Lawrence Livermore Laboratory

EVALUATION OF EXISTING POLMER CHARACTERIZATION
TECHNIQUES AND CAPABILITIES OF THE GENERAL CHEMISTRY
AND ORGANIC MATERIALS DIVISIONS IN THE CHEMISTRY
AND MATERIALS SCIENCE DEPARTMENT

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AUGUST 25, 1976

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TO: H. F. Rizzo, Organic Materials Division
K. Ernst - General Chemistry Division

FROM: F. N. Larsen, Bendix Resident Consultant to LLL

SUBJECT: EVALUATION OF EXISTING POLYMER CHARACTERIZATION TECHNIQUES AND CAPABILITIES OF THE GENERAL CHEMISTRY AND ORGANIC MATERIALS DIVISIONS IN THE CHEMISTRY AND MATERIALS SCIENCE DEPARTMENT

SUMMARY

TO PROVIDE BETTER POLYMER CHARACTERIZATION CAPABILITIES IN THE ORGANIC MATERIALS AND GENERAL CHEMISTRY DIVISIONS OF THE CHEMISTRY AND MATERIALS SCIENCE DEPARTMENT, F. N. LARSEN (BENDIX, KANSAS CITY, MATERIALS EVALUATION LABORATORY) HAS BEEN REQUESTED, AFTER A YEAR'S RESIDENCY AT LLL, TO EVALUATE EXISTING CAPABILITIES FOR POLYMER CHARACTERIZATION AT LLL. THIS REPORT BEGINS WITH DEFINITIONS OF CHARACTERIZATION AND TESTING, THEN CONTINUES WITH THE EVALUATION OF THIRTEEN SPECIFIC TECHNIQUES INCLUDING VARIOUS SPECTROSCOPY, THERMAL, SOLUTIONAL PROPERTIES, WET CHEMISTRY, CHROMATOGRAPHY AND MISCELLANEOUS PROCEDURES. COMMENTS AND RECOMMENDATIONS ON THE NEED FOR AN ANALYTICAL SERVICES FOCAL POINT IN GCD, A POLYMER CHARACTERIZATION EXPERT IN OMD AND THE USE OF CONTRACTOR FACILITIES AS A SOURCE OF DATA GATHERING ARE MADE.

IT IS CONCLUDED THAT SUBSTANTIAL CAPABILITIES FOR POLYMER CHARACTERIZATION DO EXIST AT LLL, BUT LACK OF ADEQUATE INTERFACING BETWEEN OMD AND GCD IS PREVENTING THEIR EFFECTIVE USE. ACQUISITION OF A POLYMER CHEMIST WITH EXPERIENCE IN CHARACTERIZATION TECHNIQUES APPEARS TO BE THE BEST SOLUTION TO THIS PROBLEM.

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TWO TABLES OUTLINING SCHEMES FOR A CHECK LIST FOR POLYMER CHARACTERIZATION TECHNIQUES ("CHARACTERIZATION FOR MATERIAL SELECTION") AND LIST OF TECHNIQUES AND INFORMATION NEEDED FOR AGING EFFECTS STUDIES ("CHARACTERIZATION FOR COMPATIBILITY AND/OR LONG TERM AGING EFFECTS") ARE INCLUDED FOR REFERENCE.

A SEPARATE ATTACHMENT BRIEFLY DISCUSSES PERSONNEL AND POLYMER CHARACTERIZATION SKILLS.

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INTRODUCTION

The many demands for polymeric materials in LLL programs require an adequate capability to analyze, characterize and test. These compounds include: adhesives coatings, encapsulants, elastomers, fibers, films, fluids, foams and resins, all requiring various testing to determine their purity, properties and integrity. Particularly, this is true when the applications are in weapons programs. At LLL this responsibility falls to the General Chemistry and Organic Materials Divisions of the Chemistry and Materials Science Department. GCD has the responsibility for the elemental, instrumental and spectroscopy analyses. This group, also, is responsible for the compatibility efforts. Organic Materials Division with its fiber composites, polymer materials and HE formulation groups has prime responsibility for "polymer characterization" data gathering and interpretation, even though some capabilities are resident within the groups; i.e., thermal analysis, mechanical properties, etc.

