Polymer nanocomposites for high-temperature composite repair

by

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ABSTRACT

A novel repair agent for resin-injection repair of advanced high temperature composites was developed and characterized. The repair agent was based on bisphenol E cyanate ester (BECy) and reinforced with alumina nanoparticles. To ensure good dispersion and compatibility with the BECy matrix in nanocomposites, the alumina nanoparticles were functionalized with silanes. The BECy nanocomposites, containing bare and functionalized alumina nanoparticles, were prepared and evaluated for their thermal, mechanical, rheological, and viscoelastic properties.

The monomer of BECy has an extremely low viscosity at ambient temperature, which is good for processability. The cured BECy polymer is a highly cross-linked network with excellent thermal mechanical properties, with a high glass transition temperature (T_g) of 270 °C and decomposition temperature above 350 °C. The incorporation of alumina nanoparticles enhances the mechanical and rheological properties of the BECy nanocomposites. Additionally, the alumina nanoparticles are shown to catalyze the cure of BECy.

Characterization of the nanocomposites included dynamic mechanical analysis, differential scanning calorimetry, thermogravimetric analysis, rheological and rheokinetic evaluation, and transmission electron microscopy. The experimental results show that the BECy nanocomposite is a good candidate as repair agent for resin-injection repair applications.

CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

Composites are structures in which two (or more) materials are combined to produce a new material whose properties would not be attained by conventional means. The continuous constituent of the composite, the matrix, serves to surround the other phases and provides bulk form to the material. The major structural constituents are typically fibers or particles. Fiber-filled composites are often laminates, formed from stacks of individual plies or lamina, which provide continuous in-plane reinforcement. The strength and rigidity of a composite can be controlled by varying the shape, amount, surface functionality and orientation of the major structural constituent in the matrix. This ability to tailor properties, combined with the inherent low density of composites and their relative ease of fabrication, makes these materials extremely attractive alternatives for many applications, such as boats, sports equipment, automotive components, biomedical products, underground pipes, and aircraft/aerospace structures.

Composites have different modes of failure from conventional materials. Polymer matrix composites (PMCs) are especially susceptible to matrix micro-cracking when subjected to repeated thermo-mechanical loadings. Often these matrix micro-cracks coalesce and lead to other damage modes including fiber/matrix debonding and ply delamination [1-5]. Delamination (also known as interlaminar fracture) often occurs in composite laminates as a result of low energy impact or manufacturing defects. It is difficult to detect and repair interlaminar fractures because the defects are typically confined to subsurface locations. Normally, localized delaminations are repaired by scarf removal of material and subsequent rebuilding, or by resin injection. The former repair method requires cleaning and paint removal with solvents containing hazardous volatile organic compounds (VOCs). Additionally, resin-injection repair requires a very low viscosity resin, which is injected into the failed area via an access hole. In some cases, the repair resin is diluted with volatile organic solvents or reactive diluents to achieve the required low viscosity. Once the resin solution is infiltrated, volatile solvents evaporate or remain in the resin as it subsequently cures.

There are lots of applications for polymer-matrix high temperature composites, e.g. engine cowlings and thrust reversers. Recent applications of high temperature composites in aircraft propulsion systems, such as General Electric's F-404 engine, have resulted in substantial reductions in both engine weight and manufacturing costs. For high-temperature composites which require stability at elevated temperatures up to 250 °C, the resin used in repair should have the ability to survive for a long time at such conditions, with a glass transition temperature (T_g) above 250 °C. Low viscosity resins currently used for repair applications usually have lower T_g 's than the matrices in many military grade composites, limiting their application for elevated temperature service. For very high temperature composites, such as bismaleimides, field repairs are not even attempted with current repair resins because of the low T_g of the cured adhesive.

The goal of this research is to develop a novel repair agent for resin-injection repair of high temperature structural composites. The repair agent is based on bisphenol E cyanate ester (BECy), reinforced with alumina nanoparticles. Polymerization of BECy results in a highly cross-linked thermoset with excellent mechanical properties. The high T_g (> 270 °C) and decomposition temperature (> 350 °C) of cured BECy allow for repair of high T_g composites. Additionally, the BECy monomer is very stable at room temperature and facilitates reduced waste due to spoilage compared to conventional resins. To improve the performance of the repair agent, alumina nanoparticles with average primary particle diameter of approximately 40nm will be used to optimize the crack filling and as reinforcement of the cured adhesive.

1.2 Dissertation organization

This work is organized into main chapters, which are each manuscripts that have either been published in or prepared for submission to scholarly journals.

Chapter 1 gives general introduction that outlines the background and motivation for developing a novel repair agent for resin-injection repair of high temperature structural composites. This chapter also includes the introduction and characterization of cyanate ester monomer: history and synthesis of monomers, VOCs and toxicity of BECy monomer.

Chapter 2 involves the curing kinetics of neat BECy. The curing kinetics of BECy is evaluated mainly by dynamic scanning calorimetry (DSC). Both isothermal cure and dynamic scanning methods were used to obtain the kinetic parameters, such as activation energy of polymerization of BECy, reaction order and reaction rate constant.

Chapter 3 also involves the curing kinetics of BECy but focuses on the effect of nanoparticles. To evaluate the catalytic effect of nanoparticles, both alumina and silica nanoparticles were used to prepare BECy nanocomposites. Alumina nanoparticles were shown to have a catalytic effect on the cure of BECy. Compared to silica nanoparticles, alumina nanoparticles are easy to absorb moisture and contain more hydroxyl groups on the surface. The catalytic effect of alumina nanoparticles is a result of hydroxyl groups on the surface and the Lewis acid property of γ -phase alumina.

Chapter 4 and 5 include the characterization of BECy alumina nanocomposites. In Chapter 4, the rheology and thermal-mechanical properties of BECy nanocomposites were evaluated. The bare alumina nanoparticles were functionalized with a epoxy functional group terminated silane. The properties of BECy nanocomposites containing functionalized alumina nanoparticles were compared with the BECy/bare alumina nanocomposites. Chapter 5 covers the creep behavior of BECy/alumina nanocomposites. A series of short-term creep tests were performed at isotherms ranged from 180 to 330 °C. The prediction of long-term creep behavior was made from short-term creep data by using time temperature superposition principle (TTS). The samples were also tested at frequency sweep mode, and then the frequency-domain dynamic data was transformed into time-domain creep data.

Chapter 6 gives a general discussion of conclusions drawn through this work, as well as recommendations for future research.

Appendix A and B deal with the research work related to self-healing agent, which would be encapsulated and embedded into the polymer matrix to form a self-healing material. Specifically, Appendix A involves the synthesis of cross-linkers and effect of cross-linkers on the glass transition temperature of polymerized self-healing agents. Appendix B discusses the dynamic mechanical analysis of self-healing agents. The polymerization of self-healing agents is monitored by rheometer. The rheological results show that cross-linkers have significantly reduced the time to reach the gel point of self-healing agents.

1.3 Background and literature review

1.3.1 Current repair technologies

Currently, composite parts that have been damaged in service are first inspected manually to determine the extent of damage. For critical parts this inspection may include such nondestructive testing techniques as ultrasonics, infrared thermography, X-ray tomography and computerized vibro thermography [6]. If the damage is too severe, the structural component is replaced entirely. For less extensive damage, repairs are attempted.

Figure 1-1 Scarf repair techniques (adapted from Ref. [7])

As mentioned above, one common repair method is the use of adhesively bonded scarf patches. In this method, the outer surface of the laminate is removed carefully with a high-speed grinder at a shallow angle, and then repair plies are used to fill the removed area (as shown in Figure 1-1). Compared to traditional external bonded or bolted patch repairs, the scarf repair provides an aerodynamically smooth surface and has a nominally uniform shear stress distribution within the joint. However, the recovery of strength for these common scarf repairs is often significantly lower than the virgin laminate because of the inherent

destruction of the outer plies during the grinding process. There are several environmental and safety concerns with scarf repairs due to the machining/grinding of the composite components which results in hazardous fiber dust. Additionally, these repairs require extensive solvent cleaning prior to bonding repair plies, generating significant VOCs and hazardous waste material. Numerous studies regarding these and other composite repair methods have been published [7-16].

Figure 1-2 Resin-injection repair technique (adapted from Ref. [7]).

Alternatively, the delamination may be repaired by injecting repair-resin via an access hole into the failed area as shown in Figure 1-2. Once the resin solution is infiltrated, the resin is cured, typically at elevated temperature. Resin-injection repairs eliminate the need to remove the outer undamaged plies and can result in higher recovery strength than scarf repairs. As mentioned earlier, resin-injection requires a special resin with a low viscosity at room temperature. Currently, volatile organic solvents are often used to dilute repair resins to obtain the required low viscosity. Therefore, as in scarf repairs, significant VOCs and hazardous waste materials are generated during the repair process. In addition, the resins and adhesives used for repairs often have short shelf lives and low decomposition temperatures which exacerbate the hazardous waste problem. These low viscosity resins usually have low T_g 's after cure, which limit their application for elevated temperature service.

Some of the demanding requirements for an ideal resin system for the resin-injection repair are listed below:

- Low viscosity. The repair resin must be drawn into the furthest reaches of the crack. The large, multi-level delaminations are separated by matrix micro-cracks that only a very low viscosity resin can infiltrate.
- Stability in the damage zone. The resin system should not evaporate or diffuse away from the cracks during the injection and curing process. A shear thinning fluid is ideal, which has a low viscosity at high shear during the injection, and a stable, high viscosity at low shear to remain in the damage zone until the curing process is completed.
- Low curing temperature. The resin should be cured at as low of a temperature as possible to reduce the requirements for field repair.
- High temperature stability. The cured resin should have a T_g above the maximum temperature that the composites experience in service.
- Compatible adhesive. The cured repair resin must be a strong adhesive to both the matrix and reinforcement, which can bond the crack surface together.
- Long shelf-life. The repair resin should be stored as a dormant liquid which does not lose its properties during storage. Expired materials will generate unnecessary expense and hazardous waste.
- Environmentally benign. Increasing environmental and safety concerns and regulations dictate that the repair process does not generate significant VOCs or hazardous air pollutants (HAPs).

