendors [2]. This happens because there is presently no secondary market for recycled plastics. Because numerous different types of plastics are used in each product, these plastics are commingled following demanufacturing. These commingled materials exhibit very poor properties, and have essentially no-value. Since about 2000, numerous groups have sought to identify and sort mixed plastics at throughput rates that would make for an economically viable process. The most notable of these is a pilot plant facility built for the Department of Defense by Concurrent Technologies Corporation. In this process [12] plastics were shredded into small pieces and then separated into various chemical classes using density separation and electrostatic techniques. This process was found to be slow and the purity level of the recovered plastic was unacceptably low. Consequently, this plant was decommissioned in 2003.

Over the past year SDR Technologies in WV has been assessing the use of optical and x-ray separation technique in place of the processes outlined above. In this method a near infrared (NIR) spectrometer scans across a conveyor belt at high speed. It identifies the chemical nature of the plastic which is then redirected, using pneumatic techniques, into the appropriate collection bin. In another operation an x-ray technique is used to separate flame retardant containing plastics from non-flame retardant materials. During the past six months SDR Technologies has demonstrated that the effectiveness of these techniques has improved dramatically with >95% separation being obtained. A pilot facility is now being built to demonstrate the process and acquire the relevant economic data. Further details of this project are described under Tasks 1.3 and 2.3.

Materials Issues Associated with Recycling. At present the EoLE recycling industry can, and does, recycle the leaded glass from CRT's, the precious metals from circuit boards and the commodity metals used in these products. The plastics used have no value and few uses have been found for them. As part of the MARCEE consortium, WVU has been actively involved in finding uses for recycled plastics. Some examples of the WVU work [14, 15] are described under tasks 1.1, 2.1, 1.2 and 2.2 discussed earlier.

EOLE Operations Management and Strategy. This has been an area that has attracted a lot of attention from the academic community. These subjects i.e. EOL Management, Collection and Logistics, Facility Operations and Product Disassembly form the heart of an efficient recycling industry. Most of the published papers deal with discrete modeling and planning methodologies for disassembling EoLE products.

The authors of these papers acknowledge that the *disassembly* process modeling and planning is more challenging than *assembly* since there is more uncertainty in the goals, systems structure and components as a result of being used. Most of these modeling efforts, described in a review by Zhou et al [16], use a graph-theoretic construct to describe the disassembly sequence with the objective of finding all disassembly sequences, and then defining an optimal disassembly sequence. As far as I am aware, these theoretical papers have not used any practical recycling data for comparison and the recycling planning disassembly sequence methodology does not seem to have been applied to a practical recycling facility. This is evidently an ongoing project where a tighter coupling between theory and experiment would be helpful for the recycling industry.

In another approach, Gutowski et al [17] have developed a probabilistic model to estimate the performance of any binary separation process. Using this model they have derived a set of equations to rigorously describe a materials separation process, which they have compared to various separation scenarios. This would appear to be an excellent model to use for the plastics separation activities that are being developed by SDR Technologies.

Many different theoretical approaches can be found in the recycling literature tackling a variety of problems [16-20]. They are not immediately useful to the industrial recycling community, because industrial practitioners do not understand these approaches. However, they do deserve further scrutiny by a knowledgeable academic community who are able to bridge the gap between theorists and practitioners.

Policy and Regulation. This has been a fruitful area for research since it's an ever changing regulatory landscape. Besides regulation, we also include societal and economic issues in this section.

There are now nine states that have enacted EoLE legislation. While there are many similarities between the legislative models there are also major differences and these have been discussed by Linnell and Alcorn [21], who are part of the MARCEE consortium. One of the major concerns of state agencies is an understanding the logistics and costs involved in implementing a statewide recycling scheme. Numerous groups have attempted to assess these schemes and provide a simple cost model. Caudill et al [22] undertook a case study of a recycling scheme that was

proposed for Snohomish County, Washington. The elements that were considered in the assessment are shown in Fig 3.

The authors outlined various collection scenarios ranging from large drop-off facilities to highly-distributed facilities using existing retailers, municipal facilities and one-off collection events. Given these scenarios, a set of cost models that estimated capital costs and the fixed and variable costs associated with these operations was developed. This allowed the incremental and marginal costs for providing electronic collection at existing facilities to be determined.

This study provided a better understanding of the collection, transportation and recycling infrastructure necessary for an EoLE recycling operation.

Figure 3: Elements Considered in the Snohomish-Tacoma County Electronics Recycling Assessment.

Turton, Logar and Ponzurick [23] at WVU developed a spreadsheet model to assess the economic feasibility of a recycling facility that processed only personal computers (PC's). These authors systematically accounted for all of the fixed and variable costs involved in operating a demanufacturing plant. Using this model they concluded that labor was the major factor in operating a recycling plant. These costs were estimated to account for 70% of the variable costs involved. They concluded that profitable operation of such a facility was not possible without a subsidy or charge being paid for each PC processed, or alternatively, some level of refurbishing and sale of newer computers needed to occur.

The policy area regarding EoLE generates a steady stream of papers on a variety of issues from legislation to public attitudes towards recycling. A lot of attention is paid to the European Union's WEEE directive [24] since this is thought of as a precursor to the type of legislation that could be enacted in the US. At present, the US Congress is discussing legislation and some people believe that a bill could be passed early in the next Congress [25]. However, State Legislatures view EoLE recycling as a growing problem and twelve States have enacted legislation and many more are discussing it. The fear in the recycling industry is that this could

lead to a smorgasbord of different recycling systems being enabled which would lead to an inefficient and costly system.

One of the most interesting papers to appear recently was authored by Dahmus and Gutowski [26] who developed a graphical representation of the material recycling potential for products at EoL. This graph is based on two measures (1) the value of the materials used in a product and (2) the mixture of materials used in a product. It is the equivalent of a Sherwood plot that was developed to understand the attractiveness of mining different ores. The representation of Dahmus and Gutowski shows the relative attractiveness of recycling different products. This paper deserves more in-depth studies of EoLE products since it yields insights which could be useful for recycling policy and for product designers.

Potential EoLE Research Projects at WVU

There are numerous research projects which WVU has the skills and background to undertake. This list is not meant to be definite. Faculty members with different backgrounds would be able to suggest a wider range of research projects which could enhance this emerging industry.

Turning EoL Plastics into Energy. Not all of the complex polymers that are found in electronic products will be recovered for reuse. Those that are not reused could potentially be turned into syn-gas using gasification. The advantage of the complex polymers used in EoLE is that they are rich in hydrogen. This could lead to a syn-gas that has a high energy density and could be useful for a variety of applications.

Feedstock Recycling Technologies. Fisher et al [27] have discussed the environmental objectives associated with the recycling of plastics from EoLE. They argue that there is a complimentary portfolio of chemical recovery technologies available to plastics, including glycolysis and enzymolysis, which could be used to affect depolymerisation or the production of useful chemicals. Few research papers have appeared which address these areas.

Brominated Flame Retardants. Many plastics used in electronic products contain bromine containing flame retardants many of which have now been banned because they are toxicologically active. This makes these plastics worthless. Is there any method of removing or converting these flame retardants into benign materials that would allow these plastics to be reused?

Plastics in Landfills. It is assumed that modern landfill management practices and the inertness of plastics mitigate against any problems occurring many years into the future. However, more studies would seem to be necessary to validate these assumptions. For example, do the brominated flame retardants remain as inert chemicals within the polymer or can they be leached out and ultimately contaminate the groundwater?

Continue to Find New Applications for Recycled Polymers. New areas which could be investigated include:

- Explore design rules to modify EoL plastics using reactive extrusion. This could lead to new inexpensive materials with properties that could be used for a variety of applications e.g. to enhance the life of paving asphalts.
- Using natural fibers to form composites with new properties e.g. could these materials be used to make stable, compatible composites from commingled plastics?

Processes for Demanufacturing Electronic Products. As described earlier, the demanufacturing process used is rudimentary. In order to improve processing, and hence the economics, newer processing technologies need to be developed. For instance, could robotics and newer technologies, such as laser cutting for example, be used in a more efficient process line? The logistics of demanufacturing also need attention since it has a major effect on the economics. This is a very important area which deserves more thought and study that it has presently received.

Policy and Economics. Recycling policy and economic studies are at the heart of this new industry. For instance, understanding the economics of recycling EoL plastics is very important and will determine the future of this waste stream. There are a large number of problems in these areas that are worthy of study by the academic community.

Concluding Remarks

It has become evident over the past twenty years that sustainability is a major societal issue. Consequently, recycling and materials reuse have become issues that are important from both an economic and an environmental perspective.

In this paper we have briefly described the research that academic groups have played in the EoLE recycling industry. To date it has not attracted much attention in academia, although that may change as the problems posed by the industry become more widely disseminated. One of the perceived reasons for this lack of interest in EoLE recycling is the lack of research funding from the federal government. This has been brought to the attention of the US Senate, but it is not clear that this will lead to a funding mandate for EoLE.

The range of tasks to be undertaken by an EoLE recycling industry is wide ranging and complex. It ranges from the logistics of collection to their efficient demanufacturing and reuse of the components. Overlaying these efforts is government legislation and how it affects the economics of recycling. At present this new industry is exhibiting growing pains and needs help on most fronts if it is to become a viable, mature industry. The academic community, with its diversified knowledge base, is well placed to play an important intellectual role in its development.

Acknowledgement

Thanks are due to Professor R. Caudill from the New Jersey Institute of Technology for sharing his data, and for his perspective on the research carried out by the academic community on EoLE.

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D. Report of the RECCON'05 Recycling Conference hosted by WVU (Subtask 2.6.1)

Introduction

RECCON '05 was held on November 29-December 1, 2005. It was established to further the goals of the MARCEE Project. The specific goals of RECCON' 05 were achieved and the conference was deemed highly successful. RECCON'05 also came in \$37,000 under budget. It was able to achieve most of the critical goals that were set for it.

Goals

- To develop working relationships with organizations in the European Union.
- To develop relationships with those organizations who are involved with and have expertise on WEEE (Waste Electrical and Electronics Equipment Directive) and ROHS (Restrictions on Use of Certain Hazardous Substances in Electrical and Electronic Equipment.).

- To work with initiatives such as *China-US Center for Sustainable Development* to achieve cradle-to-cradle recycling of EOLE.
- To work with the “Greening the US Government” initiative.

External Outputs

The main outputs of the Conference were

- A standing resource website for the recycling community worldwide which is maintained by West Virginia University and can be accessed at <http://www.wvu.edu/~RECCON05/>
- A CD with resources, contacts, presentations, and recapitulations of some of the events of the conference. The CD was mailed to each and every attendee to RECCON’ 05.

External Outcomes

The dissemination of knowledge that impacts communities and partnerships were the two most important outcomes of the conference. These outcomes are identified below:

I. Identification of Future Trends:

- Markets are changing quickly and becoming globalized
 - WEEE—international de facto standard—EU standards will raise global standards and create more awareness.
 - ROHS will reduce toxicity of used electronics
 - BAN – effect of EOL electronic exports to Nigeria
 - US/China and Trade Relations
 - Need to effect optimized cycles
 - Confluence of rapid economic growth
 - China’s vision of “circular economy”
 - Need for US to be strategic in developing international business relationships underscored.
 - Specific plastics issues relating to Asian markets
 - Implementation of recycling systems in Japan, EU, and US

II. National Infrastructure Comparisons

- Swiss system initiated in 1993. Funded through an advance recycling fee.
- Chinese domestic collection and recycling plans coming into effect in next few years.
- Japan’s collection and recycling system and division of responsibilities:
 - Consumers – pay at disposal
 - Retailers – collect/deliver products
 - Manufacturers – recycle
 - Canada – Electronic Product Stewardship
 - U.S. – Multi-state Systems and NCER’s coordination role

III. Regional Solutions in the U.S. and U.S. State Solutions:

- Success Stories/Lessons Learned – Studies and projects in U.S.
- California – electronics recycling program
- Maryland – electronics recycling financing approach
- Minnesota – developments and the movement toward a regional electronics recycling program in the mid-west
- Program and legislative activities in Washington
- Third Party Organization Concept

IV. The Presidential Challenge Program was highlighted and clarified

V. Numerous partnerships and business ventures were formed at RECCON 05.

Expenditures:

RECCON 05 had a budget that was allocated to it from MARCEE funds and from conference income from sponsor's fees. The amount budgeted for the conference was \$156,390. Program Income raised from the event was \$36,099 for a total allowable expenditure of \$192,489. This amount included the funding of all invited speakers including travel, lodging, food, and any honorarium paid. Total expenditures from the budget allocated were \$126,981. The amount from the Program Income that was spent was \$23,462 leaving \$8,335 in Program Income. The cumulative total funds remaining after accounting for all the expenses incurred was \$37,744.

Lessons Learned:

RECCON'05 was extremely successful. It was well attended, had an excellent agenda with well known speakers from around the world and came in under-budget.

- Pre-planning retreat was strong in accomplishments and dynamics. Could be improved by optimizing the date of the pre-planning retreat based on location and travel. Could refine the Committee selection process.
- Event:
 - Speakers/VIP's
 - Strengths: -Strong slate; time allowed for attendee interactions; format of communication was excellent
 - Improvements-Develop shared email proxy; have interactive speaker forms on web.
 - Vendors/Sponsors
 - Strengths: Generous package., very detailed, good vendor PR
 - Improvements: -Give vendors floor plan in advance so they can have site selection.
 - Invitations Programs
 - Strengths: -Great graphics, clear agenda format; excellent program, dividers, nametags and ribbons worked well.

- Event Location- The main location and all break-outs areas were fine. The registration location could have been improved; could have had more space, needed larger “Registration” signage. Receptions were well located, good food and décor. We could have had better attendance at the reception before dinner. Not sure why this occurred.
- Audio Visual
 - Strengths: -Good set up; Good technical equipment; good technical people
 - Improvement: -Central storage for presentations on a shared network.
- Process
 - Strengths: -Set-up enabled easy exit and entrance to sessions; setup enhanced audience views; room size aided communication; elevated speakers enabled audience views; speaker cards help control the audience
 - Improvements: -moderators and chairs at times did not enforce time limits.
- Public Relations
 - Strengths: -Good plan; Presentation for President was thorough; enough contact w/target audience; right people and agencies attended; website good.
 - Improvements: -Need to pre-plan more with the photographer.