As part of a work assignment to LLL as a resident consultant from Bendix for one year, this writer was requested to evaluate the existing capabilities for polymer characterization in the two divisions (OMD and GCD) of the C. and M.S. department. This report treats this evaluation from two points of reference. First, is the writer's background of having, through the past years, established a fairly complete and successful polymer characterization group and facility at the Bendix plant in Kansas City. Secondly, is from first-hand

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experience with the facilities at LLL, where the writer provided numerous Phase 3 polymer materials investigations on the B77, W79 and W70-3 programs during the year's residency.

It is hoped that this report with its evaluations, comments and recommendations will provide help and guidance to an improved and functional polymer characterization capability at LLL.

OUTLINE AND OBJECTIVES

1. Definition of characterization and testing
2. Specific characterization technique evaluations
3. Comments and recommendations
4. Generalized polymer characterization and testing scheme
5. Characterization scheme for long term aging effects
6. Personnel evaluation (separate attachment)

DEFINITIONS

It will be helpful to define and comment on the terms testing and characterization prior to the discussion.

CHARACTERIZATION - To describe the quality of.

Implies the utilization of a series or group of test procedures or techniques for the description of properties and behavior of (in this case) polymeric materials.

TESTING - Examination for performance evaluation.

Implies the application of a specific test method(s) for comparison to specification values, known performance criteria or expected material requirements.

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ANALYSIS - Determination of the nature or proportion of one or more constituents of a substance.

Implies the use of special instrumentation or separation schemes to identify and/or quantify constituent parts of a material.

Obviously there is some overlapping in the terms, but characterization suggests the application of a sufficient number of analyses to be able to describe the properties and behavior of the polymer sufficiently for design and application selection. Testing provides a specific set of comparative property data, while analysis gives essentially, heretofore, unknown identities or quantities.

SPECIFIC EVALUATIONS

Thermal Analysis - This group supervised by Ray McGuire with excellent technical support from Don Ornellas is in good position to provide all the thermal properties measurements. It is a full blown service group (even though in OMD) primarily due to the demand for thermal measurements and the single focus of operating personnel. This is the ideal characterization group where one person can work essentially full time with a technique such as TGA or DSC and TMA, developing a high degree of competence and expertise. It also provides better operational and maintenance efficiency for the instrumentation.

The group is to be commended for incorporating several new techniques in the past year. Namely, the use of the thermomechanical accessory (TMA) to provide phase transition data, expansion coefficients and fiber properties. Also, the applications of the DSC to measurements of thermal conductivity, the acquisition of the Perkin-Elmer DSC IIB for sensitive calorimetric measurements and a new TGA unit, show a desire to meet current demands and provide state-of-the-art capabilities; keep this group intact.

Molecular Weight and Solutional Properties - This effort, under the direction of Jack Clarkson, GCD, is based on Jack's interest in separations initially in gas chromatography but extended into liquid chromatography with acquisition of the gel permeation chromatograph and subsequently the high pressure liquid chromatograph. Jack has kept this operation up to a state-of-the-art technology and provides an expedient and well managed characterization service.

This group does need supportive absolute molecular weight instrumentation, primarily a membrane osmometry for number-average molecular weight determinations and secondly, light scattering apparatus for weight-average molecular weight. Laser source light scattering instruments are just coming on the market and should be considered for future acquisition.

Functional Group Analysis - Directed by Walt Selig and technical support from Glen Crossman, this group is performing quite satisfactorily

in providing analyses for OH, NCO, epoxy, amines, etc., in polymer materials. Walt does well in coordinating the organic and polymer analytical requests for GCD. The main limitations of the group are unfamiliarity with polymer materials and a bias towards micro-chemical techniques which assumes a homogeneity of polymer materials which is not always true.