1.3.2 Polymer materials for high temperature applications

There are a variety of polymers available for use as matrix resins in advanced high temperature composites or as repair agents. These high temperature polymers are generally composed of aromatic and/or heterocyclic rings linked by flexible bridging groups. The high temperature polymers generally have high T_g and good mechanical properties. Thermosetting resins are the vast majority of polymers which have such properties. The high temperature

thermosetting polymers used in advanced composites include epoxies, bismaleimides, PMR (Polymerization from monomeric reactants) polyimides and cyanate esters.

Epoxies are the most widely used matrix resins. The properties of epoxies can be tailored to many applications by using a wide variety of epoxides, curing agents and additives. The thermal properties of epoxy resins vary depending on the chemical composition. For example, the tetra-functional epoxy, MY 720, cured with diaminodiphenylsulfone curing agent has a T_g of 180 °C [17] (Figure 1-3a).

Figure 1-3 Chemical structures for high temperature thermosetting polymers.

Bismaleimides (BMIs) are the leading class of thermosetting polyimides (Figure 1-3b). The imide linking groups result in higher polymer backbone stiffness than epoxies and the higher cross-linking density of BMIs improves their performance at high temperature. However, brittleness and micro-crack formation in cured products are some of the problems attributed to the high cross-linking density of BMIs [18].

PMR (Polymerization from monomeric reactants) polyimides have the highest T_g among these thermosetting polymers and they are leading thermosetting resins for applications requiring long-term stability at temperature up to 300 °C. For example, PMR-15 (Figure 1-3c) has a cured T_g of 345 °C and retains mechanical properties for hundreds of hours up to 300 °C [19]. However, PMR-15 presents such processing difficulties as high cure temperature requirements (300 to 330 °C) and toxic starting materials.

Cyanate esters (Figure 1-3d) are another class of thermosetting resins for advanced composites. Cyanate esters are cross-linked through thermally stable cyanurate rings. These polymers offer several advantages over other thermosetting resins: the neat resins have relatively good toughness, high T_g 's and low dielectric constants. They absorb smaller amounts of water than other thermosets and demonstrate better long-term hot-wet stability.

Figure 1-4 T_g of cured polymers vs. temperature for the corresponding monomer with viscosity of 150 cP.
(adapted from Ref.[20])

For resin-injection repairs, the injected monomer or pre-polymer should be a liquid at room temperature. It is best if the monomer has a very low viscosity at room temperature, allowing the resin to infuse completely into the delamination and surrounding micro-cracks in the damage zone. Although the low temperature resins (low viscosity or solvent diluted) currently used for resin-injection repair meet this requirement, most high temperature thermosetting pre-polymers usually are solid or highly viscous liquids at room temperature. Figure 1-4 shows the correlation between T_g of a cured polymer and the temperature at which its monomer has a viscosity of 150 cP. Polyimides are not shown in Figure 1-4 because their lowest melt viscosities are higher than 0.15 Pa·s (150 cP) [20]. Normally, monomers which

cure into high temperature thermosetting polymers (high T_g) have high viscosities at room temperature [21]. As the glass transition temperature of the cured polymer increases, so does the viscosity of the prepolymer or monomer.

There is one exception in Figure 1-4 to this trend: a unique type of cyanate ester monomer called bisphenol E cyanate ester (BECy, 1,1'-bis(4-cyanatophenyl)ethane) and chemical structure of BECy is shown in Figure 1-5. Compared to the bisphenol A cyanate ester (Figure 1-3d) with a melting temperature of 82 °C, BECy has an extremely low viscosity of 90-120 cP at room temperature [19]. These processing characteristics make the BECy an excellent candidate for the resin-injection repair of high-temperature polymer composites.

Although cyanate esters are not capable of withstanding temperatures as high as bismaleimides, they are capable of withstanding extreme temperature variations, which is a significant improvement over epoxies. Additionally, cyanate esters have excellent adhesive properties and are more resistant to moisture absorption than other thermosets. Cyanate esters possess a good combination of high temperature stability and excellent mechanical properties, which make them a popular replacement for other thermosets in the aerospace and microelectronics sectors.

1.3.3 Cyanate ester

Cyanate ester resins are a family of high temperature resins, more accurately named polycyanurate, which bridge the gap in thermal performance between engineering epoxy and high temperature polyimide. The monomer of cyanate ester resins is an ester of bisphenol and cyanic acid, contained reactive ring-forming cyanate ($-\text{O}-\text{C}\equiv\text{N}$) functional groups. Cyanate ester monomers are generally polymerized via cyclotrimerization to form polycyanurates (Figure 1-5). They also can undergo thermally reversible additions to active hydrogen compounds and will react with epoxide functional groups to form disubstituted oxazoline structures [20].

The formation of substituted triazine rings via the cyclic addition of three aryl cyanate involves a series of step-growth reactions. Although cyanate ester monomers can undergo polymerization initiated by trace amount aryl phenol impurities [22], high purity monomers require addition of catalysts. The catalyst system includes two parts: an active hydrogen

source, such as nonylphenol, and a soluble coordination metal compound, such as zinc octoate or cobalt acetylacetonate, which “gathers” cyanate groups into ring-forming proximity.

Figure 1-5 Chemical structures of cyanate esters and polymerization scheme.

1.3.3.1 The history of cyanate ester monomer synthesis

Organic synthesis of cyanate ester monomers can be traced back more than 100 years to a reaction of an alkoxide with cyanogen chloride [23]. This procedure and later attempts with aryloxides were not successful because the excess oxide reacted with organic cyanate to yield mixtures of imidocarbonate and cyanurates (Figure 1-6).

Figure 1-6 Chemical reaction of alkoxide with cyanogen chloride forming imidocarbonate and cyanurate.

In 1960, an approach was successful when ortho-substituted phenols were used, and the first aryl cyanate was isolated [24]. The steric hindrance of substitution prevents the excess aryloxide from consuming the product under the reaction conditions (Figure 1-7).

Figure 1-7 Chemical reaction between aryloxide and cyanogens chloride to yield aryl cyanate.

In 1963, a simple and efficient synthesis was reported when addition of a base to the phenol-cyanogen halide mixture was shown to avoid the excess oxide problem, and this process was easily adaptable to an industrial scale [25,26]. A very large number of aryl and haloalkyl cyanates were readily synthesized in excellent yield and found to be remarkably stable [27]. Since then, most commercial cyanate ester monomers are prepared by the alcohol-cyanogen halide method.

Cyanogen halides, such as ClCN, BrCN, are highly toxic agents. They cause immediate injury upon contact with the eyes or respiratory organs. Symptoms of exposure are loss of consciousness, convulsions, paralysis, and death. ClCN is especially dangerous because it is capable of penetrating the filters in gas masks.

In 1987, Dow Chemical developed a synthesis where the cyanogen chloride is generated *in situ* and a polyfunctional cyante is formed, based on an addition of phenol and dicyclopentadiene [28]. Even with improvements in techniques and synthesis methods, the starting materials of cyanate ester monomer synthesis are highly toxic, which increases the cost of cyanate ester monomer and may have important impacts on the environment.

1.3.3.2 The toxicity and environmental concerns of cyanate ester monomer

It is believed that these cyanate ester based repair resins will reduce the environmental hazards associated with current composite repairs and open up new repair opportunities specifically for high temperature composites. Cyanate ester monomers are relatively low in toxicity [27], no leaving groups and volatile by-products during curing process, which makes them less hazardous than polyimides and bismaleimides.

Table 1-1 shows the oral, dermal and mutagenic test results of three commercial cyanate ester monomers, demonstrating their relatively low toxicity [28,29]. For comparison, the commonly used benchmark resin, EPON 828, is also listed in Table 1-1.

Table 1- 1 Toxicity testing of cyanate ester monomers [Error! Bookmark not defined.,29] and benchmark EPON 828 resin.

Sample	Acute oral LD ₅₀ (rat) (g/kg)	Acute dermal LD ₅₀ (rabbit) (g/kg)	Dermal irritation (rabbit)	Eye irritation (rabbit)	Dermal sensitization	Inhalation LD ₅₀ (mg/m ³)
bisphenol A cyanate ester	> 2.5	> 2.5	None	-	Negative	>440
bisphenol E cyanate ester (BECy)	0.5-1.0	> 5.0	None	Mild**	Mild**	-
RTX-366	> 5.0	> 2.0	None	None	-	-
* EPON 828 Epoxy	> 4.0	> 20.0	-	2mg/24h severe	Allergic	>2E10

* MSDS, "BISPHENOL A DIGLYCIDYL ETHER", Sigma-Aldrich.

** MSDS, "EX-1510 Liquid Resin", Tencate Ltd.

According to Table 1-1 and the MSDS data for the resins, the toxicity of BECy is much lower than the benchmark epoxy resin. Under conditions where exposure to vapors or mist is possible, BECy could cause respiratory tract irritation [30]. The long-term exposure may aggravate pre-existing eye, skin and respiratory disorders. However, the experiments of chronic effects on humans and animals are not established; the significance of mutagenic activity to man is still unknown. BECy is not a systemic carcinogen and is not listed as carcinogenic by the International Agency for Research on Cancer (IARC), National Toxicology Program (NTP), or Occupational Safety and Health Administration (OSHA).

The hydrolysis of cyanate ester does not produce hydrogen cyanide. Hydrolysis produces carbamates (or urethanes) which will rapidly liberate volatile decomposition products on heating, so shielding precautions should be taken if significant quantity of carbamate is suspected to be encapsulated in a resin during heating. Most cyanate ester monomers contain multiple aromatic rings and have very low volatility. The single ring cyanate ester monomers, such as hydroquinone dicyanate, phenyl cyanate and low molecular weight alkyl and fluoroalkyl cyanates have a noticeable, sharp odor. Bisphenol E cyanate ester (BECy) monomer contains two aromatic rings and has very low volatility and no noticeable odor.

The curing reaction of BECy is autocatalytic and highly exothermic (~ 700 J/g). Overheating, non-uniform heating and over-catalyzing can cause uncontrollable exothermal reaction and should be avoided. The uncontrollable exothermal reaction may increase temperature locally in excess of 400°C along with smoke and char formation [31].

In our work, the content of volatile organic compounds (VOCs) of BECy, various resin candidates and benchmark resins, was evaluated according to ASTM standard 1259-85 [32]. The VOCs came out during cure processing were also identified by using two different techniques: pyrolysis coupled with GC (gas chromatography)/MS (mass spectrometry) measurements and TG (thermogravimetry analysis) coupled with MS measurements.