The feedback from the participants was very positive. Representative Alan Mollohan, who funded the MARCEE Program gave an excellent after dinner speech and did an excellent job of circulating amongst the speakers and guests.

It was decided that RECCON’07 would be held in Spain. However, in 2007 this was postponed until November 2008.

E. NETL/DOE Peer Review

Introduction

After MARCEE had begun work on Phase I of the contract NETL/DOE asked that a Peer Review be held to assess progress against our objectives and suggest changes to the program since the funding level had been reduced.

It was agreed to hold the review on November 29- December 1, 2005 after RECCON’05 was brought to a close. Because a large number of speakers at the recycling conference were well known and respected in the e-scrap community, we believed that we could choose four high profile people from the conference who would agree to review the MARCEE Program. The reviewers chosen were:

1. Michael M. Fisher (Chair)

Senior Director Technology
 American Plastics Council
 (703) 741-5599
mike_fisher@plastics.org

2. Sego Jackson

Principal Planner
Solid Waste Management
Snohomish County, WA
(425) 388-6490
sego.jackson@co.snohomish.wa.us

3. Bassam J. Jody

Project Manager
Separation and Recycle Processes
Argonne National Laboratory
(630) 252-4206
bjody@anl.gov

4. Dewey Pitts

Product Take Back and Recycling Program Manager
Lenovo International
(919) 543-6629
odpitts@us.lenovo.com

The reviewers were chosen because they spanned the range of e-waste activities from policy to research to recyclers as well as covering many of the different institutions, namely federal and local government, private industry and trade organizations. This diversity would allow for different points of view to be heard. It would also allow an expert to review each aspect of the MARCEE Program and render a knowledgeable judgment.

The Peer Review Agenda**Wednesday, November 30, 2005**

2:00 p.m.	Introduction / Purpose of Review	M. Croucher
2:15	Financial State	A. Martin
2:30	Polymer Alliance Zone (PAZ)	B. Graham
3:00	SDR Technologies	D. Ritchie
3:30	WVU Research	R. Gupta / H. GangaRao
4:15	<i>Break</i>	
4:30	DN American	J. Tucker
5:00	NCER	J. Linnell
5:30	Adjourn	

Thursday, December 1, 2005

8:30 a.m.	Review Committee Discussion with DOE representatives	D. Maynor
9:00	Peer Review Committee Meeting	
10:30	Feedback Session	
12:00	Adjourn	

Questions for the Reviewers

These were agreed ahead of time with the NETL/DOE Program Manager for this project. Given that there was not an unlimited time for the review, it was decided to ask two specific questions regarding the MARCEE Project while a third question would allow the reviewers to draw attention to activities they thought should be changed. They were asked to be forthright in their comments.

The questions given to the review team were:

- 1. Give a brief assessment of the progress of each of the Partners to the MARCEE project against their objectives.**
- 2. What recommendations does the Review Team have for the MARCEE project regarding specific adjustments to the Statement of Work and/or the technical priorities based on the available funding for the next fiscal year?**
- 3. Are there any other specific comments that the Review Team would like to make about the MARCEE project?**

Before the review was held the review team was given the questions they needed to answer, quarterly reports from the last four quarters and the MARCEE Business Plan. They were also provided with some background information, and a list of accomplishments regarding the MARCEE Program.

Peer Review Feedback

The feedback from the review team came in a letter giving some details about the review process and a written documents that gave a list of comments/suggestions and recommendations to the program. These documents were also sent to the NETL/DOE as well as WVU. These documents are reproduced below:

January 5, 2006

Dr. Melvin D. Croucher
Director, Polymer Research Center
WVU Research Corporation
West Virginia University
886 Chestnut Ridge Road
PO Box 6216
Morgantown, WV 26506-6216

Dear Dr. Croucher:

The DOE Peer Review Team for the Mid-Atlantic Recycling Center for End-of-Life Electronics (MARCEE) Project is pleased to submit the enclosed report. In general, we find this project to be addressing key opportunities and filling important gaps on the way to establishing an environmentally and economically sound infrastructure for the recovery of end-of-life electrical and electronic products in the United States. This is a challenging activity, and the MARCEE Project partners appear to be uniquely positioned to realize technical and commercial success. It is time to refocus efforts through the development and acceptance among all of the collaborators of a clear vision for the program and associated strategic objectives. It is also time to ensure an effective project management and leadership team is in place to maintain momentum along a defined critical path.

This MARCEE Peer Review report expresses the views of the review team from a 5,000 foot level. All of the team members were familiar with the MARCEE Project, some since its inception, but none have been intimately involved in the Project. All of the team members possess expert knowledge in the field of EOL EEE recycling.

The Team met together for the first time in Morgantown, West Virginia on November 30 and December 1 in conjunction with RECCON '05, heard presentations from several of the project partners, and engaged the partners in informative discussions. The team was also given access to MARCEE Quarterly Project Reports and the MARCEE Business Plan (2002) for review. On the second day in Morgantown, the Peer Review Team orally presented its preliminary findings to the MARCEE stakeholders.

Subsequent to the Morgantown meeting, the review team prepared a preliminary draft report based on its oral remarks, circulated and commented individually on the preliminary draft report, and finally met by conference call to agree on the scope and content of the final report. The final draft report does not provide a task-by-task assessment of the status of the MARCEE Project, but instead goes directly to more fundamental issues that appear to the review team to be critically important to the Program's future success. We welcome further discussions of our findings and conclusions with the project partners or other public and private sector stakeholders.

Thank you for allowing us the opportunity to contribute to the MARCEE Project. If you have any questions or require additional information, please do not hesitate to contact any of the Peer Review Team members. Contact information can be found at the end of the report.

Sincerely,

Michael M. Fisher (Chair)
Senior Director Technology
American Plastics Council

Sego Jackson
Principal Planner
Solid Waste Management
Lenovo International
Snohomish County, WA

Bassam J. Jody
Project Manager
Separation and Recycle Processes
Argonne National Laboratory

Dewey Pitts
Product Take Back Program Manager

DOE Peer Review
The MARCEE Project
Morgantown, WV
November 30 – December 1, 2005
Peer Review Committee Report

Submitted January 5, 2006

1. The Peer Review Team appreciates the significant accomplishments of the Mid-Atlantic Recycling Center for End-of-Life Electronics (MARCEE) Project in helping to advance a sustainable infrastructure for the recycling of end-of-life electrical and electronic (EOLE) products in the United States. The Project has addressed significant issues and filled important vacuums nationally and within the Mid-Atlantic Region. The need to expend significant time and effort in such an undertaking is to be expected and has been beneficial. The project is now at a critical point where it is possible to harvest some of the early accomplishments and results.
2. There is a pressing need to more clearly define the overall program objective and achieve buy-in from all of the participants. There needs to be clear sub-goals for each of the participating entities that link to the overarching objective. The MARCEE Project Team should agree on a Vision and corresponding Strategic Objectives. In light of the significant domestic and international changes that have occurred over the past five years relative to electrical and electronic equipment (EEE) recovery, a new Situation Analysis should be undertaken to better define the program objective and sub-goals.
3. The MARCEE Project is a very important project and needs a highly qualified Project/Program Manager selected from either within or outside the partners. In light of the value of the Project, a national search for a Project/Program Manager should be considered. There is a sense of urgency given the funding issues and integration challenges that are before the Project today. A dedicated Project/Program Manager can bring needed focus to the effort. If available, a committed interim Manager could be identified while the search is underway. The interim Manager should have a broad knowledge of EOLE issues and significant stakeholders and have a good repore with all MARCEE partners.
4. A critical role of the Project/Program Manager will be to establish efficient and effective coordination among the program participants and their respective tasks. Periodic meetings involving all of the participants will be essential to ensure coordination and focus on key objectives. Each of the partners (“primary contractor”/”subcontractors”) should appoint a lead person to report to the overall Project/Program Manager.
5. The DOE National Energy Technology Laboratory (NETL) and other funding sources rely on project reports to ensure appropriate and effective use of funds. The MARCEE Project should examine its reporting process to ensure that it is timely and thorough and

meets the requirements and needs of funders. Existing reporting responsibilities and processes should be examined and adjustments made if needed.

6. The Peer Review Team is comfortable with the national scope inherent in the National Center for Electronics Recycling (NCER) and the DN American effort and sees both bringing important value to the West Virginia centered MARCEE Project. DN American also provides important support services to the MARCEE Project partners that will need to be maintained. (Please see point 11 for additional comments on the value NCER and DN American bring to the overall MARCEE effort.)
7. The location of Amandi Services within the “project walls” in West Virginia is a positive step and provides a real world, commercially oriented foundation to build on to establish the more holistic EEE recovery infrastructure envisioned by the MARCEE Project.
8. In the absence of a MARCEE Project/Program Manager, PAZ has taken on many different roles (e.g., recruitment of commercial recyclers to the technology park, facilitating and providing services to ongoing national EOLE dialogues, pursuing additional project funding, identifying & evaluating new recycling technologies) which have helped to bring the MARCEE project to where it is today. However, PAZ should now redefine its mission to best serve the project by focusing its efforts on polymer recovery issues. The organization needs to renew its outreach to and desired engagement by its members in a way that strategically captures the inherent value of having a strong WV polymer industry at the table. This engagement will be critical in defining the polymer industry’s role in addressing EOLE plastics issues and in obtaining the necessary commitments (e.g., funding, equipment, materials, and recovery expertise) from this industry to support MARCEE project efforts in establishing a demonstration process at the technology park for the recycling of EOLE plastics.
9. SDR Technologies needs to think more broadly with respect to the following issues: Technology development and technology integration for plastics recovery that supports a sustainable polymer recovery infrastructure in WV with appropriate consideration given to the management of substances of concern; Sources of recoverable plastics beyond EEE to help achieve critical volumes of feedstock; Partnerships to improve efficiencies, effectiveness, and funding opportunities related to a the portfolio of resource recovery options appropriate to the project. SDR should define a clear objective such as the establishment of an effective demonstration process at the MARCEE technology park for the recycling of EOLE plastics generated from the Amandi Services dismantling operations. Their activities should focus on separating EOLE plastic parts into multiple streams based upon available capabilities, economics, and viable end-use applications and implementing the appropriate recovery processes for each respective stream (e.g., high value single resin type, commingled). West Virginia University’s capabilities may be of assistance to SDR in developing more efficient separation techniques to produce higher value products. SDR Technologies provides a key link between quality of feedstock supply (Amandi/others) and viable end-use applications. Project technical objectives should focus on both the recovery of high value recyclates and on the recovery of mixed plastics for commercial use.

10. The Peer Review Team is excited about the West Virginia University application work on mixed plastics. This work should continue to be supported and the research team expanded in order to define and bring the most promising project(s) to an end-point. Since it is likely that a large percentage of the total EOLE plastics will end up in the commingled stream in the short term, it is critical that SDR work closely with the University team to prove technical and economic feasibility in using these materials in composite applications. Accordingly, SDR and the University partners should develop and complete the necessary analytical and processing studies to establish the feasibility of using commingled EOLE plastics in commercial composite end-use applications and define the required properties (e.g., maximum level of contamination, plastic resins allowed in the mixture, processing parameters) for recovered EOLE plastic to be successful. In parallel, a search for higher value applications should be pursued for those EOLE plastic streams which can be separated easily and economically. The application development work should be better integrated with the interests and technical capabilities of SDR Technologies and the EOLE plastics generated from the Amandi Services demanufacturing operation. Once SDR has sufficiently demonstrated the effective recycling of this stream, they should expand their project scope to the recycling of EOLE plastics from other IT recyclers (e.g., mixed plastic parts, baled IT plastics).
11. Economics are at the heart of many EOLE recycling issues. Currently the value of the materials recovered in recycling electronics often does not pay for the entire costs to collect, transport and process these products. Therefore the efforts of NCER and IMTS to assist various parties that are trying to understand financing mechanisms, their implications, and management of those systems, are essential to the eventual success of electronics and electronic product polymer recycling nationally and in the Mid-Atlantic Region. While the NCER and IMTS can not resolve these issues, they have provided very valuable services and information to those who are attempting to resolve them. Examples of activities that are key next steps that have been undertaken by NCER and/or IMTS include:
- establishing a web-based standardized e-waste recycling and pilot program data system
 - analysis of white box share of obsolete electronics and market share, and implications to funding systems
 - analysis of corporate brand share
 - analysis of and business plan development of Third Party Organizations (TPOs) as an option to manage legislated recycling systems
 - analysis of how to develop a TPO structure that can be implemented for multiple states
 - establishing the data base and web tool for the Electronic Product

Environmental Assessment Tool (EPEAT). This tool has been designed to assist institutional purchasers to procure equipment with certain environmental attributes, some

of which assist with end of life management and market development. Agencies representing over \$20 billion in annual information technology purchases have committed to using the tool when it becomes operable in 2006. Already, these activities are generating additional funding and deserve continued grant project support during this early incubation period, while they rapidly establish their national and regional identity and utility, and attract more significant funds.

12. The MARCEE Project, while regional in scope, has had national, indeed international, impact both in terms of stakeholder engagement, reach and influence, and federal agency support. As the Federal Electronics Challenge takes shape involving a multitude of Federal Agencies, the MARCEE Project should be examined as a resource for helping to identify sustainable end-of-life product management options.

Concluding Remarks on MARCEE Tasks 1.6 and 2.6

In 2005 NETL/DOE requested that MARCEE hold a Peer Review of its activities. Four well known people in the e-scrap area were brought together and a review was held in Morgantown during 4Q'05. The review team was impressed with the progress MARCEE had made in certain areas and made suggestions as to changes they felt should be made going forward. The main recommendation was to appoint a Director to oversee all of the MARCEE activities with the authority to build a regional recycling industry in West Virginia. This recommendation to the MARCEE Governing Council was given serious consideration but was rejected on financial grounds. Other recommendations that were suggested by the Peer Review Committee were adopted individual participants to MARCEE. The review team also pointed out that MARCEE was a "brand name" in recycling circles, which should be preserved if at all possible. No decisions as to what to do with the MARCEE name have been made.