The group needs capability to do reductive combustion of organics for phosphorous and sulfur determinations in fluorocarbons.

Trace Metals - Essentially emission spectroscopy (ES) with some atomic absorption for specific elements. This group performs an expedient, reliable, excellent service, particularly the ES under Ed Peck. Their ability to do trace metals in organic and polymer materials is outstanding.

Infrared - Russ Sanborn, GCD, does very capable work on the identification of organic and polymer materials. He is very skilled at sample handling and has an extensive reference file of IR spectra for polymers, plastics, rubbers, solvents, additives, etc. His capability should be made more aware and this technique should be used more for polymer characterization.

OMD has the use of a Carey UV-visible-near IR recording spectrophotometer and a Beckman IR which are used with some regularity, but inefficiently due to lack of adequate sampling accessories, no reference file and oftentimes inexperienced personnel.

Nuclear Magnetic Resonance - Here is an example of an excellent

capability (state-of-the-art instrumentation, skilled personnel - Jim Happe) that is going unused. This is for two reasons: one is that Jim is not expected to find NMR applications to polymer problems (this implies some knowledge of polymer chemistry) and second, personnel associated with, and responsible for, polymer characterization are not knowledgeable enough about NMR to request the service. Jim indicated he has had no requests for service in the last year until very recently when he had two requests -- one for KELF-800 copolymer composition by fluorine NMR and some amine cure agent structural analysis from Jim Rinde. Further discussion of this problem will be found in the comments.

Water Analysis - Lew Gregory is doing a very satisfactory job of the requests for moisture analysis using the Karl Fischer technique and a Beckman Aquameter. It is recommended that this instrumentation be upgraded to include the Aquatest II apparatus supplied by Photovolt Corporation. The Aquatest is more automated, sensitive and less skill required for its use in case other operators need to use it. It is also a widely used instrument, currently in use in all the contractor facilities (BKC, Y-12, PX).

There is glaringly absent a technique for determining moisture in solids.. The CEC 26-321A is capable of such measurements, but was recently surplussed. Roy Althouse now has the instrument and

it is recommended that it be made operational and its usefulness be made known. It is a specific measurement for moisture by a coulometric (P_2O_5) detector and can be time and temperature programmed to 1000°C.

Ash Content - Again, Lew Gregory does an excellent job for this determination of non-combustible matter or ash residue in organic and polymer materials using either platinum or ceramic crucibles and muffle furnaces.

Carbon, Hydrogen and Nitrogen Analysis - This analytical procedure currently being performed by Miles Waggoner, is providing reliable data for polymer materials. He is routinely providing good service. However, it would seem advisable to upgrade this combustion gas analysis system with a modern commercial elemental (C, H, N & O) analyzer such as the Perkin-Elmer Model 240. This instrument is particularly useful for infrequent operation such as the demand at LLL. It also can provide direct oxygen analysis utilizing the Unterzaucher technique.

Mass Spectrometry - is not used routinely for polymer applications.

At BKC our experience has shown that using a direct probe, solids inlet sampling procedure and a high resolution instrument (CEC 110) that a vast amount of information can be obtained about polymer structure, composition, impurities, degradation, etc. This technique, like others mentioned before, is most efficient when sample demand is high enough to justify essentially continuous

operation. It also requires a sufficient skill on the operator's part to interpret organic and polymeric structures, rearrangements and fragments. For polymer work, it is particularly desirable to have chemical ionization capabilities to emphasize parent ions.

LLL needs to upgrade and improve their mass spectrometry support effort in polymer characterization.

Mechanical Properties - Don Breithaupt in OMD provides some service support, primarily in tensile, compressive and shear modulus measurements of HE's and HE binders. OMD personnel also have access to Instron and similar mechanical testing equipment in Building 231 on a do-it-yourself basis. These arrangements are probably satisfactory even though it would be more efficient to have a full time service group particularly since the workload would appear to support such a service group. Perhaps with the acquisition of the Rheometrics Mechanical Spectrometer a new appraisal of mechanical properties measurements can be made.