Table 1-2 Comparison of volatile content from TG.

	TG (105°C for $\frac{1}{2}$ h)	TG (ramp until 100% wt. loss)	
	Change in wt.%	Time (min)	Temperature ($^{\circ}\text{C}$)
BECy	0.7	36.2	741
EPON	0.4	28.4	584
EPON/BGE	24.8	27.0	556

The ASTM standard calls for the heating of a certain geometry of material at 105°C for half hour and measuring the mass loss. TG experiments under the same isothermal conditions were also performed as a concomitant measurement of the volatile content [33]. The isothermal TG results are shown in Table 1-2. The BECy has just 0.7% volatile content (as defined by the ASTM standard isotherm for 30 min) while the butyl glycidyl ether (BGE)

diluted epoxies had a volatile content of 24.8%. While the neat EPON 828 resin did have a lower volatile content than the neat BECy resin (0.4% vs. 0.7%), that system has a much higher viscosity and is not being considered as a suitable benchmark system unless it is diluted with the reactive diluent (BGE) so that the two resins have the same viscosity (for injection requirements). The last two columns in Table 1-2 are the time (and corresponding temperature) at which the sample is completely volatilized i.e., the entire sample is gone. While the ASTM and TG testing confirm that there is very little volatile content of the BECy resin at the 105 °C isotherm (~0.7%)

The total number of compounds detected by py-GC/MS was 38. Yet, only five compounds made 98% of the total volatiles. These five compounds with most likely composition and relevant characteristics are summarized in Table 1-3. Concentration of the remaining 33 compounds were < 0.4% each and most < 0.1% each may have been fractioned from larger molecules when the volatile gas was injected into the GC at 300 °C.

Table 1-3 Volatile components of BECy present in greatest amounts. % volatile is based on the area of the GC peak compared to the total area.

RT (min)	Compound	Formula	CAS No.	MW	volatile %	of total sample
7.01	Hexanoic acid, hexyl ester	C ₁₂ H ₂₄ O ₂	6378-65-0	200	16.88	0.068%
10.39	3,5-Diamino-1,2,4-triazole	C ₂ H ₅ N ₅	1455-77-2	99	76.28	0.305%
19.91	5-hydroxytryptophan	C ₁₁ H ₁₂ N ₂ O ₃	4350-09-8	220	1.66	64ppm
20.29	Acetophenone, 4' - hydroxy	C ₈ H ₈ O ₂	99-93-4	136	1.6	64ppm
29.52	4,4' - ethylenediphenol	C ₁₄ H ₁₄ O ₂	2081-08-5	214	1.65	66ppm
Total :					98.07%	0.4%

TG/MS results showed similar five most abundant volatiles (as shown in Table 1-3) for BECy during temperature ramped to 500 °C at a rate of 1 °C/min under 100ml/min nitrogen flow. Using the instruments database and the parent resin BECy's chemical structure, most probable compositions were assigned to each of the five most abundant volatiles. Literature was screened for toxicity assessment of the evolved gases. None of the

five significant components was “regulated.” Only five of the remaining 33 compounds were on the list of “regulated” compounds. Concentration of each of these compounds is 0.07% of total volatiles (or 5 ppm of resin) or less.

1.3.4 Nanoparticles for composite enhancement

In many systems, nanocomposites have been shown to have increased thermal stability and mechanical performance (strength, stiffness and dimensional stability) compared to neat resin [34-40]. Compared with many other nano-fillers, alumina nanoparticles are low cost and can be functionalized for nanocomposite fabrication [41]. It is important that nanoparticles have the ability to be functionalized because surface functionalization can not only stabilize the nanoparticles to eliminate agglomeration but also enhance the compatibility of the nanoparticles with the polymer matrix. Additionally, alumina nanoparticles may have catalysis effects on the cure kinetics of BECy. Because of the abnormally coordinated Al cations of γ -alumina, the surfaces of alumina act as Lewis acids (electron-acceptors) [42]. Lewis acids have been shown to catalyze the polymerization of cyanate esters [27]. The growth of polymers from the surface of the alumina nanoparticles, a “grafting from” process, would result in strong interfacial bonding between the nanoparticles and the polymer matrix, improving the thermal mechanical properties of nanocomposites.

There are several reports comparing polymer composites containing nano-size alumina particles with micro-size alumina particles, as well as some reports of the effects of functionalized alumina nanoparticle on the mechanical properties of polymer nanocomposites. Ash *et al.* [43] reported that at an optimum weight percent, alumina nanoparticle/poly(methylmethacrylate) nanocomposites showed a 600% increase in strain-to-failure and a decrease in T_g and Young’s modulus compared to neat polymer; the composites containing micro size particles did not show the phenomenon. Appropriate surface functionality will aid in nanoparticle dispersion, increasing the mechanical properties of the resulting polymer composites. Guo *et al.* [41] used a bi-functional coupling agent (3-methacryloxypropyl-trimethoxysilane) to functionalize the alumina nanoparticles. The Young’s modulus and strength of resulting vinyl-ester resin nanocomposites increased with particle loading. Similar results were reported by Vassileva [44] *et al.* They used two different types of silane coupling agents to separately functionalize the surface of alumina

nanoparticles, one of which could react with the polymer matrix to form covalent bonding. The nanocomposites with nanoparticles covalently bonded to the polymer matrix showed the best improvement of flexural strength, strain to failure, and wear resistance.

There are conflicting experimental results reported on thermal properties of alumina/polymer composites. In Ash's same paper [43], which reported increases of the strain-to-failure for alumina nanoparticle/PMMA composites, the T_g of the nanocomposites decreased by 25 °C compare to neat PMMA at certain nanoparticle loadings. Other researchers reported an increase in the T_g of nanocomposites with increasing nanoparticle loading [45-47]. The effect of nanoparticles on the T_g of nanocomposite is far more complex than the simple increase/decrease trend with particle loading. For example, Jang *et al.* [48] reported that T_g of alkyl ester/alumina polymer composites initially increased with alumina content; however, after reaching a certain loading, T_g decreased. The effect of nanoparticles on the T_g also depends on the polymer matrix. Rittigstein *et al.* [49] observed a T_g increase in P2VP/alumina and a decrease of T_g in PMMA/alumina nanocomposites.

The interfacial interaction between the nanoparticles and the polymer matrix plays a critical role in determining the quality and properties of the nanocomposites. In the nanocomposites, the well-dispersed nanoparticles are surrounded by polymer chains, which are in contact with the particle surface. If the polymer chains have a strong contact with the surface of particles, they lose some of their mobility and a region of low mobility polymer will exist around each particles [50]. The polymer chains in this region have different behavior from those in bulk form. It is obvious that the interaction region between polymer chains and nanoparticles has a large influence on thermal and mechanical properties. Surface functionalization of nanoparticles makes the interface between the polymer matrix and the nanoparticles stronger. This can be used to optimize the properties of resulting nanocomposites.

For resin injection applications, it is important to understand the rheological behavior of monomer/nanoparticle suspensions. Compared to micro-particles, nanoparticles can easily infiltrate the cracks. Numerical simulations using molecular dynamics suggest that the inclusion of nanoparticles into a polymer mixture results in an increased volume fraction of nanoparticles near the crack tip due to depletion attraction effects. This results in a

subsequent significant reduction in the stress concentration at the crack tip due to the presence of these nanoparticles [51].

Generally, the rheological behavior of colloidal suspensions is affected by the following factors [52]: 1) medium of suspension; 2) shape, density, size and size distribution of the particles; 3) volume actually occupied by the particles in suspension; 4) thermodynamic conditions of the system; 5) presence and concentration of electric charges in the system; and 6) shear rate. For a given suspension system, the viscosity is a function of volume fraction and the interactions both between particles with one another and between particles with the suspension medium.

Figure 1-8 Thixotropy caused by nanoparticles. (Fumed silica, courtesy of Cabot Corp.)

Colloidal dispersions, such as the dispersion of alumina nanoparticles in low viscosity BECy monomer, often have Bingham plastic and thixotropic properties exhibiting a stable form at rest but becoming fluid when agitated. Thixotropy is the property of some non-newtonian pseudoplastic fluids to show a time-dependent change in viscosity; the longer the fluid undergoes shear, the lower its viscosity. A thixotropic fluid is a shear-thinning fluid which takes a finite amount of time to reach an equilibrium viscosity when introduced to a step change in shear rate. As shown in Figure 1-8, the dispersion of silica nanoparticle forms a network while standing, but with the application of shear, the network is broken down and the dispersion displays the shear-thinning behavior.

Although little experimental data exists in the literature for the rheological behavior of nanoparticles suspended in low viscosity monomers, the dispersion of nanoparticles in aqueous solutions can be used as an approximate model. The majority of the literature on the

role of particle size on rheology focuses on particles in the micro or sub-micro range [53-57]. The conclusion of the literatures suggest that alumina aqueous suspensions with particle sizes ranging from the sub-micron to microns exhibited shear thinning behavior approaching a constant value at high shear rates, but the thixotropic behavior is much more pronounced as the particle size decreases. Such behavior has additional benefit for resin-injection repair, since the thixotropic behavior will allow easy injection of the resin to the damaged region and provide sufficient integrity to the suspension after the injection pressure (shear force) is removed and the monomer is cured.

1.4 Research objectives

1.4.1 Curing kinetics of bisphenol E cyanate ester

The cure kinetics of BECy is investigated by differential scanning calorimetry (DSC). Both dynamic and isothermal experiments are carried out to obtain the kinetic parameters. Several reaction models are used to model isothermal curing. The parameters of cure kinetics, such as activation energy and reaction order, are obtained from model analysis. The empirical DiBenedetto equation is used to evaluate the relationship between T_g and conversion. Changes in activation energy are evaluated from Isoconversional analysis

1.4.2 The effect of alumina nanoparticles on the curing kinetics of bisphenol E cyanate ester

In this stage, the cure kinetics of bisphenol E cyanate ester with various loadings of alumina or silica nanoparticles without catalysts are investigated. Alumina nanoparticles are shown to have a catalytic effect on the cure of BECy. The silica nanoparticles are used as control, to evaluate the catalytic effect of alumina nanoparticles. Dynamic DSC experiments are performed to obtain kinetic parameters. Similar to the analysis of BECy cure kinetics, an autocatalytic model is used to describe the cure process. The kinetic parameters obtained from the model gives the information about the catalytic effect of alumina nanoparticles on the cure reaction mechanism of BECy. By using the kinetic parameters obtained from dynamic experiments, the isothermal cure of BECy/nanoparticle composites is predicted.