E-Scrap is now becoming established as an important and viable industry across the US. It appears likely that a bipartisan federal e-waste bill will be passed in the next Congress (2009-2011). Part of the bill could be the appropriation of research funding for e-waste studies which is being advocated by this emerging industry. If this occurs, WVU could be well placed to compete for such funding. In response to a request from the Dean of Engineering, a report was written outlining areas where research is presently being carried out, and where WVU could play an important role with its present faculty.

3.0 New Research Activities Sponsored by the WVU Polymer Research Center

In the 4th quarter 2008 funding was allocated for polymer research projects at WVU. An RFP was written and circulated in December 2008. Eight proposals were received which were externally reviewed and four were chosen to be funded as of February 2009.

They were:

Polymer Nanocomposites for Carbon Dioxide Capture (PI is R. Gupta)

Polymer Films and Thin-Laminates for Renewable Energy and “Green” Infrastructure (PI is D. Cairns)

New Functional Polymers based on Triazoles (PI is X. Shi)

Genetic Modification of Woody Biomass and Isolation of Cellulosic Fibrils in Micro/Nano Scales for Biofuels Development (PI is J. Wang)

Each of these proposals has an *energy* theme. The reason for this is to tie the WVU Polymer Research Center activities to a major new initiative within the university known as the *Advanced Energy Initiative (AEI)*.

The following reports chart the progress made in these research projects over the past year:

Polymer Nanocomposites for CO₂ Capture (PI/R.Gupta)

Summary

The main objective of this project was to develop nanoclay-based polymer nanocomposites for CO₂ capture. This involves treating nanoclays with amine-containing compounds so that the resulting material is able to adsorb CO₂ from a gas stream by chemisorption. The treated nanoclays can then be dispersed in a suitable polymer matrix to make polymer nanocomposite solid sorbents. In this report, results are presented from experiments performed on the surface treatment of montmorillonite and Perkalite nanoclays and the resulting CO₂ adsorption behavior. It was found that 3-aminopropyltrimethoxysilane (APTMS), an amine compound, could be successfully grafted on to the surface of both the montmorillonite and Perkalite, with the extent of grafting being greater on Perkalite nanoclay. Also, various grafting methods resulted in different amounts of amine grafting. For the APTMS treated montmorillonite clay, about 25wt% CO₂ capture capacity could be achieved at high pressures which compares well with the desired CO₂ sorbent capacity of about 22wt%. At atmospheric pressure, the capture capacity is about 8wt%. These results validate the essential idea behind the research reported here. Surprisingly, though, the APTMS-grafted Perkalite showed very little CO₂ capture capacity. Clays grafted with other amine compounds, such as polyethylenimine (PEI), Ethylenediaminetetraacetic acid tetrasodium dihydrate (ETDA) and aminobenzoic acid sodium salt (AAS), also resulted in montmorillonite and Perkalite clays which showed only a small CO₂ capture capacity. From these results it can be concluded that while the potential exists for developing polymer nanocomposites for CO₂ capture, the reason why some amines work but others do not needs to be investigated in order to increase both the amine grafting on the nanoclays and the CO₂ capture capacity of the resulting solid sorbents.

Background and Objective

To reduce the emission of carbon dioxide from anthropogenic point sources, such as coal-fired power plants, one approach is to remove the CO₂ from flue gases by separation processes before releasing the CO₂-free gases into the atmosphere. Captured CO₂ could then be compressed and transported for use in applications such as urea production or enhanced oil recovery or be sequestered for an extended period of time in geological formations.

Liquid sorbents, solid sorbents and membrane separations are commonly proposed to capture CO₂ from the post-combustion flue stream. Indeed, liquid sorbents, such as aqueous amine solutions, have been industry standards for a long time. Here, CO₂ is captured by chemical absorption due to the reaction between the amine and CO₂. CO₂ is subsequently desorbed from the solution by heating to a high temperature, regenerating the amine solution for reuse. Though liquid amine processes are capable of removing almost 98% of the CO₂ from flue gases, they have high equipment costs, corrosion problems, amine deactivation due to the presence of SO₂ and NO_x and the high energy cost of regeneration. Consequently, there is an urgent need to develop better CO₂ capture technologies. Membrane separation and solid sorbents are alternative technologies that are being pursued to replace the liquid amine adsorption process. Our focus in this research is on solid sorbents. The advantages that they offer over amine solvents include the

absence of corrosion and the relatively low cost of regeneration. Solid sorbents have actually been used in enclosed environments such as those in submarines and spacecrafts to remove CO₂ from the atmosphere. However, they have low adsorption capacities and, to the best of our knowledge, no solid sorbent is commercially available that can satisfy the post-combustion CO₂ capture requirements of industrial power plants. Some other concerns are: (1) deleterious effect of acid gases, such as SO₂ and NO_x, present in flue gases on the solid sorbent (2) effect of fly ash (3) sorption temperature (4) effect of adsorption/desorption cycling (5) attrition resistance and (6) possible catalytic effect of the solid sorbent. Research work is ongoing at NETL-DOE and various other research institutions to solve these problems and to develop useful, high capacity solid sorbents for CO₂ capture.

Our main research objective is to develop low-cost nanoclay-based polymer nanocomposites to work as high-capacity solid-adsorbents to capture carbon dioxide from post-combustion flue gases. Polymer nanocomposites are typically made by dispersing montmorillonite, a layered silicate, into a polymer. Since montmorillonite occurs in nature as micron-sized particles, the platelets making up these particles have to be exfoliated or separated from each other in order that the nanocomposites possess superior mechanical, barrier and flammability properties. This is done by chemical treatment of the clay followed by the use of shear mixing in an extruder. Each platelet is 1 nm thick, has hydroxyl groups on the edges and is composed of an alumina octahedral layer sandwiched between two silica tetrahedral layers. The different platelets contain adsorbed Na⁺ ions between them, and these ions can be exchanged with organic cations to make the clay compatible with polymers. When the clay is fully exfoliated, the specific surface area can reach 800 m²/gm. Another nanoclay used for this purpose is hydrotalcite layered double hydroxide (LDH) clay which is available commercially as Perkalite. Perkalite can have a surface area as high as 1600 m²/gm when fully exfoliated. If use can be made of these large surface areas to adsorb CO₂, result should be a high capacity solid sorbent. However, nanoclays by themselves do not have any significant CO₂ capture capacity at low temperatures. Hence they have to be chemically treated with organoamine compounds to graft amine groups on the nanoclays. Amine groups react with CO₂ in a reversible fashion which results in CO₂ capture. The relevant reactions are as follows:

Thus, one mole of CO₂ requires two moles of amine to react. However, if water is present, the reaction proceeds according to following scheme to form bicarbonate:

Nanoclays contain various reactive groups and exchangeable ions that can be used for grafting amino groups. Montmorillonite contains hydroxyl groups on the edges of the platelets and exchangeable cations in the inter-gallery space of the platelets. Perkalite contains hydroxide groups on the surface and exchangeable anions in the inter-gallery space. Based on this, 3-aminopropyltrimethoxysilane (APTMS) is a logical compound to react with the hydroxyl groups, while polyethylenimine (PEI) can be used to substitute for the cations present on the faces to maximize amine grafting. For Perkalite clay, Ethylenediaminetetraacetic acid tetrasodium dihydrate (ETDA) and aminobenzoic acid sodium salt (AAS) can be used for anion exchange.

After grafting, these amine compounds are expected to act as capture sites for CO₂. Our aim was to maximize the amine grafting to increase the CO₂ capture capacity. The following section describes the experimental details of amine grafting and CO₂ adsorption experiments.

Experimental Methods and Materials

Materials

Montmorillonite clay was purchased from Southern Clay products as Cloisite NA. Perkalite clay was provided by Akzo-Nobel. Amine compounds APTMS, PEI, ETDA and AAS were purchased from Sigma-Aldrich.

Experimental Methods

APTMS grafting was performed by two methods. In the “dry method”, the nanoclay was dispersed in either toluene or dimethyl formamide (DMF), and APTMS was then added and the mixture was stirred for 24 hrs to allow grafting to take place. In the second method, called the “slurry method”, the nanoclay was first dispersed in water to swell the clay so that more surface area becomes available for grafting. After filtration and drying, APTMS grafting was performed as described above. Grafting reactions by other three amine compounds were performed in an aqueous medium.

The following methods of CO₂ adsorption were used to evaluate the nanoclay performance:

High pressure saturation

Nanoclay samples were weighed and then enclosed in a pressure vessel. The pressure vessel was then pressurized with pure CO₂ at 280psi. Samples were left for up to 3 days for CO₂ adsorption to take place. After that, the pressure vessel was depressurized and the samples removed. They were weighed immediately after removal and then periodically after every 15 minutes.

Thermogravimetric analysis

CO₂ adsorption was also studied using TA Instruments Q50 thermogravimetric analyzer (TGA). The nanoclay sample was loaded into a TGA, and the temperature was ramped to 100°C under N₂ flow and then held at this temperature for 1 hour. This was done to remove any adsorbed moisture. Once moisture was removed, the sample was cooled down to 30°C under N₂ flow. Now the gas flow was switched from N₂ to CO₂, and the weight gain was observed as a function of time at a constant temperature since CO₂ adsorbs on the clay particles for up to 18 hours; thereafter, equilibrium is reached.

The TGA was also used to determine the amount of amine grafting on the treated nanoclays. To determine the amount of amine grafted onto the clays, the treated nanoclay was loaded in the TGA and the temperature was ramped up to 600°C at a rate of 20°C/min and then held constant for 30 minutes. At this temperature, all the organic material undergoes thermal decomposition. The difference between the starting weight (after accounting for moisture) and the final weight is the amount of amine compound immobilized on the nanoclays.

Results and Discussion

Grafting of APTMS on Montmorillonite Nanoclay

Experiments were performed to see the effect of various solvents and APTMS concentration on amine grafting. Solvents such as acetone, toluene and DMF vary in their polar-nonpolar behavior which can affect the nanoclay dispersion. Results obtained with the use of different liquid media are shown in Figure 1. It is found that the maximum amount of amine grafting is achieved when DMF is used as the solvent, and approximately 27 wt% APTMS is immobilized on the nanoclay surface. Figure 2 shows the effect of the amount of added APTMS in the reaction mixture. As the amount of APTMS used is increased, the amount of amine grafting also increases, but eventually saturation is observed.

Figure 1: Effect of dispersion solvent on the amount of amine grafting.

Figure 2: Amount of amine grafting as a function of added APTMS.

The fact that montmorillonite is easily swollen by water can be used to promote the separation of clay platelets. We evaluated the effect of dispersing the nanoclay first in water and then dispersing it in the chosen organic liquid. This method is designated as the “slurry method” as opposed to the “dry method” described above where only an organic liquid was used. Figure 3 shows the difference in amine grafting obtained by the use of the two methods. Clearly, more amine grafting is achieved by the slurry method, and this may be due to access to additional grafting sites in the presence of water.

Figure 4 shows the observed CO₂ adsorption for amine-grafted clays in the TGA experiment. It can be seen that up to ~8wt% CO₂ capture capacity can be obtained for the nanoclay sorbent prepared by the slurry method. The corresponding results when CO₂ adsorption was performed at 270 psi CO₂ pressure at room temperature are shown in Figure 5. It can be seen that up to ~25wt% CO₂ capture was obtained. This figure also shows that the best performance is obtained for the nanoclay sorbent prepared by the dry method. Desorption of CO₂ is also shown in the same figure. It can be seen that CO₂ desorbs rapidly simply by exposing the spent sorbent to atmospheric conditions. The very high CO₂ capture capacity obtained in our preliminary experiments demonstrates the utility of the chosen approach.

Figure 3: Effect of preparation method- “dry” vs. “slurry method”.

Figure 4: CO₂ adsorption capacities at atmospheric pressure for various amine grafted nanoclay sorbents. The adsorption capacity of untreated nanoclay is not shown as it is negligible.

Figure 5: CO₂ adsorption capacities at 270 psi CO₂ followed by desorption.

The effect of reusing the amine-grafted nanoclay after one adsorption-desorption cycle is shown in Figure 6; only a very small decrease in adsorption capacity is observed.

Figure 6: Effect of sorption-desorption cycling on capture capacity at high pressure CO₂ adsorption.

Some additional experiments were also performed with montmorillonite clay using polyethylenimine (PEI) as the grafting material. PEI is a polyamine containing many amine groups; therefore it may show a higher CO₂ capture capacity. PEI of various molecular weights was evaluated in these preliminary experiments. Since PEI is water soluble, grafting was performed in aqueous medium. The following table summarizes our initial findings:

Table 1: PEI grafting on montmorillonite clay and CO₂ adsorption

Sample	Clay Amt. (g)	Grafting Compound	Grafting Comp. Amt.	pH	% CO ₂ Adsorbed
AR	0.502	PEI Mn 1200	1.0 g		1.03
AS	0.506	PEI low MW	1.0 g		0.41
BK	0.502	PEI Mn 1200	1.0g	11.1	0.30
BN	0.501	PEI High MW	1.15 g	10.6	0.23

Clearly, for these materials, the CO₂ capture capacity is very small, and the reason for this observation needs to be understood.