Rheological Properties - The capillary rheometer accessory to the Instron tester is used little or none at all. The main problem is that it ties an Instron tester up for an extended period of time. Some very useful studies on thermoplastic polymers could be performed with this equipment (rheological studies on W-70 polycarbonate performed at BKC, for example). Melt flow rate (melt indexer) apparatus is available for use in the Polymeric Materials Group.

Dielectrometry - A technique used rather extensively by Roy Althouse and some others to measure relative degree of cure in polymers, phase transitions and establish cure parameters (time/temperature) for a variety of resin systems. This apparatus though furnishing empirical data only is a workhorse and should be upgraded and automated.

TECHNIQUES NOT BEING USED

X-Ray Diffraction (XRD) and its associated techniques of small angle x-ray diffraction (SAXD) and wide angle x-ray diffraction (WAXD) are not being used. (L. Penn has just recently used the XRD techniques for Kevlar evaluation.) This writer was intending to explore XRD applications to polymer characterization while on assignment at LLL, but due to an administrative assignment of the cognizant XRD scientist (Quintin Johnson) during the period no progress on this activity was made. It is still felt that the XRD techniques should be explored and be available on request for those measurements of polymer crystallinity, unit cell dimensional measurements and crystalline orientation. These properties are very important to the overall characterization data for polymers. The equipment is essentially available with some modification. What is needed is an interested and qualified person to initiate such a program.

Fourier Transform Infrared (FTIR) instrumentation is another state-of-the-art technique that should be acquired. Once again, lack of a sufficient workload appears to be the main reason for not incorporating this technique.

A modern Gas Chromatography/Mass Spectrometer system (Hewlett-Packard, Finnigan) would seem to be a necessity for future requirements (as well as those current applications) not only in polymer characterization, trace analysis, but also in compatibility programs. The availability of a search/file/reference of thousands of mass spectra and ease of operation make this instrumentation extremely useful.

COMMENTS AND RECOMMENDATIONS

It was apparent during this writer's residency at LLL that there was no visible focal point for analytical services in GCD. Walt Selig coordinated most of the polymer analytical requests, but there was no general awareness of his role. A designated (on organization chart) group with a section head who will interface with other departments well and be familiar with weapons and other program needs is essential to the analytical services support effort at LLL.

To adequately utilize the analytical and characterization facilities it is necessary to have personnel not only formally trained in polymer chemistry, but sufficiently knowledgeable with characterization techniques

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and analytical chemistry. OMD should have someone in this category, if an adequate polymer characterization program is to be established.

It is this writer's opinion and observation that with a very few exceptions, sufficient capabilities (instrumentation and techniques) exist currently in GCD and OMD to carry on an adequate polymer characterization program. These facilities are not being used because of the lack of an interface between GCD and OMD. One cannot for the most part write a request for some analytical service or characterization technique and "dump" the sample on the analyst. A careful explanation by the requestor of the background problem, need, program, accuracy, replication, end use of data, etc., goes a long way to get the right data or analysis.

This writer had no difficulties with analytical services requests and in all cases the information was completed in the time requested. In no case did service take longer than two weeks.

It would appear quite justifiable to use contractor facilities (i.e., BKC, Y-12, Pantex) via SANL funding to obtain characterization and analytical data. This implies, of course, that LLL personnel are cognizant of the analytical capabilities at the other agency facilities. It is recommended that some provision be made for better familiarization by LLL of those capabilities at BKC, Y-12 and Pantex. An illustration of the type of information and support at BKC is given in a recent report by this writer on a \$20,000 SANL for materials characterization in the B-77 program. A PDO (NPD) endeavor is being undertaken at Pantex

this year to explore their interest and capability to do polymer characterization. If one could circumvent the horrible data reporting situation at Y-12, they do have some very capable personnel who could be sources of help in polymer characterization.