1.4.3 Rheology and dynamic mechanical analysis of cyanate ester/alumina nanocomposites

The 3-Glycidyloxypropyltrimethoxysilane (GPS) is immobilized on the surface of alumina nanoparticles. The functionalized alumina nanoparticles are characterized by using Fourier transform infrared (FTIR) and thermogravimetric analysis (TG). The alumina

nanoparticles are dispersed into BECy monomer. The rheology and rheokinetic of BECy suspensions are evaluated. The thermal-mechanical properties of cured BECy/bare alumina and BECy/functionalized alumina nanocomposites are evaluated by dynamic mechanical analysis. The relationship of storage modulus increased and loading of nanoparticles for both bare and functionalized alumina is analyzed by using different equations. While, the change of T_g is investigated. The dispersion status of alumina nanoparticles in BECy matrix is observed by using transmission electron microscopy (TEM).

1.4.4 Creep behavior of cyanate ester/alumina nanocomposites

The creep behavior of neat bisphenol E cyanate ester (BECy) and BECy/alumina nanocomposite is studied through tensile creep testing by using dynamic mechanical analysis (DMA). The tensile creep compliance is measured at isothermal conditions between 190 and 320 °C with 10 °C interval. The long-term creep behavior in a high temperature environment is predicted by following temperature-time superposition principle (TTS). The frequency dependent dynamic properties of neat BECy and BECy/alumina nanocomposite are also evaluated at isothermal conditions as same as tensile creep testing. Based on the frequency-time transformation method, the frequency dependent dynamic data can be transformed into time-domain creep compliance data. The transformed creep compliance data is useful for the prediction of long-term creep behavior because the frequency dependent dynamic test eliminates the possible physical and/or chemical aging of the material due to the aggressive testing conditions.

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CHAPTER 2: CURING KINETICS OF THERMOSETTING BISPHENOL E CYANATE ESTER

A paper published in *Journal of Thermal Analysis and Calorimetry*¹

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2.1 Abstract

Resin injection repair is a common method to repair delamination damage in polymer matrix composites (PMCs). To repair high-temperature PMCs, the resin should have a very low viscosity, yet cure into a compatible adhesive with high temperature stability. Normally, thermosetting polymers with high glass transition temperatures (T_g) are made from monomers with high room temperature viscosities. Among the high temperature resins, bisphenol E cyanate ester (BECy, 1,1'-bis(4-cyanatophenyl)ethane), is unique because it has an extremely low viscosity of 0.09-0.12 Pa·s at room temperature yet polymerizes as a cross-linked thermoset with a high T_g of 274 °C. BECy monomer is cured via a trimerization reaction, without volatile products, to form the high T_g amorphous network. In this study, the cure kinetics of BECy is investigated by differential scanning calorimetry (DSC). Both dynamic and isothermal experiments were carried out to obtain the kinetic parameters. An autocatalytic model was successfully used to model isothermal curing. The activation energy from the autocatalytic model is 60.3 kJ/mol and the total reaction order is about 2.4. The empirical DiBenedetto equation was used to evaluate the relationship between T_g and conversion. The activation energy of BECy from the dynamic experiments is 66.7 kJ/mol based on Kissinger's method, while isoconversional analysis shows the activation energy changes as the reaction progresses.

Keywords: activation energy, cure kinetics, cyanate ester, differential scanning calorimetry

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2.2 Introduction

Polymer matrix composites (PMC) are especially susceptible to matrix micro-cracking when subjected to repeated thermo-mechanical loadings. Often these matrix micro-cracks coalesce and lead to other damage modes including fiber/matrix debonding and ply delamination [1-5]. Low velocity impacts from events, such as a tool drop or a glancing bird strike on an aircraft, are common causes of delamination damage in fiber reinforced PMC. Currently composite parts that have been damaged in service are first inspected manually to determine the extent of damage. For critical parts this inspection may include such nondestructive testing techniques as ultrasonics, infrared thermography, X-ray tomography and computerized *vibro* thermography [6]. If the damage is too severe, the structural component is replaced entirely. For less extensive damage, repairs are attempted.

One common repair method is the use of adhesively bonded scarf patches. In this method, the surface material of the laminate is carefully removed to the bottom of the delamination region with a high-speed grinder at a shallow angle. Then repair plies are used to fill the removed material. Another repair method is resin-injection repair, where delamination damage is repaired by injecting resin via an evacuated access hole into the failed area. The resin-injection repair eliminates the need to remove the outer undamaged plies and can result in higher recovery strengths than repairs made by the scarf repair method. However, the use of the resin-injection repair method for high temperature PMCs (loosely defined as composites that maintain their useful properties after thousands of hours in air at 200 °C) has been limited to date because of the low T_g 's of the cured adhesives which are available.

There are several special requirements for an ideal resin system for the resin-injection repair of high temperature PMCs: 1) *low viscosity and wettability*, easy to infiltrate the damage area; 2) *high temperature stability*—the cured resin should have a T_g above the maximum temperature that the composites experience in service; 3) *compatible adhesive*—the cured repair resin must be a strong adhesive to the matrix and reinforcement, to bond the crack surface together; and 4) *long shelf-life and environmentally benign*. Among these requirements, the low viscosity of the monomer resin and the high temperature stability of

the resulting polymer network are critical, yet competing, properties for an ideal system for resin-injection repair applications.

Normally, a monomer which cures into a high temperature thermosetting polymer with a high T_g also has a high viscosity at room temperature [7, 8]. As a general rule, the higher the cured glass transition temperature, the higher the viscosity of the prepolymer at a given temperature. For example, bismaleimide (1,1'-(methylene-di-4,1-phenylene)bismaleimide) resin cures into a polymer network with a high T_g of above 300 °C, but the temperature of the resin must be raised to 160 °C for the viscosity of the resin to reach an injectable viscosity of 0.15 Pa·s [7]. There is one exception to the trend: a unique type of cyanate ester monomer: bisphenol E cyanate ester (BECy, 1,1'-bis(4-cyanatophenyl)ethane). Compared to the more common bisphenol A cyanate ester (Figure 2-1) with a melting temperature of 82 °C, BECy has an extremely low viscosity of 0.09-0.12 Pa·s at room temperature [9]. These processing characteristics make the BECy an excellent candidate for the resin-injection repair of high-temperature polymer composites.

Figure 2-1 Cyanate ester chemical structures and cyclotrimerization reaction scheme.

The monomer of cyanate ester resins is an ester of bisphenol and cyanic acid, containing reactive ring-forming cyanate ($\text{—O—C}\equiv\text{N}$) functional groups. Cyanate ester monomers are generally polymerized via cyclotrimerization to polycyanurates (Figure 2-1). The formation of substituted triazine rings via the cyclic addition of three aryl cyanates involves a series of step-growth reactions. Cyanate esters have low toxicity and no leaving groups or volatile by-products during the polymerization, which makes them less hazardous than many other high temperature polymers, such as bismaleimides. Although cyanate esters are not capable of withstanding temperatures as high as bismaleimides, they are capable of withstanding extreme temperature variations, which is a significant improvement over epoxies. Additionally, cyanate esters have excellent adhesive properties and are more resistant to moisture absorption than other thermosets. Therefore, we believe that BECy is a good candidate for the resin injection repair of high temperature composites. In this study, the cure kinetics of BECy is investigated mainly by differential scanning calorimetry (DSC). Both isothermal and multi-heating-rate dynamic cure experiments are used to obtain the cure kinetic parameters. The obtained kinetic parameters can be used as a guide to determine the processing time and temperature profile in the actual repair processes.

2.3 Experimental

BECy monomer is obtained from Bryte technologies, Inc. (Morgan Hill, CA) as EX1510 cyanate ester. BECy is mixed with catalyst (Bryte technologies, Inc., supplied with EX1510 cyanate ester) in a weight ratio of 100:3 at room temperature by magnetic stirring.

Thermogravimetric analysis (TG) measurements were performed on a TG model Q50 (TA Instruments, Inc., New Castle, DE) to determine the decomposition temperature of polymerized BECy and volatile contents during the polymerization. About 20 mg uncured resin was placed in platinum pans and heated from 25 °C to 800 °C at a rate of 20 °C/min under nitrogen or air purge at 60 mL/min.

Differential scanning calorimetry (DSC) measurements were made on a model Q2000 DSC (TA instruments, Inc.) for isothermal and dynamic cure experiments. A helium flow of 25 mL/min was used as purge gas for all the DSC experiments. Fully or partially cured solid BECy samples were sealed into standard aluminum DSC pans. The liquid samples, uncured

mixture of BECy monomer and catalyst, were transferred into hermetic aluminum pans using a pipette and sealed with lids.

Uncured samples were tested first by DSC in the dynamic scan mode from -80 to 350 °C at a heating rate of 10 °C/min. This temperature scan range allowed for observation of the glass transition of BECy monomer and was below the decomposition temperature of the polymerized BECy. Integration of the exothermal peak gives the value of the total reaction heat ΔH_T . A fully cured sample was also performed under these dynamic scan conditions to determine the T_g of the fully cured BECy.

Two different methods were used to evaluate conversion versus time of BECy under isothermal cure conditions. In method I, partially cured samples were prepared by pouring catalyzed BECy into silicon rubber molds followed by isothermal cure in an oven at a preset temperature ($T_c = 180, 200$ °C). After various curing times, ranging from 1 min to 6 hrs, samples were removed from the oven and quenched to room temperature with liquid nitrogen. A small piece (~ 10 mg) was cut from the sample for subsequent dynamic DSC evaluation from -80 to 350 °C at 10 °C/min. From these experiments both the residual reaction heat ΔH_r and T_g of partially cured samples were obtained simultaneously.