Perkalite Clay

Some initial experiments have also been performed on Perkalite nanoclay. Here APTMS, PEI, EDTA and AAS were used to graft amine groups. APTMS and PEI are supposed to react with hydroxyl groups while EDTA and AAS may attach by anion exchange reactions. The following table summarizes results from these experiments:

Table 2: Amine grafting on Perkalite clay and CO₂ adsorption

Sample	Clay	Clay Amt. (g)	Clay	Solution Medium	Grafting Compound	Grafting Comp. Amt.	pH	% CO ₂ Adsorbed
	Perkalite LD							0.22
AJ	Perkalite LD	0.508	Dry	DMF	APTMS	0.820 g		0.90
AK	Perkalite LD	0.517	Dry	Acetone	APTMS	0.830 g		0.42
AL	Perkalite LD	0.5	15 ml Slurry	DMF	APTMS	0.818 g		2.94
AM	Perkalite LD	0.5	15 ml Slurry	DMF	APTMS	0.409 g		0.49
AN	Perkalite LD	0.500	Dry	DMF	APTMS	0.815 g		0.75
AP	Perkalite LD	0.514	Dry	Water	Aminobenzoic acid	0.312 g		0.53
AQ	Perkalite LD	0.505	Dry	Water	Aminobenzoic acid	0.250 g	10.5	0.57
BM	Perkalite LD	0.523	Dry	Water	EDTA	0.232 g		1.06

Here also, these initial experiments show very small CO₂ capture capacity. Still, APTMS-Perkalite made with the slurry method shows the highest CO₂ capture capacity. Experiments to determine the amount of amine grafting have not been performed yet. It may be possible to use a combination of these organoamine compounds to attach amines to the edges, faces and inter-gallery spaces simultaneously which should result in significantly more grafting of amines.

Conclusions

- From the experimental results detailed in the previous sections, the following observations and conclusions can be made:
- Nanoclays can be chemically treated to graft or immobilize amine containing compounds for CO₂ capture.
- Amount of amine grafting on montmorillonite nanoclay varies depending on the method of preparation- dry vs slurry method.

- APTMS is immobilized more effectively on montmorillonite clay than other amine compounds tested in this work.
- APTMS treated montmorillonite clay is the most effective in capturing CO₂. Up to 25wt% CO₂ adsorption is possible at high pressure saturation which compares well with the desired CO₂ sorbent capacity of about 22wt%.
- At atmospheric pressure, the APTMS-montmorillonite clay capture capacity is about 8wt%.
- For Perkalite clay also, APTMS treatment shows the most promising capture capacity as compared to other amine treatments.

Polymer Films and Thin-laminates for Renewable Energy and 'Green' Infrastructure (PI/D. Cairns)

Introduction

The initiation of a new research and fabrication project that will yield prototype conformable polymer based structures with increased durability and efficiency was proposed in the past and initial funding was obtained through MARCEE.

The proposed structures can be used in numerous energy-related and optoelectronic applications such as solar reflectors and flexible solid state lighting devices.

A common feature of such structures is the increased light-guiding capability that will be introduced on their surface using micro embossing and surface modification techniques. In addition, increased corrosion resistance and mechanical durability will significantly enhance the lifetime of such components. It is very important to manufacture such thin structures since increased device durability and efficiency is a key parameter.

Our preliminary work is focused on three major areas. At first, the enhancement of corrosion resistance of silver based films is a priority since these films are forming a base for most applications. The inclusion of Pd, around 3%, to the Ag films is critical since it greatly enhances the corrosion resistance. Also, the development and characterization of mechanically durable transparent conductors based on carbon nanotube films (CNT) is a major step towards improving the mechanical durability of flexible optoelectronic devices. Increased mechanical durability will in turn increase the device lifetime thus increasing energy efficiency. Finally, micro embossed surface films with increased light guiding ability are characterized. Microembossed surfaces could hold the key for next generation devices since they can significantly improve light-guiding capabilities even when they are bent or flexed.

This final report will address all the above issues. The flexible devices lab at WVU under the direction of Dr. Darran Cairns and Dr. Kostas Sierros is currently developing polymer films and thin polymer laminates for a range of energy applications including: flexible solid state lighting for automotive applications; dynamic roughness surfaces for drag reduction in aerospace; dust mitigation systems for lunar solar arrays; corrosion resistant solar reflecting films; and aerogel insulation materials for high efficiency windows. We are currently collaborating with experience industrial partners CP Films (Martinsville, VA), Grote (Madison, IN) and Unidym (Sunnyvale, CA) for developing the next generation of mechanically durable, corrosion resistant and energy efficient optoelectronic devices.

Results and discussion

Initial corrosion screening

Research and development of corrosion resistance silver based films are currently under way. We work closely with industrial partners (CP Films, Grote Industries) in order to develop the next generation of corrosion resistant silver based films for energy and green optoelectronic applications.

As shown in figure 1, when using Ag-Pd (1% Pd atomic ratio) coatings we can significantly reduce corrosion. Ag coatings are currently used as the mirror layer in solar reflector stacks. Accelerated salt spray monitoring of various Ag and Ag based alloy systems was conducted in a salt spray chamber (Ascott, UK) under the ASTM B117 protocol with the temperature increased to 45° for more accelerated results. Test duration depends on the corrosion resistance of the coating; the more corrosion resistant the coating is, the longer the period in testing without showing signs of corrosion. Resulting corrosion mechanisms can then be analyzed using microscopy, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS).

Figure 1: Corrosion resistance enhancement (right hand side) using Ag alloy coatings. Note increased corrosion when using pure Ag coating (left hand side). Both samples have been in an accelerated corrosion environment for 15 days.

From figure 1 we observe that corrosion initiates from the edges of the coating and progresses towards the center of the sample. It is limited on the edges of the sample when adding 1% Pd to pure Ag film. This has been also observed in dental material applications.

Microscopy and chemical analysis of corroded surfaces

Optical microscopy can greatly enhance our understanding regarding corrosion mechanisms. As shown in figures 2, a corroded surface of an Ag film immersed in NaCl for 15 minutes can develop pitting corrosion.

Figure 2: Pitting corrosion of a pure Ag film after immersion in NaCl (0.1 M) for 15 minutes.

Corroded regions ranging from a few μm to around 70 μm in diameter can be observed. There are also regions on the surface of the film that appear to be intact and non-tarnished. A critical question that arises is how corrosion progresses in the ‘bulk’ of the film. We attempted to answer this question later on this project with some encouraging preliminary results as will be explained later on this report.

Figure 3: Pitting corrosion of a pure Ag film after immersion in NaCl (0.1 M) for 24 hours.

When samples are immersed for longer periods (24 hours) as shown in figure 3, corrosion propagates and tends to cover larger areas on the surface of the film. Large salt crystals forming on the surface can be observed. Therefore, salt crystal formation and coalescence is the dominating mechanism in this case. In order to confirm this, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS) were performed. An SEM Hitachi S4000 was used equipped with a liquid nitrogen free Evex QDD-Violin Detector.

As shown in figure 4, a detailed SEM image showing the Ag film surface with the large salt crystals formed on it as confirmed by EDS chemical analysis. Also, it was confirmed that AgCl was formed as a corrosion product on the surface of the film. This is important since it further strengthens the characterization of corrosion mechanisms due to salt spraying.

Figure 4: SEM of a corroded Ag film surface and EDS analysis of the inset area.

Mechanical durability of transparent conductors

We work closely with industrial partners (Unidym, Grote Industries) in order to develop the next generation of transparent conducting materials. Transparent conductors need to be mechanically durable in order to remain functional when deformed to various shapes, figure 5. Up to date flexible devices are based on transparent conducting oxides which are brittle and prone to cracking when deformed.

Figure 5: Flexible lighting device under bending (right hand side) and twisting (left hand side) mode.

Replacing transparent conducting oxides with carbon nanotube based films, which exhibit superior mechanical properties, we will be able to enhance the mechanical reliability of such devices and be able to develop the next generation of flexible devices that can be bent and twisted significantly more than their predecessors.

Figure 6 shows the difference between ITO (a common transparent conducting oxide) and carbon nanotube (CNT) based films when they are both deformed under tension. By monitoring the electrical resistance of such films we can determine the onset tensile strain for mechanical failure. It is observed that the ITO electrical resistance increases at around 2% strain whereas significant increase of the CNT electrical resistance is observed at around 25% tensile strain. This indicates that the CNT based material can withstand significantly higher deformation strains than its ceramic counterpart.

Figure 6: Uniaxial tensile electromechanical testing of transparent conducting electrodes.

Using this advanced CNT film network we aim to introduce the next generation of highly durable (ITO-free) electrodes which can be used in various optoelectronic applications and can withstand high externally applied strains and thus deformations. Therefore, the manufacturing of extremely durable and corrosion resistant flexible LEDs is very close to completion. We anticipate that the use of CNTs will increase the lifetime of such devices from 1-2 years to 5-10 years. Also, the use of ITO which is a scarce will be eliminated.

Surface patterned films

There is significant interaction with our industrial partners (Unidym) in order to develop microembossed high-aspect ratio features on polymer surfaces, figure 7 left, for light-guiding and optoelectronic applications.

Figure 7: Schematic of microembossed prisms (left hand side) and CNT based film coated prisms (right hand side).

As shown in figure 8, preliminary microembossed prism structures have been developed and further, in detail, mechanical and optical characterization is following.

Figure 8: Scanning electron microscope image of a microembossed polymer surface.

The microembossed structures were coated with CNT-base films as schematically shown in figure 7 (right hand side). Coating, such high aspect ratio features, with CNT based films is highly beneficial since tip-to-tip conductive bridging can be achieved as can clearly be observed in figure 9 below. The extremely high strength of the CNTs will ensure the durability of the bridging. It has to be noted that bridging using ITO for example is extremely difficult and cost ineffective. The light-guiding capabilities of the film can be an additional advantage.

Figure 9: Scanning electron microscope image of CNT coated polymer prisms

EIS measurements for corrosion characterization

Ag and Ag-based alloy films were tested using EIS in order to determine their resistance to corrosion and their corrosion rates. EIS is a more quantitative test method than salt-spray for corrosion characterization. Tests were performed in a 0.1M NaCl solution. Figure 10 shows the corresponding Nyquist plots for pure Ag and Ag-alloy films. Nyquist plots obtained from EIS measurements provide a more quantitative measure of the corrosion resistance. The larger the diameter from the origin the more corrosion resistant the material. In this particular case, it is evident that the Ag-alloy sample is more corrosion resistant than the pure Ag sample. In more quantitative terms the Ag-alloy is approximately 3 times more corrosion resistant than the pure Ag film. It is therefore important to underline that adding a small amount, around 1%, of alloy to Ag films we were able to significantly increase corrosion resistance.

Figure 10: Nyquist plots for pure Ag film and Ag-alloy film

Electromechanical testing of surface patterned films

Mechanical durability of CNT coated and embossed films is of paramount importance since these structures will be flexed, bent and conformed in service. Figure 11 shows a monotonic uniaxial loading graph. An abrupt increase in resistance is observed at 25% uniaxial strain. This is because the sample fractures at this strain. The CNT film performs satisfactorily for up to 25% strain and the loss of functionality is a result of substrate rupture.

Cyclic loading between 0 and 10% uniaxial strain, figure 12, confirms that the film performs satisfactorily for up to 25 cycles with no significant loss of functionality. Then, a fatigue related gradual loss of functionality is observed until the 37th cycle when the substrate ruptures.

Figure 11: Monotonic tensile testing of patterned CNT coated film

Figure 12: Cyclic tensile testing of patterned CNT coated film.

XPS Characterization of Ag-alloy films

Finally, XPS characterization was performed in order to determine the salt migration in the ‘bulk’ of the structure and thus characterize the corrosion progression in the ‘bulk’ of the films. Figures 13 and 14 show XPS spectra performed on a corroded and on a non corroded area of a sample surface that was salt sprayed for several days. Interestingly enough, we observed Na migration in the bulk of the sample. This indicates a diffusion mechanism for the Na ions. Therefore, it was found that Na tends to migrate inside the ‘bulk’ of the film and is not limited to only forming crystals on the surface. In particular, a concentration of around 30% of Na ions was measured, figure 14. This is a very important result which leads to the conclusion that effective hardcoats have to be developed in order to stop the Na migration.

Figure 13: XPS spectrum for a non tarnished region.

Figure 14: XPS spectrum for a tarnished region. Note the increasing Na concentration (red line) as the sputter time (thickness) increases.

Conclusions

During this project various experiments were performed with the aim to characterize and improve the mechanical and corrosion durability of thin structures that are used in demanding flexible optoelectronic applications.

It was found that Ag-alloys, in particular small amount of Pd added in Ag, improve the overall corrosion resistance of the coating. This is critical in applications such as solar concentrators and photovoltaic's. Also, it was demonstrated that CNT networks greatly enhance the mechanical durability. Corrosion mechanisms were described and patterned polymer films with light guiding capabilities were introduced.

New Functional Polymers based on Triazoles (PI/X. Shi)

Introduction

The goal for this research supported by the MARCEE program is to develop novel materials and molecule building blocks with potential unique chemical and biological properties. The overall support from the MARCEE program allowed the Principal Investigator (PI), Xiaodong Michael Shi of the Chemistry Department of West Virginia University, to hire a postdoctoral research associate to conduct the proposed research. Though with limited time, the research project went well and significant research progress has been made. In addition, the support provided a solid foundation for the synthesis of triazole-based novel polymeric materials. Overall, this generous support has allowed the PI to initiate a new program to apply 1, 2, 3-triazoles as novel building blocks in functional materials and in the synthesis of biological molecules.

1) Synthesis of triazole ligands and radical polymerization:

Our first goal toward the triazole based new materials in to polymerize the vinyl-substituted triazoles through either radical polymerization or anion mediated chain extension. During the last ten months, a series of vinyl modified triazoles were prepared and the key building block, compound **1**, was prepared in gram scales through multiple step synthesis as shown in **Scheme 1**.

Scheme 1 Preparation of scaled-up triazole ligands

With the preparation of large scale of triazole monomer, the radical polymerization conditions were investigated. Various different reaction conditions were investigated. With AIBN as the radical initiator in toluene at 120 °C, triazole polymer has been successfully prepared.