Finally, it is specifically recommended that John Newton, GCD, visit Bendix and review the GC/MS analytical system and its applications to polymers and organic analysis with Charles J. Cook and Stan Dubiel of the BKC Materials Evaluation Laboratory, Department 816. It would be helpful for Carlos Colmenares, GCD, to visit Bendix also and review the extensive capabilities for surface analysis (ESCA, SEM, TEM, Auger, Microprobe). Perhaps these facilities could be used in times of work overload at LLL.

CHARACTERIZATION SCHEMES

Two tables are included in this report for reference. Perhaps they contain nothing new, but are given here as guidance to personnel not familiar with polymer characterization techniques, who might want a check-list for their specific materials requirements.

Table I lists those items routinely investigated or requested by this writer when a material candidate needs "characterization." The properties are listed in a general order of priority.

Table II lists techniques and information applicable to the long term aging effects and/or compatibility of polymeric materials. Again, the items are listed in general order of priority.

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TABLE I

CHARACTERIZATION FOR MATERIAL SELECTION

1. MASS SPECTROMETRY - Analysis for composition, additives, volatiles, degradation
2. THERMAL ANALYSIS
 - a. TGA (dynamic) - weight loss, stability, volatiles
 - b. DSC - phase transitions, T_g, T_m, reactions
 - c. TMA - softening point, T_g
3. SOLUBILITY - Acetone, hexane, isopropanol, toluene, chloroform, tetrahydrofuran. Solubility gives basis for potential solutional property measurements. Determines cross-linked versus linear or branched polymers. If insoluble, solvent swell tests can be applied.
4. SOLUTIONAL PROPERTIES
 - a. GPC - molecular weight, distribution of molecular weights, purity, number of components.
 - b. Membrane osmometry or light scattering for absolute molecular weight.
5. RESIDUE ON ASHING (approx. 900°C) - fillers, additives, "Z" elements
6. EMISSION SPECTROSCOPY - For trace metals analysis, "Z" elements
7. DYNAMIC MECHANICAL TESTING - Dynamic shear modulus for G', G'' and tan delta over temperature range approx. -70°C to -150°C.
8. STATE OR DEGREE OF CHEMICAL CURE - functional group and/or end group analysis.
9. MOISTURE CONTENT - Weight percent water versus percent relative humidity.
10. EFFECT OF ELEVATED TEMPERATURE ON STATE OF CURE OR "ANNEALING" EFFECTS.

TABLE II

CHARACTERIZATION FOR COMPATIBILITY AND/OR
LONG TERM AGING EFFECTS

1. CHEMICAL REACTIVITY - to near neighbor materials - salt, HE, metals.
Canned assembly gas analysis and surface chemistry examination.
2. SOLVENT EXTRATION - low molecular weight material, potential migratables, also as a function of time/temperature.
3. DEGRADATION MECHANISM - from mass spectrometry and/or TGA/RGA or TGA/EGA.
4. MIGRATION STUDIES - utilize solubility parameter data and diffusional experiments.
5. DETERMINE ACTIVATION ENERGIES - various phenomenon - dissociation, degradation, decarboxylation, etc. - obtain from gas analysis, mass spectrometry, isothermal TGA and various other thermoanalytical techniques.
6. EQUILIBRIUM MOISTURE CONTENT - function of % RH
7. MOISTURE GAIN AND LOSS RATES - from solids moisture analyses.
8. MOLECULAR WEIGHT CHANGES - function of time, temperature, environment (H_2O , NO_x , etc.) - ester hydrolysis, polymer unzipping, chemical attack - GPC best technique, if soluble.

TABLE II

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9. MORPHOLOGICAL STUDIES - crystalline growth by IR, XRD, SEM.
10. LONG TERM CREEP OR
STRESS RELAXATION
EXPERIMENTS - development of "master" modulus curves.
11. MOISTURE VAPOR TRANS-
MISSION RATE
12. GAS PERMEABILITY DATA -

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