To perform the isothermal curing method II, uncured BECy samples (~ 8 mg) were sealed in a hermetic pan with a lid and loaded into the DSC cell. The DSC cell is heated up to the cure temperature ($T_c = 160, 170, 180, 200$ °C) at a heating rate of 100 °C/min, and then isothermally soaked from 1 to 6 hours depending on the cure temperature used. After the first scan is finished, the DSC cell is cooled down to 25 °C, and a second scan with the same temperature profile as the first is performed to obtain the baseline for analysis. Finally, the same sample is evaluated in dynamic mode from room temperature to 350 °C at 10 °C/min. The residual reaction heat ΔH_r is used to calculate the final conversion of the sample at the various isothermal cure temperatures. The cure kinetics of uncured BECy samples is also evaluated from dynamic scanning experiments at multiple heating rates of 2, 5, 10, 15 and 20 °C/min.

2.4 Results and discussion

2.4.1 Thermogravimetric analysis

The decomposition temperature and volatile content of uncured bisphenol E cyanate ester was measured by TG (Figure 2-2). The minimal mass loss below 200 °C is mainly volatile content in the BECy monomer and catalyst, such as water and residual volatile solvents. At this temperature range, BECy shows very low (less than 1%) volatile content before curing. Above 400 °C, the cured BECy decomposes, with 5% mass loss occurring at 438 °C and 437 °C in nitrogen and air respectively. In nitrogen, the decomposition rate reaches the highest value at 446 °C and showed a large mass loss to about 46% of the initial sample mass by 800 °C. When the sample was tested under air, it exhibited a similar sudden drop in mass. Under the air atmosphere, oxidation is involved and the entire sample is burned off by the end of the experiment. TG results confirm that the BECy does not generate significant volatile organic compounds (VOCs) and has a very high decomposition temperature, which is desirable for high temperature resin repair applications. It also indicates that the upper temperature limit for subsequent DSC experiments should be below 400 °C to prevent sample decomposition in the cell.

Figure 2-2 The TGA curves (at 20 °C/min) of catalyzed BECy under nitrogen and air.

2.4.2 Isothermal curing method

The isothermal curing method I allows for the calculation of residual reaction heat and determination of glass transition temperature from a single DSC scan. Typical dynamic DSC scans of BECy samples, which had first been partially cured isothermally in the oven at 180 °C, are shown in Figure 2-3. The T_g (pointed out by arrows) of partially cured BECy increases with increasing isothermal cure time at 180 °C. The exothermal peak area, which occurs after the T_g , represents the residual reaction heat ΔH_r , and decreases with increasing isothermal cure time. The increase of T_g and decrease of ΔH_r indicates how the reaction progresses with the cure time. The conversion of BECy monomer is calculated by

$$\alpha = \frac{\Delta H_T - \Delta H_r}{\Delta H_T} \quad (2-1)$$

where the total reaction heat ΔH_T is determined as 720 J/g by scanning of uncured sample in the DSC cell at a heating rate of 10 °C/min. After first scanning partially cured samples to determine T_g and ΔH_r , a second scan was performed to measure the T_g of fully cured BECy. The T_g and ΔH_r of partially cured samples and their subsequent T_g from the second experiment are plotted versus isothermal cure time in Figure 2-4.

Figure 2-3 Typical DSC curves for partially cured BECy samples that were cured at 180 °C for various times.

Figure 2-4 Residual reaction heat ΔH_r and T_g of BECy samples isothermally cured at 180 °C for various times.

For short isothermal curing times, it is clear that the residual reaction heats, ΔH_r , decrease as the preceding isothermal cure time increases. After curing for one hour at 180 °C, the residual reaction heat, ΔH_r , reaches a plateau. Based on these isothermal cure experiments, the highest conversion at a cure temperature of 180 °C is 91%. Therefore, a post-cure process is needed to reach the fully cured state. In Figure 2-3, the exothermal peak areas, which are proportional to the residual reaction heats, have peak temperatures above the isothermal cure temperature. Additionally, the samples which cured longer than 1 hr at 180 °C all show peak temperatures closed to 250 °C, indicating that a post-cure process should be carried out above 250 °C for the samples to reach the fully cured state.

Isothermal curing method II was performed at four cure temperatures: 160, 170, 180, and 200 °C, respectively. As mentioned previously, three individual scans are required to get enough information to plot conversion vs. time for the isothermal curing method II: (1) a first isothermal measurement of uncured BECy sample at the cure temperature for an extended period of time, (2) a second isothermal scan following the same temperature profile to obtain the baseline for data analysis, and (3) a third dynamic scan at 10 °C/min, to measure T_g and ΔH_r (to determine the value of final conversion). The highest possible conversions without subsequent post-cure processes were found to be 87%, 89%, 91% and 94% at cure temperatures of 160, 170, 180 and 200 °C, respectively. The analyzed isothermal cure plot of

conversion vs. time at different curing temperatures is showed in Figure 2-5 (only the data at the beginning stage of the isothermal cure are shown). The experimental data of conversion vs. time obtained from isothermal cure method I (the residual heat method) is also shown in the Figure 2-5, which matches very closely with the data obtained from isothermal cure method II at the same isothermal cure temperature of 180 °C.

Figure 2-5 Plot of conversion vs. time for isothermal cures of BECy at different curing temperatures.

The conversion rate can be defined as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_T} \quad (2-2)$$

where, dH/dt is the heat flow rate and can be measured directly by DSC. Modeling equations for the cure kinetics of thermosetting polymers generally have two categories: n th order and autocatalytic. If more than one chemical reaction occurs during cure, the kinetic model may represent an overall process when these chemical reactions occur simultaneously [10].

For the cure of thermosetting polymers that follow n th order kinetics, the rate of conversion is proportional to the concentration of unreacted materials:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2-3)$$

where, n is the reaction order, and k is the temperature dependent reaction rate constant given by the Arrhenius relationship:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2-4)$$

E_a is the activation energy, R the gas constant, T the absolute temperature, and A the pre-exponential or frequency factor. Eq. (2-3) indicates that the maximum conversion rate occurs at $\alpha = 0$. The conversion rate is dependent only on the amount of unreacted materials and assumes that the reaction products are not involved in the reaction.

Figure 2-6 Autocatalytic modeling of isothermal cure data.

If the reaction products are involved in the reaction, the autocatalytic model will apply:

$$\frac{d\alpha}{dt} = k'(1-\alpha)^n \alpha^m \quad (2-5)$$

where, similarly, reaction rate constant k' follows the Arrhenius relationship and m is a component of the reaction order. According to Eq. (2-5), the conversion rate is zero at the beginning of the reaction and reaches a maximum value at an intermediate conversion.

To determine which models best describe the cure kinetics of BECy, a plot of conversion rate (da/dt) versus conversion (α) is made and shown in Figure 2-6. As shown in Figure 2-6, the conversion rate has a maximum value between 10 and 20% depending on the isothermal cure temperature (T_c). These characteristics indicate that the isothermal cure of BECy follows an autocatalytic model. The fitting results by the autocatalytic model are also shown in Figure 2-6 as solid lines. The autocatalytic model has a good agreement to the

experimental data, with the degree of fit $R^2 > 0.98$. The kinetic parameters k , n and m obtained by least squares regression are listed in Table 2-1. Obviously, the reaction rate constantly increases with cure temperature. The isothermal cure of BECy has a total reaction order ($m+n$) of 2.4. Based on the logarithmic form of the Arrhenius relationship, a plot of $\ln k$ vs. $1/T$ (Figure 2-7) gives the activation energy E_a as 60.3kJ/mol and $\ln A$ as 11.2.

Table 2-1 Kinetic parameters at different isothermal cure temperature.

Cure temperature (°C)	$k \times 10^{-4}$ (s ⁻¹)	n	m	$n+m$
160	36	2.0	0.3	2.3
170	54	2.1	0.3	2.4
180	74	2.1	0.3	2.4
200	150	2.1	0.4	2.5

While the residual reaction heat, ΔH_r , is difficult to measure when the reaction reaches a high degree of conversion ($\alpha > 95\%$), the T_g measurably increases with cure state and serves as a more sensitive measure of conversion than residual reaction heat at the latter stages of cure. There is a one-to-one non-linear relationship between T_g and conversion α , independent of cure temperature for this high T_g BECy system. Therefore, T_g can be used as a primary variable to transform T_g to conversion and vice versa, via the one-to-one relationship obtained from a theoretical or empirical fit of the experimental data.

To evaluate the relationship between T_g and conversion, samples were prepared following the isothermal cure method I procedure: the uncured samples were isothermally cured at 180 and 200 °C, respectively, for various periods of time; and then dynamic DSC scans were performed to measure the partially cured sample T_g and conversion α . A plot of T_g vs. conversion α is shown in Figure 2-8 with the T_g increasing monotonically with conversion.

Figure 2-7 Arrhenius plot obtained by autocatalytic model.

Figure 2-8 T_g vs. conversion plot with DiBenedetto equation fitting.

In Eq. (2-6), the empirical DiBenedetto equation, which is often used to fit T_g vs. conversion data [11], is rewritten by assuming the partially cured system as a mixture of fully cured polymer and monomer:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda)\alpha} \quad (2-6)$$

where, T_{g0} is the T_g of the uncured monomer and $T_{g\infty}$ is the maximum T_g for the fully cured sample. The parameter λ is a structure dependent constant, theoretically equal to $\Delta C_{p\infty}/\Delta C_{p0}$, where $\Delta C_{p\infty}$ and ΔC_{p0} are the differences in heat capacity between the glassy and rubbery states at T_g for fully cured sample and uncured sample, respectively.

Taking the T_g and α values experimentally, T_{g0} , $T_{g\infty}$ and λ were determined by least squares regression as -56 °C, 277 °C and 0.32 respectively. The values of T_{g0} and $T_{g\infty}$ are very close to the experimentally measured values (as shown in Figure 2-8). The parameter λ is difficult to measure accurately with traditional DSC techniques because of the large measurement uncertainties in $\Delta C_{p\infty}$ and ΔC_{p0} ; however, modulated DSC may be pursued in further experiments to experimentally measure the value of λ and compare it with the value obtained through the model fit.

2.4.3 Dynamic scanning method

While the isothermal measurements have the advantage of a complete separation between the variables of time and temperature, dynamic scanning experiments allow for improved investigation of the kinetics at the start and end of the reaction, and the kinetic parameters can more easily be interpreted by a comparison of measurements at different heating rates [12]. Multiple dynamic DSC experiments were performed at heating rates of 2, 5, 10, 15 and 20 °C/min, respectively, to test uncured BECy samples. Figure 2-9 shows the DSC scans for all of the experimental multi-heating-rate runs for the BECy samples.