Scheme 2 Developing polymerization conditions

The GPC measurements gave molecular MW>80K and NMR studies indicated that a carbon-nitrogen bond was formed which suggested the structures shown in **Scheme 2**. However, this process suffered from low yields and problem in robust repeating the reaction. With averaging

10 different batches, one 2 of them successfully gave the polymer and with low yields. Giving the unique structures of this new material, significant efforts have been made in optimizing the reaction conditions with better performance and easy repeatability. These conditions include different solvents, temperature and radical initiators. With these efforts, we concluded that the polymerization impurity in the triazole monomer from the synthesis shown in **Scheme 1** quenched the reaction and those impurities, even trace amount and was very hard to get rid of. We therefore made the further modification of the monomer by introducing a removable N-protecting group as shown in **Scheme 3**.

Scheme 3

With great efforts in purify the monomer, a readily removable pivolate methyl bromide was selected as the optimal linkers and the monomer ligand could then be purified from column chromatography followed by the recrystallization to get rid of the polymer impurity in the triazole monomers that quench the radical process. Deprotection of the pivolate group is currently under investigation in the group and triazole monomer with high purity is expected in the near future.

Another concern for the challenges in the polymerization process is the rather significant steric hindrance on the vinyl group (with the 1,1-diaryl substitution). An alternative synthetic route with much less hindered vinyl group on the triazole C-5 position was then developed as shown in **Scheme 4**.

Scheme 4

With the success in discovery the optimal method to pure vinyl substituted triazoles, the polymerization will be conducted again and efficient polymerization is expected. Once the proposed polymer is made the characterized, a manuscript will be submitted regarding the above-mentioned studies and a patent release would be also considered once the polymer become available.

2) Triazole-based polymer from condensation approach:

Besides the radical polymerization process, another valid strategy in applying functional 1,2,3-triazole as building block to achieve new material is the cross condensation with dual functional linkers. One approach is to develop triazole based di-acids as shown in **Scheme 5** to conduct cross condensation with di-amines. We were particularly interested in the N-2-aryl triazoles since we have recently demonstrate that these molecules possessed co-planar conformation between the triazole ring and the N2-aryl ring (Liu, Y.; Yan, W.; Chen, Y.; Petersen, J. L.; Shi,

X.* *Org. Lett.* **2008**, *10*, 5389-5392.). Moreover, efficient fluorescence emission was obtained with the N-2 aryl triazoles. Although detailed fluorescence studies are currently under investigation in PI's group, it is likely that the polymer formed from this new building block will be of great interest with potential unique photo and electronic properties.

Scheme 5 proposed novel triazole modified linkers for polymer synthesis

While this new polymer is very promising, the biggest challenge here is to develop an effective synthesis for the synthesis of the triazole-based ligands, such as the di-acids shown in **Scheme 5**. During the last a couple of months, we successfully developed an efficient synthetic route to reach the desired di-acids as shown in **Scheme 6**.

Scheme 6 Synthesis of novel di-acids monomer for polymerization

Notably, this route will not only gave the desired di-acids, but also provide a valid synthetic protocol to other di-acid derivatives, such as di-esters and di-cide chlorides. Moreover, with this route, different substitution, such as o-carboxylate and m-carboxylate (**Scheme 7**) could also be prepared, which allowed the proposed triazole derivatives as general building blocks for the new polymer construction.

Scheme 7. Alternative triazole building blocks that could be prepared from this route.

3) Unexpected, interesting novel triazole-based vinyl-Au complexes:

During the development of functionalized triazoles, we successfully prepared the alkyne-modified triazole as potential monomers in polymerization. Our initial attempt was to apply the more reactive alkyne derivatives for the polymerization. However, with the application of Au catalysts (one well known Lewis acid for alkyne activation), the unexpected green solution was observed. With good efforts in try to identify the products, we successfully isolated the intramolecular cyclization product of triazole as novel vinyl-Au complexes. The Au-carbene complexes were determined by X-ray crystallography (**Scheme 8**).

Scheme 8. Preparation of alkyne-triazole analogues un-expected vinyl-Au complex formation
Preparation of alkyne functionalized triazole for polymerization

An un-expected, intramolecular cyclization for the preparation of novel carbene complexes

The recent surge of homogenous gold catalysis brought a series of new transformations that significantly enriched the field of organic synthesis. Besides the efforts in discovering new type of Au catalyzed reactions, more and more efforts have been put in understanding the mechanistic reason behind unique reactivity of cationic Au, which gave great electrophilic activation toward alkyne and allene with a d^{10} metal center. Although the vinyl-Au intermediates, from nucleophilic addition to alkynes, were long believed as the reaction intermediate in Au activation of alkynes, unambiguous structural evidence was not obtained until very recently when X-ray crystal structures of several vinyl-Au complexes were reported (**Scheme 9**).

Scheme 9. Literature reported vinyl-Au complexes

The first successful isolation of vinyl-Au complex was reported by Hammond and coworkers (**9a**) in the late 2008 through intramolecular allene-ester cyclization. Shortly after, Hashmi and coworkers reported the X-ray crystal structure of **9b** through Au-catalyzed 6-endo-dig amide-alkyne cyclization. Very recently, Blum and coworkers isolated complex **9c** by Pd catalyzed carboauration. With the presence of C-Au bond, these vinyl-Au complexes were not stable under acidic condition, giving the corresponding protonation products when expose to water or acids.

Although the vinyl-Au compounds were only recently isolated as mentioned above, complexes with C-Au bond have been reported with a much longer history. Similar to the vinyl-Au complexes, almost all alkyl-gold compounds suffered from acid stability. Probably the only exception was the N-heterocyclic carbenes, where rather stable C-Au bond was formed due to the effective back bonding. This discovery revealed a unique C-Au bond, which survived from strong acids. With this absolute novel discovery, efforts were therefore put into further elucidation for the mechanism of this reaction. As shown in **Scheme 10**,

Scheme 10. Proposed reaction mechanism for the formation of the unique vinyl-Au complex

It was a great surprise that the C-Au bonds were stable under acidic condition, even with the presence of HSbF₆, which is the strongest acid existing with pK_a = -25. These structures have been unambiguously confirmed by the X-ray crystal structures shown in **Scheme 11**.

Scheme 11. X-ray crystal structures of the novel triazole-based vinyl-Au complexes

With the unambiguous evidence from the X-ray crystal structures, we discovered a new type of vinyl-Au complexes. This discovery will lead to the preparation of a series of novel gold complexes that potentially can catalyze a series of novel transformations for chemicals that are challenging to be prepared using previous methods. A manuscript is under preparation and will be submitted within in two weeks.

4) 1,2,3-triazole as special X-factor in catalyzing alkyne activation:

Our group has recently reported 1, 2, 3-triazole bound Au complexes as the effective, thermally stable catalysts in intermolecular alkyne hydroaminations. Partial support from the MARCEE was allocated to the further development of this new catalytic approach. To our please, even with the limited time, we discovered a new application of these complexes as effective pre-catalysts in promoting chemo-selective intramolecular furan-alkyne cyclization, which provided a) clear evidence for Au(I) cation as possible catalyst in this transformation and b) a practical alternative solution that allows simple, inexpensive PPh₃ as effective ligand.

As well documented in literature, the cationic Au activation of alkynes usually proceeded through two reaction paths: a) Lewis acid (or p-acid) activation of alkyne for nucleophilic addition and b) Au back bonding to alkyne that led to the formation of carbene-like intermediates. One good example for this interesting dual reactivity is the Au catalyzed intramolecular alkyne-furan arrangement, first reported by Hashmi and coworkers (**Scheme 12**).

Scheme 12. Dual reactivities of cationic Au catalysts

The furan-ynone **12a** could rearrange to form aromatic substitution product **12b** and phenol **12c** with the presence of proper Au catalysts. Although with some debates, it was generally believed that product **12b** was formed through arene addition to the gold (Lewis acid) activated alkyne (Friedel-Craft type addition). The formation of phenol **12c**, on the other hand, proceeded through the Au-carbene like intermediates followed by cyclopropane ring opening and gold carbene C=O bond insertion. Compared with reaction path A, the formation of phenol **12c** is a much more interesting transformation, which involved four bonds breaking and formation of four new bonds in one step. Hashmi and coworkers performed extensive investigations of this transformation. Remarkable works have also been performed regarding the elucidation of the reaction mechanism including the successful isolation of several key intermediates. Our interest in spending efforts on this rather “well studied” transformation was initiated by the “un-conventional” and “picky” ligand effect, along with unclear argument in literature whether Au(I) cation itself could promote this reaction or the *in situ* formed Au(III) (from Au(I) pre-catalyst decomposition) were the only viable catalysts for this reaction.

According to literature, the AuCl₃ was first reported as the effective catalyst for the isomerization of **12a**, giving phenol **12c** as the major products in good yields. Later developed Au (III)-pyridine complexes led to improved reaction efficiency. Meanwhile, the Au (I) complexes, such as Ph₃PAuOTf, were reported as less-effective catalysts with “slow reaction rate” and poor chemoselectivity. One hypothesis was that Au (I) underwent disproportionation and generated active Au (III) *in situ*, which then served as the active catalyst for this reaction. The successful application of Au(I) complexes as the pre-catalyst was first reported in 2006, while Uson–Laguna salt **13b** and Schmidbaur–Bayler salt **13c** were used to promote the reaction, giving modest to good yields (up to 72%) of the phenol products. Interestingly, with a more sterically hindered ligand, catalyst **13c** provided better chemoselectivity, favored the formation of the phenol (>20:1). Therefore, very recently, new Au (I) complexes with steric hindered ligands (such as **13d** and **13e**) have been applied as effective catalysts for phenol synthesis. These results led to the concerns: *were Au (I) cations themselves effective catalysts for alkyne 1 activation? Whether the application of the rather complicated steric hindered and electron enriched phosphorus ligands necessary?*

Scheme 13: Representative Effective Gold Catalysts for Hashmi Phenol Synthesis

It was reasonable to rationalize that Au(III), a better Lewis acid, should favor alkyne activation in the Friedel-Craft type cyclization (formation of A). The Au(I) cation, in theory, would be a better catalyst for carbene intermediate formation due to its high electron density on the gold atom (d^{10} for Au^{I} and d^8 for Au^{III}). But this hypothesis was not consistent with current literature reports. To investigate the reaction mechanism, ^{31}P NMR studies were performed with substrate **12a** and simple $\text{Ph}_3\text{PAu}^+\cdot\text{TfO}^-$ catalyst as summarized in **Scheme 14**.

Scheme 14. ^{31}P NMR spectra of catalyst $\text{Ph}_3\text{PAu}^+\cdot\text{TfO}^-$ interactions with substrate **14a**

^a Ph₃PAuCl (20 mg, 0.04 mmol) was dissolved in 1 mL CDCl₃, then AgOTf (10 mg, 0.04 mmol) and **14a** (24 mg, 0.08 mmol) was added sequentially (see supporting information).

To ensure the accuracy of these NMR experiments, the H₃PO₄ in a sealed capillary tube was applied as the internal standard (0 ppm signal). The Ph₃PAu⁺•TfO⁻ sample was freshly prepared. As shown in **Scheme 14B**, the Ph₃PAu⁺, though it decomposed over time (up to 10 h at rt), could be prepared in good purity. The integration ratio of the signals provided direct measurement of PPh₃Au⁺ cation concentration. Upon the addition of 2.0 equiv alkyne **14a**, formation of gold-mirror occurred *instantly*. A new 43.5 ppm signal was observed in NMR (**Scheme 14C**), which likely was attributable to the corresponding phosphorus oxidation products. The decomposition of the Ph₃PAu⁺•TfO⁻ occurred much faster with the presence of alkyne **14a** and almost no Ph₃PAu⁺ left after 2 hours (**Scheme 14E**). Importantly, **14a** was completely consumed and the products **12b** (26% NMR yield) and **12c** (28% NMR yield) were both formed, though with low yields and poor chemoselectivity. Upon addition of extra **14a** into the fully decomposed sample (**Scheme 14E**), a slower reaction of **14a** was observed, which was consistent with literature reports that in situ formed Au(III) or Au(0) from Au(I) decomposition could still catalyze this transformation, though with a slower reaction rate. These NMR experiments indicated that a) the reaction between Ph₃PAu⁺•TfO⁻ and **14a** was fast and b) the resulting low yields were caused by the decomposition of the Au(I) catalyst, especially with the presence of **14a**. These results were also in agreement with the facts that more bulky phosphorus ligands (i.e. **13d**, **13e**) gave better yields due to the improved stability of Au (I) cations.

Scheme 15. ^{31}P NMR spectra of complex **15a** with addition of **15b**

Considering the main problem for simple $\text{Ph}_3\text{PAu}^+\cdot\text{TfO}^-$ in promoting Hashmi phenol synthesis was the decomposition of catalysts, we wondered whether the X-ligand coordination strategy could be applied. This would provide an alternative solution to promote this useful transformation with the very simple, inexpensive PPh_3 ligand. The NMR experiments between triazole-Au complex **15a** and **14a** were then performed to evaluate the stability of the triazole-Au complex (**Scheme 15**).

To our great delight, no triazole Au decomposition was observed with the presence of **1a** even after 24 hours and isomerization products **15c** and **15d** were formed in modest yields (50%, 1:1). Later screening of the reaction conditions revealed with MeNO_2 as the solvents under dilute condition, the desired phenol product **15c** was prepared with nearly quantitative yield (>99%) with only 1% of catalyst loading.

Therefore, instead of tuning the phosphorus ligands, an alternative strategy was developed by using the 1, 2, 3-triazole as a coordination factor to stabilize the catalyst. Excellent yields and chemo-selectivity were obtained. This new approach not only provided a simple solution for the reported transformation, but also, more importantly, revealed a new strategy in fine-tuning catalyst reactivity. Influences on the reactivities of other gold catalyzed transformations by this X-factor effect are expected and currently under investigation.

Using Hybrid Poplar for More Efficient Biofuels and Bio-Nanocomposites Production (PI/J. Wang)

1. Overview

Poplar trees (native cottonwood and aspen species) are suitable candidates for genetic improvement for biofuels production due to their modest genome size, fast growth, amenability to genetic engineering and vegetative propagation, and adaptability to a wide range of planting conditions. In order to examine the potential of hybrid poplar for efficient production of biofuels and bio-nanocomposites, hybrid poplar samples were collected from a plantation at the West Virginia University Agronomy Farm (Fig. 1-1), including stumps and roots from a two-year old plantation, and stem-wood specimens from one-year coppice growth in a stool bed (Fig. 1-2). The hybrid poplar plantation (*Populus trichocarpa* x *Populus deltoides*) was established from vegetative cuttings at in July of 2007 from materials produced at the University of Minnesota (B. McMahon, personal communication). The plant material consisted of a single interspecific family produced from a pseudobackcross crossing design (Fig. 1-3). Flowering branches were collected from female *P. trichocarpa* tree clone 93-968 (clone PT1 in this report), from Washington state. Pollen was collected from a male *P. deltoides* clone, number ILL-101 (clone PD1), and used for crosses in a greenhouse setting (Stanton & Villar 1996). This produced an F₁ hybrid, clone 52-225 (clone F1), which has been used extensively in commercial plantations (van Oosten 2000). To dissect the factors contributing to hybrid vigor in this commercial clone, the F₁ hybrid was backcrossed to a different *P. deltoides* tree, clone D124 (clone PD2), from Minnesota (Riemenschneider et al. 2001). This produced the pseudobackcross family 52124 (collectively referred to as clone BC1 in this report), which was used for establishing the plantation and stool bed at West Virginia University. The plantation consists of 755 genotypes arranged in two randomized blocks at 2 m x 2 m spacing. Samples were collected in August of 2009 from stumps of trees that were harvested in December 2008. In addition, primary coppice shoots were collected from a stool bed that was established at 0.5 m spacing in 2007.

An anatomic analysis for each sample was conducted in cross section, radial section, and transverse section using a scanning electron microscope (SEM) (Figs 1-4 to 1-8). Although the vessel distributions in cross sections are visually different among the five types of poplar, the anatomic result tends to suggest that the hybrid poplar has more resemblance with *Populus trichocarpa* with fewer vessels per unit area, than to the pedigree father (*Populus deltoides* clone PD1). In general, all other anatomic features such as vessel size, fibers, and pits located at the cross, radial, and transverse sections did not reveal much difference among the five types of poplar. Future study may include the comparisons of average sizes of vessels with variations, void contents among the five samples. It is also necessary and important to perform an experiment to further study and in-depth anatomical properties like fiber length, fiber strength, rays and pits.

Figure 1-1: Two-year old hybrid poplar plantation (top) and one year old coppiced poplar in a stoolbed.

Table 1-1. Samples of five genotypes of poplar.

Generation	Grandmother	Grandfather	Mother	Father	Offspring
Code	PT1	PD1	F1	PD2	BC1
Latin or cross	Populus trichocarpa	Populus deltoides	Hybrid poplar 1 PT1*PD1	Populus deltoides	Hybrid poplar 2 PD2*F1
Number	93-968	ILL-101	52-225	D124	52124

Figure 1-2: Poplar roots (top) and one year old stem-wood specimens (bottom).

QTL Mapping Population

Figure 1-3: Crossing design for production of the QTL mapping pedigree

Female clone 93-968 was crossed to *P. deltoides* male clone ILL-101 to produce the F1 tree clone 52-225, a female tree. This tree was then crossed to another *P. deltoides* male clone, D124, to produce 796 progeny comprising family 52124.

Figure 1-4: SEM images of *Populus trichocarpa* (PT1, grandmother): a) Cross section, b) Radial section, c) Transverse section.

Figure 1-5: SEM images of *Populus deltoides* (PD1, Grandfather):
a) Cross section, b) Radial section, c) Transverse section.

Figure 1-6: SEM images of first generation hybrid poplar (F1-PT1*PD1, Mother): a) Cross section, b) Radial section, c) Transverse section.

Figure 1-7: SEM images of *Populus deltoides* (PD2, Father): a) Cross section, b) Radial section, c) Transverse section.

Figure 1-8: SEM images of second generation hybrid poplar (BC1- PD2*F1, Offspring):
a) Cross section, b) Radial section, c) Transverse section.

2. Thermo-Chemical Comparisons among Juvenile Hybrid Poplar, *Populus deltoids*, and *Populus trichocarpa* in Relation to Their Bioenergy Utilization Potentials

Introduction

Demand for alternative energy in the U.S. is growing due to a concerted effort to reduce the nation's dependency on fossil fuels. Currently, woody biomass is a potentially important feedstock for bioenergy (Perlack et al. 2005). The benefits of using biomass as feedstock for bioenergy include reduction of the use of nonrenewable fuels, less dependency on foreign fuels, stabilization of income in rural areas, and reduced carbon emissions to the atmosphere (Office of Technology Assessment 1993). The challenge with using biomass for transportation fuel production is due to the recalcitrant nature of the Lignocellulosic carbon. Currently, cellulase enzymes produced from a host of microorganisms can be used to hydrolyze wood into fermentable sugars provided an appropriate pretreatment is used. Pretreatment alters the structure of cellulose making it more accessible to enzymes, increases surface area of cellulose, disrupts cellulose crystallinity, solubilizes hemicelluloses, and removes lignin (Demain et al. 2005). The productivity of enzymes is limited by lignin content in pretreated wood and thus there is a need for biofuels feedstock with naturally low lignin content. Poplar trees (native cottonwood and aspen species) are suitable candidates for genetic improvement for biofuels production due to their modest genome size, fast growth, amenability to genetic engineering and vegetative propagation, and adaptability to a wide range of planting conditions. It is necessary to assess the anatomic, thermo-chemical related properties of hybrid poplar trees and their potential for biofuels and bioproducts.

Materials and Methods

This study utilized a hybrid poplar pedigree that was produced to identify genes that control lignin composition and recalcitrance properties for biofuel production, as described in chapter 1. This study was set up as a randomized complete block design (RCBD) with 4 replicates. In this design, two main factors were considered: genotype and wood source. There were five genotypes, all of which were part of a two-generation pedigree: *Populus deltoides* (PD1-the grandfather of the pedigree, and PD2-the father of the pedigree), *Populus trichocarpa* (PT1-pedigree the grandmother of the pedigree), an F1 cross between the grandparents (F1, mother),

and backcross offspring (BC1-PD2*F1, offspring). The second source of variation (block) factor is wood sample location within the various wood sources i.e. stem and stump. The experimental samples used for this study were collected from a two-year old hybrid poplar plantation and one year old coppice sprouts from a stool bed, both of which are located on the West Virginia University Agronomy Farm. After the samples were collected from the designated site, each specimen was processed into small blocks of wood for moisture content (MC) and density determination using a gravimetric method. Lignin, extractives, and holocellulose in the wood were determined in accordance with ASTM D 1110-84; 1106-96 (ASTM 2001).

Proximate analysis, i.e. content of volatile matter, carbon, and ash in wood, was evaluated based on ASTM procedures, designation (D3172, 2006 and D1102-84 2001). All pulverized samples used for heat value determination were oven-dried to 0% MC. One gram of each sample was placed in an oxygen bomb calorimeter (Parr 6300) for heat determination. After running each sample through the bomb calorimeter, corrections were made based on the calorimeter gross and net heat of combustion (Eqs. 1 and 2) for hydrogen, nitric acid, and sulfuric acid, and fuse wire consumption for the final computation of the gross and net heating value of each wood specimen following ASTM E711-87 (2006). At the completion of all physical, chemical, proximate, and thermal tests on the wood samples, analysis of variance with a Duncan multiple comparison was performed using SPSS statistical software (SPSS Inc., Chicago, IL).

$$H_c = (WT - e_1 - e_2 - e_3)/kg \quad (1)$$

$$H_n = 1.8H_c - 92.7H \quad (2)$$

Where;

H_c = gross heat combustion (J/kg)

T = observed temperature rise ($^{\circ}\text{C}$)

W = energy equivalent of calorimeter used (J/kg)

e_1 = heat produced by burning nitrogen in air (J)

e_2 = heat produced by formation of sulfuric acid in bomb (J)

e_3 = heat produced by heating wire and tread (J), m = mass of sample (kg)

H_n = net heating value (J/kg)

H = hydrogen (%)

Results and Discussion

The physical and chemical properties of juvenile hybrid poplar showed some differences among genotypes as shown in table 2-1 and Fig. 2-1. High densities of 0.44 g/cm^3 , 0.43 g/cm^3 and 0.42 g/cm^3 were observed in pedigree parents (PD2, PT1) and hybrid poplar (BC1) stumps respectively, while lower density range of $0.35\text{-}0.39 \text{ g/cm}^3$ were observed throughout the stem samples of all the five poplar genotypes. Stump densities of the first and second generation hybrid poplar (F1, BC1) of 0.43 g/cm^3 were 2% lower than the other genotypes. For generation 1 hybrid poplar (F1) compared with BC1, the stem density is higher (0.39 vs. 0.35 g/cm^3); stem and stump extractive content range of 11.5% to 12.51 were about 14% higher than its pedigree parents (PD1, PD2, PT1) (12.5 vs. 11.5%). BC1 stump lignin is lower than PD1 (24.67% vs. 25.6%), but higher than PD2, PT1, and F1. Stump holocellulose content observed are 67%, 66%, 65%, and 64% respectively for pedigree grandmother (PT1), mother (F1), father (PD2),

grandfather (PD1) and offspring (BC1); stem holocellulose content observed ranged from 63.2% to 65.5% across all the genotypes measured.

Proximate analysis indicated similar volatile matter, carbon, and ash content among the various poplar genotypes (Table 2-2). The values obtained were within the range those reported previously for hardwood species (Sjostrom 1981; Adebayo et al. 2008). Generally, the observed stem/stump volatile matter content which ranged from 72 to 74.7% showed little variation within the genotype wood (stem vs. stump) but with slightly higher volatile matter content of 74.7% for first generation pedigree mother (F1) and father (PD2). Stump volatile content of hybrid poplar (BC1) was slightly higher than *Populus deltoides* at the expense of lower carbon content. PD1, PT1, and BC1 had high carbon content values of 28.5%, 27.7%, 27.4%, and 27.2% respectively when compared to the other poplar genotypes. The least carbon content value of 25.2% was found in PD2 stem. Ash content (i.e. minerals like magnesium, calcium, potassium etc) varies significantly among the genotypes; stump ash content (0.8-1.7%) was higher than stem ash content (1.1-1.3%) in most of the genotypes. Hybrid poplar (F1 and BC1) showed slightly lower ash content when compared with their parents (1.1-1.2% vs. 0.8-1.7%).

The measured heating value varies significantly among the poplar genotypes. The values observed among the stem of the three poplar species indicated a slightly higher gross heat values at the stem than at the stump; the values ranged from 4,540.0 cal/g to 4,686.0 cal/g at the stem and 4256.1 cal/g to 4673.9 cal/g at the stump of the five genotypes. Hybrid poplar (F1, BC1) had higher gross heating values than their pedigree parents (PD1, PD2, PT1). The reason for the slightly higher gross heating value could be due to the proportionately higher lignin content in them. Lignin had been previously reported to have a strong correlation to higher heating value of wood, (White 1987). Heat related properties of the poplar genotypes are further illustrated in thermogrametric analysis (TGA) of the samples at various pyrolysis temperatures (from 0-400°C). In Fig. 2-2. TGA graph indicated two main phases in wood decomposition viz; phase 1-equilibrium moisture content loss phase 4.7% wood weight loss= % moisture content (MC). Phase 2-loss of wood volatiles otherwise called synthetic gases (CO₂, CH₄, NO_x, etc).

Table 2-1: Physical and chemical properties of hybrid poplar (F1 and BC1), *Populus deltoides* (PD1-pedigree grandfather, PD2-pedegree father) and *Populus trichocarpa* (PT1-pedegree grandmother).

Properties	PD1		PD2		PT1		F1		BC1	
Generation name	Grandfather		Father		Grandmother		Mother		Offspring	
	Stem	Stump	Stem	Stump	Stem	Stump	Stem	Stump	Stem	Stump
Dia. (mm)	14.50	65.00	14.00	31.00	19.00	65.00	16.00	85.00	13.50	31.00
Density (g/cm)	0.35	0.35	0.39	0.44	0.36	0.41	0.39	0.43	0.35	0.43
Green MC (%)	73.90	73.90	63.40	63.40	74.00	74.00	68.50	68.50	73.00	75.00
Extractive (%)	10.71	10.64	10.98	10.98	11.11	10.15	11.89	12.51	11.89	11.45
Lignin(%)	25.60	25.60	23.64	23.64	23.38	23.10	24.98	22.58	24.98	24.67
Holocellulose(%)	63.29	64.00	65.24	65.24	65.51	67.00	63.91	66.32	63.88	63.44

Table 2-2: Proximate and heat related properties of hybrid poplar (F1 and BC1), *Populus deltoides* (PD1- pedigree grandfather, PD2-pedigree father) and *Populus trichocarpa* (PT1-pedigree grandmother).

Properties	PD1		PD2		PT1		F1		BC1	
Generation name	Grandfather		Father		Grandmother		Mother		Offspring	
	Stem	Stump	Stem	Stump	Stem	Stump	Stem	Stump	Stem	Stump
Dia. (mm)	14.50	65.0	14.0	31.0	19.0	65.0	16.0	85.0	13.5	31.0
Density (g/cm)	0.35	0.35	0.39	0.44	0.36	0.41	0.39	0.43	0.35	0.43
Volatile (%)	72.3	71.5	74.7	73.6	72.9	72.6	74.7	74.6	72.4	73.3
Carbon (%)	27.7	28.5	25.2	26.4	27.1	27.4	25.3	25.4	27.2	27.2
Ash (%)	1.3	1.2	1.2	1.7	1.2	0.8	1.2	1.1	1.1	1.2
N. Heat (Cal/g)	4384.2	4236.8	4246.9	40070.6	4328.8	3952.6	4381.9	4233.2	4369.8	4342.4
G. Heat (Cal/g)	4688.2	4540.0	4549.0	4374.7	4632.9	4256.1	4686.0	4537.3	4673.9	4646.4

Figure 2-1: Chemical properties comparisons among *Populus deltoides* (PD1-pedegree grandfather, PD2-pedegree father) and *Populus trichocarpa* (PT1-pedegree grandmother, F1-pedegree mother) and BC1-offspring

Figure 2-2: Thermal degradation of hybrid poplar (BC1) at ramp temperature of 0-400°C in TGA Q50 V20.10 build instrument.