The isothermal experimental data were well fit by an autocatalytic cure model. By combining Eq. (2-2), (2-4) and (2-5), the heat flow can be expressed as:

$$\frac{dH}{dt} = \Delta H_T A \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n \alpha^m \quad (2-7)$$

Using the kinetic parameters obtained from the isothermal experiments (E_a , A , n , and m) the experimental dynamic DSC data can be compared to the model, which are shown as solid lines in Figure 2-9. The modeling curves fit the experimental data reasonably well throughout most of the temperature range, but deviate significantly in the high temperature regions. This deviation from the experimental data suggest that more complex cure mechanisms are involved and that BECy may not be characterized by an autocatalytic model through the whole curing process under dynamic scanning conditions.

Figure 2-9 Dynamic scanning method: experimental DSC curves of uncured BECy (symbols) and model fittings (solid lines).

An isoconversional method, which assumes the activation energy and pre-exponential factor are both functions of the degree of cure, can be used to analyze the multi-heating-rate scan data [13,14]. This makes it equally effective for analyzing both n th-order and autocatalytic reactions.

In the analysis of experimental data from multi-heating-rate dynamic scans, there are two approaches often used to determine curing kinetic parameters: Kissinger's approach [15] and Ozawa's [16-19] approach.

The exothermal peak temperature, T_p , is shifted to higher temperatures with increasing heating rate. According to Kissinger's approach, the maximum reaction rate $d\alpha/dt$ occurs at T_p , where $d^2\alpha/dt^2 = 0$, and the kinetic equation can be expressed as

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (2-8)$$

Based on Kissinger's approach, a plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ gives the values of the pre-exponential factor A and activation energy E_a (where β represents the heating rate in K/s). Figure 2-10 shows the plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$.

Figure 2-10 Plots based on Kissinger's approaches.

Ozawa's approach gives a simple relationship between the activation energy, the heating rate and isoconversion temperature:

$$\log \beta = -\frac{0.4567 E_a}{RT_i} + A' \quad (2-9)$$

where for each degree of conversion, A' is a constant that can be expressed as

$$A' = \log \left[\frac{AE_a}{g(\alpha)R} \right] - 2.315 \quad (2-10)$$

and $g(\alpha)$ is a function of the dependence of conversion [19]. Similarly, a plot of $\log \beta$ vs. $1/T_i$ at each degree of conversion gives a slope proportional to the corresponding activation energy E_a and an intercept of the pre-exponential factor A' (Figure 2-11). Therefore, the relationship of activation energy and conversion can be measured through the whole reaction. The activation energy initially decreases with the increase of conversion, reaching a minimum value at around 30% conversion. It then increases, until about 70% conversion, before decreasing again at high conversions. The decrease of activation energy at the beginning may be due to the autocatalytic effect of the curing process and the subsequent increase of activation energy may be caused by the formation of the cross-linked network which restricts diffusion of the unreacted monomer. The decrease of activation energy at high

conversions is still in question. At high conversions, the reaction no longer follows the autocatalytic kinetics and more complex mechanisms, such as diffusion control, are involved in the cure process. The A shows a similar trend as E_a with conversion in Figure 2-11. This is due to the kinetic compensation effect [20], which suggests that the value of $\ln A$ varies linearly with E_a . Both Kissinger's and Ozawa's plots show a very good linear relationship between parameters based on the experimental data. The calculated results based on Kissinger's approach are listed in Table 2-2. Ozawa approach gives an average value of 61.2 kJ/mol, which is slightly higher than the activation energy obtained from the isothermal curing method, but lower than that obtained from Kissinger's method.

Table 2-2 Cure kinetic parameters calculated from Kissinger and Flynn-Wall-Ozawa approach.

Heating rate (°C/min)	T_p (°C)	Kissinger	
		E_a (kJ/mol)	$\ln A$
20	202.0	66.7±0.4	12.4±0.1
15	195.5		
10	185.6		
5	169.8		
2	150.3		

Another isoconversional method is the Friedman's analysis [20]:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln f(\alpha)A - \frac{E_a}{RT} \quad (2-11)$$

where, $f(\alpha)$ is an unknown reaction model. Similar to Ozawa's approach, the activation energy and $\ln f(\alpha)A$ can be calculated from the slope and intercept of a $\ln d\alpha/dt$ vs. $1/T$ plot (Figure 2-12). Friedman's analysis shows that activation energy versus conversion is qualitatively similar to that found by Ozawa's method: the activation energy decreases first and then increases to a maximum value with the increase of conversion, and finally, decreases again at the highest conversion stages. Friedman's approach gives a lower average activation energy: 56.8 kJ/mol.

Figure 2-11 Isoconversional analysis: Ozawa approach.

Figure 2-12 Isoconversional analysis: Friedman plot.

The activation energy E_a of BECy is lower than the 80 kJ/mol of the similar bisphenol A cyanate ester system and close to the reported value of 68.5 kJ/mol calculated from a WLF diffusion-controlled model in Ref. [21]. The lower activation energy E_a implies lower required cure temperatures to polymerize the resin, which is favorable for composite repair applications.

2.5 Conclusions

BECy has low viscosity at room temperature and can polymerize into a thermosetting polymer with a high glass transition temperature and good thermal stability. Fully cured BECy has a T_g of 274 °C and reaches the highest rate of decomposition at 446 °C in air. The relationship of conversion vs. time at different isothermal cure temperatures shows how increasing the curing temperature increases the reaction rate and a post-cure process above 250 °C is needed to fully cure the resin. The kinetic parameters are calculated by applying an autocatalytic model to fit the isothermal cure data. The analysis gives an activation energy of 60.3 kJ/mol and a total reaction order around 2.4. Isothermal curing experiments also shows a one-to-one relationship between the T_g of partially cured BECy and conversion. Multi-heating rate scans were analyzed by Kissinger's and Ozawa's approaches. The overall activation energy calculated from Kissinger's approaches is 66.7 kJ/mol, which is higher than the value obtained from the isothermal cure method. Ozawa and Friedman analysis give a relationship of activation energy vs. conversion, and an average value of 61.2 , 56.8 kJ/mol, respectively.

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CHAPTER 3: THE EFFECTS OF ALUMINA NANOPARTICLES ON THE CURING KINETICS OF BISPHENOL E CYANATE ESTER

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3.1 Abstract

The cure kinetics of bisphenol E cyanate ester (BECy) with various loadings of alumina or silica nanoparticles without catalysts is investigated by differential scanning calorimetry (DSC). Alumina nanoparticles are shown to have a catalytic effect on the cure of BECy. The greater catalytic effect of alumina nanoparticles, compared to silica, is attributed to the increased number of hydroxyl groups on the surface and the Lewis acidic character of γ -phase alumina. Dynamic DSC experiments were carried out to obtain kinetic parameters. For an autocatalytic model of the cure process, the kinetic parameters obtained from the model suggest that the addition of alumina nanoparticles changed the cure reaction mechanism of BECy. By using the kinetic parameters obtained from dynamic experiments, the isothermal cure of BECy/nanoparticle composites is predicted.

3.2 Introduction

Bisphenol E cyanate ester (BECy) is a unique cyanate ester monomer with an extremely low viscosity, 0.09-0.12 Pa s at room temperature [1], differing from other high-temperature thermosetting polymers. The cured BECy has a high glass transition temperature (~ 270 °C) and excellent thermal-mechanical properties [2]. The combination of excellent processability and thermal-mechanical properties make BECy an excellent candidate for many applications ranging from aerospace to micro-electronics.

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The curing of BECy is accomplished by the cyclotrimerization of three cyanate groups (-OCN) and results in a highly cross-linked network. Figure 3-1 shows the chemical structure of BECy monomer and the cyclotrimerization scheme. The rate of the cyclotrimerization reaction is catalyst dependent. The most common types of catalyst used for the dicyanate ester are carboxylate salts and chelates of transition metal ions [3,4]. However, the polymerization of cyanate ester can be carried out in the absence of catalyst [5-13]. When cyanate ester monomers are heated, small amounts of impurities (e.g. H₂O/phenol) in the monomer will react with a cyanate ester to form an intermediate iminocarbonate, which can react with two -OCN groups to form a triazine ring and the abstracted phenol is then able to enter the polymerization again (Figure 3-2).

Figure 3-1 Cyanate ester chemical structure and cyclotrimerization reaction scheme.

Figure 3-2 Reaction scheme: the polymerization of cyanate ester by a small amount phenol in the monomer.

Fillers are often used to modify thermosetting polymers. They serve not only as reinforcements to enhance the mechanical properties but also as processing additives to alter rheological properties. Recently, a growing number of reports have focused on nano-size fillers, such as exfoliated clays, carbon nanotubes, and silica nanoparticles [14,15,16]. Because of their huge specific surface area, nanoparticles have been shown to enhance physical, thermal-mechanical and processing characteristics of the resulting polymer nanocomposites beyond traditional rule of mixture estimates [17]. Oxide nanoparticles, such as alumina, silica, and titania, usually contain substantial hydroxyl groups on the surface. Because of their low cost and ability to be functionalized, alumina nanoparticles are often used as fillers with a broad choice of polymer matrices, such as epoxy [18], PMMA [19-22], PS and PVE (poly vinyl ester) [23]. Additionally, the nanoparticles may catalytic impact the formation of the organic matrix due to surface functionalities, which under certain conditions, affect the cure kinetic of the monomers in which the particles are dispersed [24-30]. In our previous study on BECy/silica nanocomposites, silica nanoparticles also showed a slight catalytic effect on the cure behavior of BECy [31].

In this study, alumina nanoparticles are added to BECy as a reinforcement and additive to adjust rheological properties. The catalytic effects of alumina nanoparticles on the cure kinetics of BECy are investigated primarily by differential scanning calorimetry (DSC). Silica nanoparticles with similar particle size as the alumina are also added to BECy monomer as a control to compare the catalytic effects of alumina relative to silica on the BECy cure kinetics.

3.3 Experimental

3.3.1 Materials

BECy monomer was supplied by BRYTE technologies, Inc. (Morgan Hill, CA) as EX1510 resin, which was used as received without further purification. Alumina nanoparticles were supplied by Nanophase Technologies, Inc. (Romeoville, IL) as NanoTek aluminum oxide, which is γ -phase alumina with an average particle size (diameter) of 40 nm and a specific surface area of 44 m²/g. Silica nanoparticles are obtained from Degussa, Inc. (Essen, Germany) as Aerosil-OX50 fumed silica with an average particles size of 40 nm and

a specific surface area of 50 m²/g. Before use, the nanoparticles were dried *in vacuo* at 120 °C for 24 hr unless otherwise stated.

3.3.2 Specimen preparation

The dried nanoparticles were first weighed in a vial. Then, BECy monomer was added according to the desired nanoparticle loading. The total weight of mixture was c.a. 3 g. The vial containing the mixture of BECy and nanoparticles was sealed with a lid, and then subjected to two hr ultrasonic treatment in a water bath. To further disperse the particles, the mixtures were sonicated with a high intensity ultrasonic tip intermittently for a total of 30 s to prevent excessive temperature rise. The power output ranged between 16 and 18 W during sonication. The well-dispersed suspensions of BECy/nanoparticles were stored in a desiccator.

3.3.3 Experimental procedure

The nanoparticles were characterized by a Fourier transform infrared (FTIR) spectrometer (VERTEX 70, Bruker Inc., Madison, WI). The nanoparticles (~ 1 mg) were mixed with KBr powder at an approximate ratio of 1:100, ground and compressed into a pellet. FTIR spectra were recorded in transmission mode under vacuum.

The moisture content of the nanoparticles was determined by thermogravimetric analysis (TG, model Q50 TA Instruments, Inc., New Castle, DE). About 10 mg of nanoparticles were placed in a platinum pan and heated at a rate of 20 °C/min from 25 °C to 800 °C under nitrogen purge at 60 mL/min.

To assess the catalytic effects of nanoparticles alone, no additional catalyst was added to the well-dispersed BECy/nanoparticles suspension. The suspensions were prepared in hermetic aluminum DSC pans and sealed with lids. The lids were crimped and had uniform tiny holes to relieve the pressure built up during heating. DSC measurements were made on a model Q20DSC (TA instruments, Inc.) for dynamic cure experiments. A nitrogen flow of 50mL/min was used as purge gas for all the DSC experiments. Heating rates of 1, 2, 4 and 6 °C/min were used from room temperature to 350 °C to evaluate the cure of BECy/nanoparticle suspensions in a controlled fashion.

3.4 Results and discussion

3.4.1 FT-IR and TG analysis

Since both physically adsorbed water and hydroxyl groups on the nanoparticle surface may contribute to the catalysis of BECy curing, the alumina and silica nanoparticles were dried at low and high-temperature. This was done to determine their ability to absorb moisture and to evaluate the surface hydroxyl group concentration.

Figure 3-3 FTIR spectra of dried nanoparticles: (a) alumina nanoparticles; (b) silica nanoparticles.

The drying process affects the moisture content of the nanoparticles. After drying at 350 °C for 4 hr, the Silica-H sample shows a diminished –OH stretching peak at $\sim 3500\text{ cm}^{-1}$ (Figure 3-3b) compared to Silica-L sample. The drying process was expected to have similar effect on alumina nanoparticles, but the Alumina-H sample does not show a significant difference from Alumina-L sample. The sharp peak at 1385 cm^{-1} in Figure 3-3a, which is probably related to physically adsorbed water [32], are also unchanged. During the preparation of FTIR pellet, the nanoparticles are briefly exposed to the lab environment, which may cause the tiny amount ($\sim 1\text{ mg}$) of alumina nanoparticles to quickly adsorb moisture. These results suggest that alumina nanoparticles adsorb moisture more quickly than silica nanoparticles.

Figure 3-4 TGA of alumina and silica nanoparticles dried at different conditions.

The content of physically adsorbed water and hydroxyl groups of nanoparticles is evaluated quantitatively by TG (Figure 3-4). The TG curves of alumina can be separated into four regimes [33]: a) room temperature-150 °C, gas desorption; b) 100-400 °C, desorption physically of adsorbed water; c) 400-800 °C, dehydrolysis of adjacent –OH groups on the surface; d) $>800\text{ °C}$, diffusion and desorption of isolated –OH groups. Because the weight loss caused by desorption of isolated –OH groups is less significant and due to the limitation of the instrument's temperature range, the TG tests were performed from room temperature to 800 °C. The TG curves of alumina and silica nanoparticles in Figure 3-4 are divided into 3

regimes: below 100 °C, between 100 °C and 450 °C, and above 450 °C. The measured mass loss values are listed in Table 3-1. The amount of physically adsorbed water and density of hydroxyl groups on the nanoparticles can be estimated from mass loss at certain temperatures, as shown in Table 3-1. The three mass loss regimes overlap with each other, so the exact water content and densities of hydroxyl groups are hard to determine precisely; however, the estimated values are still useful for comparison purposes. The densities of hydroxyl groups on the alumina nanoparticles are calculated as 5.1 (Alumina-H) and 4.0 (Alumina-L) $\mu\text{mol}/\text{m}^2$, which are close to the reported value of 4-7 $\mu\text{mol}/\text{m}^2$ for Al_2O_3 [34,35]. The high temperature drying process helps to reduce the water content of the nanoparticles, but dried alumina quickly adsorbs moisture during preparation of pellets for FT-IR and contain more physically adsorbed water and hydroxyl groups than silica nanoparticles. The ability to easily adsorb moisture is a result of the strong Lewis acidity (electron acceptor character) of the surface of γ -alumina. This Lewis acidity is expected to significantly influence the role that alumina nanoparticles play in the BECy curing.

Table 3-1 TGA measurement results and calculated amount of physically adsorbed water and hydroxyl groups on the surface of nanoparticles.

Sample	Mass loss at 100°C (%)	Mass loss at 450°C (%)	Mass loss at 800°C (%)	Physically adsorbed water ($\mu\text{mol}/\text{m}^2$)	Hydroxyl group density ($\mu\text{mol}/\text{m}^2$)
Alumina-L	0.32	1.33	1.51	11.2	4.0
Alumina-H	0.41	1.07	1.30	7.3	5.1
Silica-L	0.05	0.26	0.29	2.3	0.7
Silica-H	0.01	0.13	0.19	1.3	1.3

3.4.2 DSC measurements and cure kinetic analysis

Differential scanning calorimetry (DSC) is a useful tool to characterize the cure kinetic of polymer cross-link network formation. Usually, there are two experimental methods used to investigate the cure of thermosetting resins: isothermal and multi-heating-rate dynamic cure methods. In the isothermal curing method, the sample is cured at several

constant temperatures (T_c) for various lengths of time. The isothermal cure process can be done in an oven or in the DSC cell for real time monitoring of monomer conversion (α) vs. time. The cured or partially cured samples then undergo a dynamic scan in the DSC, the residual reaction heat (ΔH_r) and glass transition temperature (T_g) are used to determine the monomer conversion for further analysis of the curing process. In the dynamic scan method, samples are heated in the DSC cell at multiple heating rates. The isothermal measurements have the advantage of a complete separation between the variables of time and temperature, while dynamic scanning experiments allow for improved investigation of the kinetics at the start and end of the reaction, and the kinetic parameters can more easily be interpreted by a comparison of results at different heating rates.

The cure kinetics of catalyzed BECy without nanoparticles was investigated by using both dynamic and isothermal experiments in our previous paper [36]. An autocatalytic model is used to describe the reaction mechanism. The activation energy from the autocatalytic model was determined to be 60.3 kJ/mol and the total reaction order was about 2.4. The present study is focused on the effects of nanoparticles on cure of BECy and no catalyst is added to the BECy/nanoparticle suspensions. There are some difficulties for the isothermal cure method: the reaction heat is too small to detect and it takes a very long time to cure at the manufacturer suggested isothermal conditions; increasing the isothermal cure temperature to get higher heat flow signals causes the evaporation of uncured monomer, which introduces significant errors. As a result, the dynamic scan method was used in this study to evaluate the cure kinetic of the BECy/nanoparticle composites. The slow heating rates of 1, 2, 4 and 6 °C/min were used from room temperature to 350 °C to ensure a controlled cure of the BECy/nanoparticle suspension and to prevent volatilization of the monomer.

The suspensions of BECy/alumina nanoparticles and BECy/silica nanoparticles were prepared at equivalent volume loadings to ensure adequate comparisons. The compositions of samples are listed in Table 3-2. According to Table 3-2, the samples discussed below will be designed by their fill type (A for alumina, S for silica) and loading (1 for 0.16 vol.% to 4 for 3.2 vol.%). For example, BECy/alumina suspension at 0.16 vol.% is labeled as A1, while the BECy/silica suspension at 3.2 vol.% is designated as S4.

Table 3-2 Composition of BECy nanocomposite samples.

Sample No.	Volume percent (%)	Alumina nanoparticles Weight percent (%)	Silica nanoparticles Weight percent (%)
1	0.16	0.5	0.3
2	0.7	2	1.2
3	1.6	5	3.0
4	3.2	10	5.8

Figure 3-5 shows typical DSC dynamic scan thermograms of A4 at multiple heating rates (Figure 3-5a) and BECy samples containing different loadings of alumina nanoparticles at a single heating rate of 1 °C/min (Figure 3-5b). As shown in Figure 3-5a, with increasing heating rate, the exothermal peak shifts to high temperatures, but the total reaction heat (ΔH_r) remains constant at c.a. 820 kJ/g. Other samples were also tested at multiple heating rates, and Figure 3-5b shows DSC thermograms of BECy/alumina nanoparticle suspension and neat BECy (without catalyst) at a heating rate of 1 °C/min.

With the addition of alumina nanoparticles, the exothermal peak shifts to lower temperatures. Addition of 3.2 vol.% alumina nanoparticles shifts the peak temperature (T_p) by 70 °C compared to neat BECy. Both A2 and A3 samples show two peaks: Peak 1 (at low temperature) and Peak 2 (at high temperature). Peak 1 becomes more pronounced as the alumina loading increases from 0.7 to 1.6 vol.% and Peak 2 diminishes. The changes of peak position and shape indicate that the reaction mechanism is changing with addition of alumina nanoparticles. The silica nanoparticles also affect the cure of BECy, but increasing the silica nanoparticles loading from 0.16 to 3.2 vol.% decreases the T_p by only 7 °C at a heating rate of 1 °C/min. Furthermore, all BECy/silica nanoparticle samples show a single exothermic peak (not shown here) regardless of the nanoparticle loadings and the heating rates used.