Conclusions

The cross between poplar species *Populus deltoides* and *Populus trichocarpa* resulted in a hybrid poplar tree with substantially different physical, chemical, and thermal properties from its parent trees. The limitation of this study is that the samples used are a year old. These trees are expected to undergo some physiological changes that may result in some chemical alterations in the wood. However, our comparison of wood from two-year old stumps and one-year old coppice sprouts do not support this expectation. Future studies should examine variation among the 52124 progeny to enable mapping of genes underlying the control of lignin and cellulose content, thus enabling genetic engineering of feedstock for efficient biofuels production using streamlined industrial processes. Future work may also include examination of variations among a three year old 52124 progeny using a more robust experimental design and analysis to enable mapping of genes underlying the control of lignin and cellulose content in order to produce an economically efficient biofuel feedstock. It is also very important to perform an experiment to further study and in-depth anatomical properties like fiber length, fiber strength, rays and pits, and the chemical nature/type of lignin variations in 52124 progeny as influenced by age and soil. In addition, it is needed to study the behavior of lignin and cellulose variations in 52124 progeny to commercial bio-conversion enzymes to sugar.

3. Cellulosic Fibrils Isolation and Its Nanocomposites from Hybrid Poplar and Appalachian Hardwood Residues

Introduction

Fast growing hybrid poplar is a suitable candidate for genetic engineering for biofuels and bioproducts production. Additionally, there are about 2.41 potential million dry tons of wood residues per year, which is 72.7% of the total biomass in West Virginia (Wang et al., 2006). The challenge is determining the best use for this potential woody biomass. This study is intended to investigate high-value nanocomposites reinforced with micro/nano-scale cellulosic fibrils and nanocrystals isolated from this hybrid poplar and wood wastes. Many terms have been used to describe different types of cellulose fibrils, such as microcrystalline cellulose (MCC), microfibrillated cellulose (MFC), cellulose nanocrystal, cellulose nanofibril, cellulose whisker, cellulose crystallites, and bacterial cellulose (BC). A cellulose nanocrystal is part of a microfibril, sometimes called elementary microfibrils, while the nanofibers are bundles of nanocrystals or microfibrils.

Bio-based nanocomposites are considered one of the green materials for the next generation. The market for these bio-based nanocomposites has the potential for dramatic growth with a green concept in recent years. The bio-based nanocomposites can be produced from renewable resource-based polymers in combination with nano-filler reinforcement, such as cellulose nanocrystals and nanofibers, for a variety of applications. Nanocomposites of this category are expected to possess improved strength and stiffness with little sacrifice of toughness, reduced gas/water vapor permeability, a lower coefficient of thermal expansion, and an increased heat deflection temperature (Ray et al., 2003; Samir et al., 2004; Zimmermann et al., 2004). Market for these bio-based nanocomposites has the greatest growth potential in industries, especially, in areas where biocompatibility and environmentally responsible design and construction are required. The potential applications include biomedical tissue, car interiors, packaging materials, electronics, and housing appliances.

Several methods have been developed to obtain cellulose nanocrystals and nanofibers: 1) chemical methods: such as strong acid hydrolysis - cellulose nanocrystals have been obtained from wood fibers (Candanedo et al., 2005) and sugar beet pulp (Dufrense et al., 1997) by this method; 2) mechanical methods: such as homogenizer (Turbak et al., 1983; Herrick et al., 1983), refining and cryocrushing (Chakraborty et al., 2005), and high-intensity ultrasonication (Cheng et al., 2007; Cheng et al., 2009; Wang and Cheng, 2009).

Cellulose nanocrystals and nanofibrils can be used to process nanocomposite materials using a polymer as the matrix. Nanocomposite is a broad concept that includes at least one-dimension of one component in the composite at the nanometer scale (1-100 nm). Because of the nanometric size effect, these composites have some unique outstanding properties with respect to their conventional microcomposite counterparts. The research on nanocomposites reinforced by cellulose fibrils/crystals has grown very fast because of its environmentally friendly feature and the improvement of stiffness and/or strength in recent years (Samir et al., 2004; Zimmermann et al., 2004). There are two major fabrications of nanocomposites. One is film casting using water-soluble or solvent-soluble polymers (Favier et al., 1995), and the other is freeze drying followed

by classical compression or extrusion processes (Hajji et al., 1996). Pure cellulose and pulp fiber are the common raw materials for the isolation of nanocrystals and nanofibers in current research. In this study, we used hybrid poplar wood and Appalachian hardwood residues as raw materials to isolate micro/nano-scale fibrils/crystals and fabricate nanocomposites.

Materials and Methods

Three wood sources were used: black cottonwood (*Populus trichocarpa* (PT1), hybrid poplar 2 (BC1 offspring in Table 1-1), and yellow-poplar (*Liriodendron tulipifera*) residues. Microcrystalline cellulose (MCC, Avicel PH-101, and FMC BioPolymer) was used as reference material. Biodegradable polymer: poly(vinyl) alcohol (PVA, 99-100% hydrolyzed, approx average M_w 86,000, Acros, New Jersey) was used as matrix.

Cellulosic fibrils in micro/nano scales and nanocrystals from yellow poplar residues and *Populus* samples were produced using mechanical pretreatment followed by strong acid hydrolysis (Fig. 3-1). An optical microscope (Fisher Scientific Micromaster I) and scanning electron microscope (SEM, Hitachi S-4700) were used for morphological characterization of cellulose particles, fibrils and nanocrystals.

Figure 3-1: Procedures to isolate cellulosic nanocrystals.

PVA water solution (10 wt%) and cellulose fibril and nanocrystal water suspension were mixed and stirred manually and then dispersed by ultrasonic treatment (Sonic Newtown, CT, 20 kHz, Model 750 W) for about one minute with 50% power level. The film casting method was used to make nanocomposite film in propylene dishes. The mixtures were degassed in a desiccator with vacuum and evaporated at room temperature (T : $\sim 20^\circ\text{C}$) and relative humidity (RH) of 30% until films were formed, and then the films were heat treated in an oven at 60°C for more than 4 hours (Cheng et al. 2007). The samples were kept in a desiccator before the mechanical properties were characterized. The composites with three levels of fibril loading (1%, 2%, and 5%) were manufactured and tested. The nominal thickness was $150\ \mu\text{m}$.

The mechanical tests were performed using an Instron testing machine (Model 5869, load cell 30kN). The crosshead speed was 2.5 mm/min. Crosshead extensions were used as the specimen deformations to calculate the tensile strain. The samples were cut to dogbone shapes with width of 5 mm for the narrow portion and total length of 40 mm (gauge length was 20 mm). Based on ASTM D1708 standard (ASTM, 2002), five specimens were tested for each composition. Tensile modulus was tangent modulus from the linear portion in the stress-strain curves with ignoring the initially unstable part. The maximum tensile stress was used as the tensile strength. The elongation to break was calculated using the extension at break of each sample divided by the original length of the sample.

Results and Discussion

Characterization of wood particles, fibrils, and nanocrystals

The wood flour was changed to white after lignin was removed (Fig. 3-2, left). The microstructure of wood particles made by milling is shown in Fig. 3-2 (right). Most particles were smaller than 200 μm and the dimensions are irregular. After hydrolysis, a turbid suspension presented for all samples, but after ultrasonic treatment, the suspensions were transparent (Fig. 3-3, left). Most cellulose crystals were still bundles of single nanocrystals as shown in the SEM image of samples dried on a silicon wafer (Fig. 3-3, right). The average diameter of the nanocrystals was about 21 nm measured by dynamic light scattering (Fig. 3-4). This further indicated that the nanocrystals were still bundles of single nanocrystals because a single cellulose crystal is about 3-10 nm in diameter (Beck-Candanedo et al. 2005).

Figure 3-2: Images of yellow poplar wood residues before and after lignin was removed (left), and microstructure under microscope (right).

Mechanical properties of the nanocomposites

Fig. 3-5 shows typical tensile curves of pure PVA and nanocomposites with 5% cellulose nanocrystals, respectively. The elongation to break decreased in different percents for all composites compared with pure PVA.

The tensile modulus and strength of neat PVA and its composites reinforced by untreated and treated MCC, and nanocrystals from MCC, yellow poplar, hybrid poplar (BC1), and *P. trichocarpa* (PT1) with 1, 2, and 5 wt% are shown in Figs. 3-6 and 3-7. The tensile modulus of neat PVA was decreased significantly by untreated MCC, while PVA modulus was increased by all cellulose nanocrystals. The tensile strength of PVA was decreased significantly by untreated and treated MCC, but it did not decreased by most of the nanocrystals. The nanocrystals from MCC were better than others for tensile strength. These demonstrated that the nanocrystals from MCC may have higher aspect ratio (length/diameter) because MCC may be made from softwood, which has higher aspect ratio of crystals than hardwoods, such as the species used here. No significant differences of reinforcement among cellulose nanocrystals from yellow poplar, hybrid poplar, and *P. trichocarpa* were detected (Figs. 3-6 and 3-7).

Figure 3-3: Cellulose suspensions in water (left) and SEM image of self assembly formed bundles of nanocrystals (right).

Figure 3-4: Nanocrystal size distribution measured by dynamic light scattering.

ASTM D1708 Plastics- Microtensile Specimen Test

ASTM D1708 Plastics- Microtensile Specimen Test

Figure 3-5: Typical stress strain curves of pure PVA (top) and cellulosic (bottom)

Figure 3-6: Tensile moduli of the nanocomposites.

Conclusions

Bio-nanocomposites, one of the green materials for the next generation, can be made from cellulosic nanofibers or nanocrystals and some biodegradable polymers. The potential applications of these green nanocomposites may include biomedical tissue, car interiors, packaging materials, electronics, and housing appliances. Cellulose nanocrystals can be isolated from MCC, yellow poplar, hybrid poplar, and *P. trichocarpa* (PT1) using mechanical and chemical methods. Most of nanocrystals were bundles of single nanocrystals and the average diameter of the crystals was about 21 nm. All the nanocrystals can be used to reinforce PVA to fabricate bio-nanocomposites, but they may have different effects on PVA tensile properties. Cellulose nanocrystals have much better performance than untreated MCC for PVA reinforcement. No significant differences of tensile mechanical properties of PVA nanocomposites reinforced with cellulosic nanocrystals isolated from yellow poplar wood residue, hybrid poplar 2 (BC1), and *P. trichocarpa* (PT1) were detected. One possible limitation of this study is that the samples from hybrid poplar 2 (BC1), and *P. trichocarpa* (PT1) were only one year old, which are expected to undergo some physiological changes that may result in some dimension changes of nanocrystals for older trees. If funding available, further study to separate and characterize nanocrystals, fabricate and characterize cellulosic nanocomposites is necessary in order to evaluate the differences and polymer reinforcement of nanocrystals from hybrid poplar (especially for several years' old or adult trees) and hardwood residues. If nanocrystal isolation process is easier from the hybrid poplar or its genetically improved hybrid poplar, the cost of bio-nanocomposites should be decreased and their commercialization will be more realizable.

Figure 3-7: Tensile strength of nanocomposites prepared

4. Future Work

Further studies are necessary in the future to investigate more hybrid poplar samples, such as three-year old trees, more details of anatomical properties, thermo-chemical properties, and biofuel conversion processes from these materials, as well as the isolation and characterization of nanocrystals and their bio-nanocomposites. Specifically, future studies will examine the variations among 52124 progenies (offspring) to enable mapping of genes underlying the control of lignin and cellulose content, thus enabling genetic engineering of feedstock for efficient biofuels production using streamlined industrial processes. Future work may also include examination of the variations among three-year-old 52124 progenies using a more robust experimental design and analysis to enable mapping of genes underling the control of lignin and cellulose content in order to produce an economically efficient biofuel feedstock. It is also very important to perform an experiment to further study in-depth anatomical properties like fiber length, fiber strength, rays and pits, and the chemical nature/type of lignin variations in 52124 progenies as influenced by age and soil. In addition, we should also study the behavior of lignin and cellulose variations in 52124 progenies to commercial bio-conversion enzymes for sugar production.

The limitation of this study is that the samples used are one-year-old. These trees are expected to undergo some physiological changes that may result in some chemical alterations in the wood. However, our comparisons of wood from two-year old stumps and one-year old coppice sprouts do not support this expectation. Future studies should examine the variations among 52124 progenies to enable mapping of genes underlying the control of lignin and cellulose content, thus enabling genetic engineering of feedstock for efficient biofuels production using streamlined industrial processes.

Further study to separate and characterize nanocrystals, fabricate and characterize cellulosic nanocomposites is necessary in order to evaluate the differences between polymer reinforcement of nanocrystals from hybrid poplar (especially for several years' old or adult trees) and hardwood residues. More powerful, robust analyses, such as using atomic force microscope (AFM) and transmission electron microscopy (TEM) need to be conducted for morphological characterization of cellulosic nanocrystals. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) will be helpful to evaluate the thermal transition property, enthalpy relaxation, and crystallization and melting behavior of the bio-nanocomposites.

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List of Figures and Reaction Schemes

2.1 Recycling Polymers from End-of-Life Electronics into Wood-Polymer Composite Materials

Figure 1: Tensile strength of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 2: Tensile modulus of 50wt% wood-ABS-WPCs with different amount of SMA and SEBS-g-MA

Figure 3: Elongation at break of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA.

Figure 4: Flexural strength of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 5: Flexural modulus of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 6: Flexural strain at maximum load of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA.

Figure 7: Reverse-notch Izod impact strength of 50wt% wood-ABS-WPCs with different amounts of SMA and SEBS-g-MA

Figure 8: Tensile fracture surface of 50wt% wood ABS-WPCs samples without coupling agents

Figure 9: Tensile fracture surface of 50wt% wood ABS-WPCs samples with 10wt% SMA to wood flour

Figure 10: Tensile fracture surface of 50wt% wood ABS-WPCs samples with 10wt% SEBS-g-MA to wood flour

Figure 11: Impact strength of ABS-WPCs with different amounts of wood

Figure 12: Moisture uptake of ABS-WPCs containing 50 wt% wood as a function of SMA amount

Figure 13: Comparison of ABS WPC with PP-WPC after 1000 hours of water immersion.

Figure 14: Moisture uptakes of wood ABS-WPCs of various wood content. No SMA is added

Figure 15: Plot of Carbon Dioxide uptake over time in various ABS/Wood material blends.

Figure 16: Relative Density versus wood composition for samples foamed at 100°C

Figure 17: Relative Density versus wood composition for samples foamed at 120°C.

Task 2.2 Manufacturing and Durability Evaluation of Structural Composites with Recycled Plastics

Figure 2.1: Granulated recycled polymers

Figure 2.2: Pellets grinder

Figure 3.1: Compression molding machine

Figure 3.2: Tension, bending, impact and compression specimen

Figure 4.1: Environmental Chamber

Figure 4.2: Temperature variation

Figure 4.3: Humidity variation

Figure 5.1: DeWALT Heavy-Duty 7"/ 9" Large Angle Sander

Figure 5.2: Manufacturing of composite sandwich

Figure 5.3: Bonding of composite sandwich components (TP/TS/TP)

Figure 5.4: Application of tabs for sandwich specimens

Figure 6.1: Stress strain graph for tension test specimens

Figure 6.2: Stress strain curve for bending specimens

Figure 6.3: Stress vs strain curve for compression specimens

Figure 6.4: Impact strengths with increasing number of fabrics

Figure 6.5: Stress strain curves for specimens aged in alkaline solution E chamber aged for one month

Figure 6.6: Stress strain curves for specimens aged in salt solution E chamber aged for one month

Figure 6.7: Stress strain graph for eight month tension specimens placed alkaline solution E chamber

Figure 6.8: Stress strain curve for salt soln E chamber aged tension specimens

Figure 6.9: Tension test specimens placed in alkaline solution in room Temperature

Figure 6.10: strength reduction graphs for aged compression specimens placed in alkaline solution E chamber

Figure 6.11: Summary for tension test specimens placed in salt solution room temperature

Figure 6.12: Strength variation summaries for tension test specimens placed in salt solution E chamber.

Figure 6.13: Stress strain graph for one month bending test alkaline solution E chamber specimens

Figure 6.14: Stress strain graph for one month bending test salt solution E chamber specimens

Figure 6.15: Stress strain curve for bending specimens placed alkaline solution E chamber for eight months

Figure 6.16: Stress strain curve for bending specimens placed salt solution E chamber for eight months

Figure 6.17: Stresses for bending test specimens placed in alkaline solution room temperature

Figure 6.18: Bending strength variations for specimens placed in alkaline solution E chamber

Figure 6.19: Stress variations for bending test specimens placed in salt solution room temperature

Figure 6.20: Graphs for aged bending specimens placed in salt solution E chamber

Figure 6.21: Stress strain graph for compression specimens placed in alkaline solution E chamber for one month

Figure 6.22: Stress strain graph for compression specimens placed in salt solution E chamber

Figure 6.23: Stress strain curve for salt soln e chamber eight months aged compression specimens

Figure 6.24: Stress strain curve for alkaline soln E chamber eight months aged compression specimens

Figure 6.25: Aged compression specimens placed in alkaline solution room temperature

Figure 6.26: Strength reduction compression specimens placed in alkaline solution E chamber

Figure 6.27: Strength variation summary for salt solution room temperature aged specimens.

Figure 2.28: Graphs for strength variation for aged specimens placed in salt solution E chamber

Figure 6.29: Impact strengths for specimens placed in alkaline solution room temperature

Figure 6.30: Impact strength variation for specimens subjected to alkaline solution E chamber aging

Figure 6.31: Impact strength summaries for specimens subjected to salt solution room temperature
 Figure 6.32: Summary for impact specimens subjected to aging under salt solution E chamber
 Figure 7.1: Thermoplastic/Thermoset/Thermoplastic tension test
 Figure 7.2: Stress strain graph for TP/TS/TP roughened tension test specimen
 Figure 7.3: Stress strain graph for TP/TS/TP roughened specimen
 Figure 7.4: Stress strain graph for TS/TP roughened tension test specimen
 Figure 7.5: Stress strain graph for TS/TP/TS roughened tension test specimen
 Figure 7.6: Stress strain curve for plain vinyl ester and virgin ABS tension test specimen
 Figure 7.7: Delamination of thermoplastic and thermoset sandwich composite

Task 2.3 Demonstration of Recycling Technologies and High Level Design

Figure 1: Two-Man Manual Identification Layout
 Figure 2: Design of Pilot Scale Facility

1.5 The Role of the National Center for Electronics Recycling in the E-Waste Industry

Figure 1: CDR Website
 Figure 2: Webpage of BMDS
 Figure 3: NCER Electronic Newsletter Webpage

Task 2.6: Development of a Polymer Research Center at WVU

Figure 1: Number of EoLE Recycling Papers Published by Year
 Figure 2: Number of papers published by category
 Figure 3: Elements Considered in the Snohomish-Tacoma County Electronics Recycling Assessment

Polymer Nanocomposites for CO₂ Capture

Figure 1: Effect of dispersion solvent on the amount of amine grafting
 Figure 2: Amount of amine grafting as a function of added APTMS
 Figure 3: Effect of preparation method- “dry” vs. “slurry method”.
 Figure 4: CO₂ adsorption capacities at atmospheric pressure for various amine grafted nanoclay sorbents. The adsorption capacity of untreated nanoclay is not shown as it is negligible.
 Figure 5: CO₂ adsorption capacities at 270 psi CO₂ followed by desorption.
 The effect of reusing the amine-grafted nanoclay after one adsorption-desorption cycle is shown in Figure 6; only a very small decrease in adsorption capacity is observed.
 Figure 6: Effect of sorption-desorption cycling on capture capacity at high pressure CO₂ adsorption.

Polymer Films and Thin-laminates for Renewable Energy and 'Green' Infrastructure

Figure 1: Corrosion resistance enhancement (right hand side) using Ag alloy coatings. Note increased corrosion when using pure Ag coating (left hand side). Both samples have been in an accelerated corrosion environment for 15 days

Figure 2: Pitting corrosion of a pure Ag film after immersion in NaCl (0.1 M) for 15 minutes

Figure 3: Pitting corrosion of a pure Ag film after immersion in NaCl (0.1 M) for 24 hours

Figure 4: SEM of a corroded Ag film surface and EDS analysis of the inset area

Figure 5: Flexible lighting device under bending (right hand side) and twisting (left hand side) mode.

Figure 6: Uniaxial tensile electromechanical testing of transparent conducting electrodes.

Figure 7: Schematic of microembossed prisms (left hand side) and CNT based film coated prisms (right hand side).

Figure 8: Scanning electron microscope image of a microembossed polymer surface

Figure 9: Scanning electron microscope image of CNT coated polymer prisms

Figure 10: Nyquist plots for pure Ag film and Ag-alloy film

Figure 11: Monotonic tensile testing of patterned CNT coated film

Figure 12: Cyclic tensile testing of patterned CNT coated film.

Figure 13: XPS spectrum for a non tarnished region.

Figure 14: XPS spectrum for a tarnished region. Note the increasing Na concentration (red line) as the sputter time (thickness) increases

New Functional Polymers based on Triazoles

Scheme 1: Preparation of scaled-up Triazole ligands

Scheme 2: Developing polymerization conditions

Scheme 3: Introduction of N-protecting group

Scheme 4: Alternative synthesis

Scheme 5: Proposed novel triazole modified linkers for polymer synthesis

Scheme 6: Synthesis of di-acid monomers for polymerization

Scheme 7: Alternative triazole building blocks that could be prepared by this route

Scheme 8: Preparation of alkyne-triazole analogues unexpected vinyl-Au complex formation

Scheme 9: Literature reported vinyl-Au complexes

Scheme 10: Proposed reaction mechanism for the formation of unique vinyl-Au complexes

Scheme 11: X-ray crystal structures of the novel triazole-based vinyl-Au complexes

Scheme 12: Dual reactivities of cationic Au catalysts

Scheme 13: Representative effective gold catalysts for Hashmi phenol synthesis

Scheme 14: NMR spectra of catalyst

Scheme 15: NMR spectra of complex 15A

Using Hybrid Poplar for More Efficient Biofuels and Bio-Nanocomposites Production

Figure 1-1: Two-year old hybrid poplar plantation (top) and one year old coppiced poplar in a stoolbed

Figure 1-2: Poplar roots (top) and one year old stem-wood specimens (bottom).

Figure 1-3: Crossing design for production of the QTL mapping pedigree

Figure 1-4: SEM images of *Populus trichocarpa* (PT1, grandmother): a) Cross section, b) Radial section, c) Transverse section.

Figure 1-5: SEM images of *Populus deltoides* (PD1, Grandfather): a) Cross section, b) Radial section, c) Transverse section

Figure 1-6: SEM images of first generation hybrid poplar (F1-PT1*PD1, Mother): a) Cross section, b) Radial section, c) Transverse section

Figure 1-7: SEM images of *Populus deltoides* (PD2, Father): a) Cross section, b) Radial section, c) Transverse section.

Figure 1-8: SEM images of second generation hybrid poplar (BC1- PD2*F1, Offspring): a) Cross section, b) Radial section, c) Transverse section

Figure 2-1: Chemical properties comparisons among *Populus deltoides* (PD1-pedigree grandfather, PD2-pedigree father) and *Populus trichocarpa* (PT1-pedigree grandmother, F1-pedigree mother) and BC1-offspring

Figure 2-2: Thermal degradation of hybrid poplar (BC1) at ramp temperature of 0-400⁰C in TGA Q50 V20.10 build instrument

Figure 3-1: Procedures to isolate cellulosic nanocrystals

Figure 3-2: Images of yellow poplar wood residues, before and after lignin was removed (left), and microstructure under microscope (right).

Figure 3-3: Cellulose suspensions in water (left) and SEM image of self assembly formed bundles of nanocrystals (right).

Figure 3-4: Nanocrystal size distribution measured by dynamic light scattering

Figure 3-5: Typical stress strain curves of pure PVA (top) and cellulosic (bottom)

Figure 3-6: Tensile moduli of the nanocomposites.

Figure 3-7: Tensile strength of nanocomposites prepared

List of Tables

Task 2.1 Recycling Polymers from End-of-Life Electronics into Wood-Polymer Composite Materials

Table 1: Mechanical properties of virgin and recycled ABS

Table 2: Composition of ABS/wood flour composites in terms of polymer, coupling agents and lubricants

Table 3: Processing conditions of 50wt% wood-ABS wood plastic composites

Table 4: Experimental data of flammability and mechanical properties of WPCs

Table 5: Experimental data on flammability and mechanical properties of WPCs with Virgin ABS with different FRs

Table 6: Experimental for flammability (AP423 as flame retardants) for WPC with recycled ABS

Task 2.2 Manufacturing and Durability Evaluation of Structural Composites with Recycled Polymers

Table 1: Tensile strength (Amarnath 2006)

Table 6.1: Tension test results

Table 6.2: Stress and tensile stiffness increment

Table 6.3: Bending test results

Table 6.4: Percentage stress and stiffness increment for bending test

Table 6.5: Compression test results

Table 6.6: Compressive stresses and stiffness

Table 6.7 Impact test

Table 6.8 Impact strength increment with fiber volume fraction

Table 6.9 Strength variations for tension test specimens subjected to various aging scenario and 1, 4, 8 and 12 months

Table 6.10 Stiffness variations for one and eight months aged tension specimens

Table 6.11 Strength variation for bending test specimens subjected to various aging scenario and different months

Table 6.12 Stiffness variations for one and eight months aged compression specimens

Table 6.13 Strength variation for compression test specimens subjected to various aging scenario and different months

Table 6.14 Stiffness variations for one and eight months aged compression specimens

Table 6.15 Impact strength under different aging condition

Table 6.16 Maximum strength reductions for tension, bending compression and impact specimens

Table 7.1 Thermoplastic thermoset (TP/TS/TP) tension test result

Table 7.2 Thermoplastic thermoset (TP/TS) tension test results

Table 7.3 Thermoplastic thermoset (TS/TP/TS) tension test results

Table 7.4 Thermoplastic thermoset (ABS and vinyl ester) tension test results

Table 7.5 Thermoplastic thermoset bending test results

Table 7.6 Thermoplastic thermoset (TP/TS) bending test results

Task 2.3 Demonstration of Recycling Technologies and High Level Design

Table 1: Comparison Performance Data of the Optical Sorting Equipment from TiTech and MSS

Table 2: Materials Throughput for the Plastics Demonstration Equipment

2.5 The Role of the National Center for Electronics Recycling in the E-Waste Industry

Table 1: Per Capita Collection Rate by State

Task 2.6: Development of a Polymer Research Center at WVU

Polymer Nanocomposites for CO₂ Capture

Table 1: PEI grafting on montmorillonite clay and CO₂ adsorption

Table 2: Amine grafting on Perkalite clay and CO₂ adsorption

Using Hybrid Poplar for More Efficient Biofuels and Bio-Nanocomposites Production

Table 1-1: Samples of five genotypes of poplar.

Table 2-1: Physical and chemical properties of hybrid poplar (F1 and BC1), *Populus deltoides* (PD1-pedigree grandfather, PD2-pedigree father) and *Populus trichocarpa* (PT1-pedigree grandmother)

Table 2-2: Proximate and heat related properties of hybrid poplar (F1 and BC1), *Populus deltoides* (PD1- pedigree grandfather, PD2-pedigree father) and *Populus trichocarpa* (PT1- pedigree grandmother)