Figure 3-5 The typical DSC dynamic thermograms: (a) A4 sample (BECy/Alumina, 3.2 vol.%) at different heating rates; (b) BECy nanocomposites with different loadings of alumina nanoparticles at 1°C/min.

By comparing the position of the peak of the exotherm for each scan, the overall activation energy, E , of the reaction can be obtained. Using Kissinger's model, which assumes that the maximum reaction rate occurs at the exothermal peak, the activation energy, E_a , is related to the heating rate (β), and peak temperature (T_p), by

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E}{RT_p} \quad (3-1)$$

where A is a pre-exponential factor [37]. Thus, the slope of a plot of $\ln(\beta/T_p^2)$ vs $1/T_p$ is proportional to the activation energy. Figure 3-6 shows this plot for sample A4 based on the DSC thermograms of Figure 3-5a. Similarly, the overall activation energy of other samples can be calculated and the results are listed in Table 3-3. Since A2 and A3 samples have two exothermic peaks on the thermograms, the activation energies were calculated separately as E_1 from peaks at low temperature (peaks of A4, and Peak 1 of A2, and A3) and E_2 from peaks at high temperature (peaks of neat BECy, A1, and Peak 2 of A2, and A3). Neat BECy (without catalyst) has an E_a of 91.5 kJ/mol. Addition of alumina nanoparticles decreases the value of E_a to 82.6 kJ/mol for A1 sample, which suggest that alumina nanoparticles have a catalytic effect on the cure of BECy. With the addition of more alumina nanoparticles, the reaction mechanism starts to shift from one reaction mechanism to another indicated by the two peaks and corresponding distinct activation energies for A2 and A3 samples. After the loading of alumina nanoparticles reach a certain level, the cure of BECy is dominated by a reaction mechanism with an E_a of 100.2 kJ/mol.

Figure 3-6 Kissinger's plot for A4 sample (BECy/Alumina, 3.2 vol.%) applied at the exothermal peak.

Table 3-3 The overall activation energy estimated by Kissinger's plot for BECy nanocomposites with different alumina loadings.

Alumina loading (vol.%)	E_{a1} (kJ/mol)	E_{a2} (kJ/mol)
0		91.5
0.16		82.6
0.7	100.4	78.5
1.6	102.8	83.8
3.2	100.2	

The polymerization of BECy can be catalyzed by: (1) trace amount of phenol in the monomer; (2) the surface hydroxyl group of alumina and physically adsorbed water; and (3) Lewis acidic catalyzing species [38], including metal ions, such as Co^{2+} , Zn^{2+} , Fe^{3+} , Al^{3+} . Since the amount of phenol in BECy monomer does not change with the loading of alumina nanoparticles, the catalytic effect of alumina nanoparticles is likely due to the last two factors. Silica nanoparticles contain physically adsorbed water and hydroxyl groups on the surface but do not show significant Lewis acidity on the surface. Therefore, silica nanoparticles were used to prepare suspensions of BECy/nanoparticles as control samples to evaluate the effects of the surface hydroxyl groups and physically adsorbed water, and Lewis acidity of alumina nanoparticles.

BECy/silica nanoparticle suspensions were prepared following exactly the same process as the BECy/alumina nanoparticle suspensions. The composition of BECy/silica nanoparticle suspensions is listed in Table 3-2. All BECy/silica nanoparticle suspensions were tested using DSC at multiple heating-rate scans.

The normalized integration of original DSC dynamic scan thermograms gives the plot of conversion vs. temperature as shown in Figure 3-7. The thermograms at multiple heating rates of A4 and S4 are showed in Figure 3-7a. Alumina nanoparticles initiate the cure of BECy at lower temperatures than silica nanoparticles at the same solids loadings. Figure 3-7b shows conversion vs. temperature at a heating rate of 1 °C/min with different alumina and silica loadings. The presence of the alumina nanoparticles decreases the temperature at which a given level of monomer conversion is reached. For example, 50% monomer conversion occurs at 247 °C for A1 and 190 °C for A4. Addition of silica nanoparticles does not show such a significant decrease with silica loading: 50% monomer conversion occurs at 256, 252

and 244 °C for neat BECy, S1 and S4, respectively. Both alumina and silica nanoparticles have a catalytic effect on the cure of BECy, but the catalytic effect of alumina nanoparticles is much more pronounced.

Figure 3-7 Plot of conversion vs. temperature: (a) same nanoparticles loading (3.2 vol.%) at different heating rates; (b) different nanoparticles loading at same heating rate of 1 °C/min.

Figure 3-8 Isoconversional analysis of A4 DSC dynamic scans: (a) Ozawa's plot; (b) Friedman's plot.

The isoconversional method is often employed for the analysis of curing kinetics [39]. Isoconversional analysis method assumes that the reaction rate for a given conversion is only a function of temperature and, hence, allows evaluation of the activation energy as a function of conversion:

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (3-2)$$

where t is time and R the universal gas constant. For multi-step kinetics, the global value of conversion does not uniquely determine the composition of the reacting system. This ultimately causes E_a to vary with α , reflecting the variation in relative contributions of single-steps to the overall reaction rate [40]. The relationship between E_a and conversion, α , is often determined by the commonly employed methods, namely Ozawa's and Friedman's methods. Ozawa's approach gives a simple relationship between the activation energy, the heating rate and temperature [41-43]:

$$\log \beta = -\frac{0.4567 E_a}{RT_i} + A' \quad (3-3)$$

where for a given degree of conversion, A' is a constant that can be expressed as

$$A' = \log \left[\frac{AE_a}{g(\alpha)R} \right] - 2.315 \quad (3-4)$$

and $g(\alpha)$ is a function of conversion [44]. A plot of $\log \beta$ vs. $1/T_i$ at a fixed conversion gives a slope proportional to the corresponding activation energy E_a and an intercept that is equal to the pre-exponential factor A' . Figure 3-8a shows such a plot based on the A4 suspension at several heating rates.

Another isoconversional method is Friedman's analysis [45]:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln f(\alpha)A - \frac{E_a}{RT} \quad (3-5)$$

where, $f(\alpha)$ is an unknown reaction model. Similar to Ozawa's approach, the activation energy and $\ln f(\alpha)A$ can be calculated from the slope and intercept of a $\ln d\alpha/dt$ vs $1/T$ (Figure 3-8b).

Both Ozawa's and Friedman's analyses can give a simple relationship between activation energy and conversion (Figure 3-9). Overall, the activation energy increases with conversion. The increase of activation energy is often attributed to the formation of the cross-linked network, which restricts diffusion of the unreacted monomer. Especially at high conversion, the diffusion mechanism dominates the process and activation energy may reach very high levels, as shown for the A4 sample in Figure 3-9. Compared to Kissinger's analysis, both Ozawa's and Friedman's analyses show that the A1 and A2 samples have

lower activation energies than A3 and A4 sample. This decrease in E_a suggests that different reaction mechanisms are involved.

Figure 3-9 Overall activation energy vs. conversion: (a) Ozawa's method; (b) Friedman's method.

With addition of silica nanoparticles, the E_a decreases, reaching a similar value as E_a for the A1 suspension. It is likely that A1, A2 and BEC/silica nanoparticles samples follow the same reaction mechanism, which is catalysis by physically adsorbed water and surface hydroxyl groups (Figure 3-10). The presence of an interaction between cyanate ester and

substrate hydroxyl groups is reported in the literature for cyanate ester composites [38]. Cyanate ester can form covalent bonds with hydroxyl groups via iminocarbonate groups [46]. According to calculated results in Table 3-1, S3 (1.6 vol.%) should contain similar amount of water and hydroxyl groups as A1 (0.32 vol.%) and show similar effect on cure kinetics if they affect the cure of BECy in the same way. The plots in Figure 3-7b and 3-9 suggest that the behavior of A1 is close to sample S4. It indicates that S4 may actually contain similar amounts of water and hydroxyl groups as A1.

Figure 3-10 Reaction scheme of BECy and nanoparticle surface through thermal curing.

The higher activation energies of A3 and A4 suggest a new reaction mechanism: perhaps the Lewis acidity of γ -alumina starts to dominate the cure of BECy. The transition between different reaction mechanisms is also indicated by the changing peak shapes in Figure 3-5b.

By using the activation energies obtained from the experiments and applying suitable reaction model, the experimental DSC dynamic scanning data can be fitted and the curing behavior of uncatalyzed BECy suspensions at isothermal conditions can be predicted.

The heat flow measured in DSC is proportional to both the total reaction heat (ΔH_t) and conversion rate:

$$\frac{dH}{dt} = \Delta H_r \frac{d\alpha}{dt} \quad (3-6)$$

where, the conversion rate $d\alpha/dt$ is expressed as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3-7)$$

where, $f(\alpha)$ is the reaction model. For the cure of thermosetting polymers, $f(\alpha)$ is usually taken in two forms: (1) $f(\alpha) = (1 - \alpha)^n$, n^{th} order reaction model; (2) $f(\alpha) = (1 - \alpha)^n \alpha^m$, autocatalytic model (n and m are the reaction order). The temperature dependent conversion rate constant, $k(T)$, is given by the Arrhenius relationship. If $f(\alpha)$ is replaced with the autocatalytic model, the heat flow can be expressed as:

$$\frac{dH}{dt} = \Delta H_r A \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \alpha^m \quad (3-8)$$

Since the heat flow is measured directly from DSC dynamic scans and the activation energy is obtained from Kissinger's model as mentioned earlier, the kinetic parameters, A , n and m , can be calculated by fitting experimental data to an assumed reaction model. The maximum conversion rate occurs at $\alpha = 0$ for the n^{th} order reaction model, while for autocatalytic model, the conversion rate is zero at the beginning of the reaction and reaches a maximum value at an intermediate conversion.

Figure 3-11 A4 sample (BECy/Alumina, 3.2 vol.%) DSC dynamic thermograms with fittings by autocatalytic model at different heating rates. Symbols: experimental data and Solid lines: model fits.

To determine which model best describes the cure kinetics of BECy, both the n^{th} order reaction and autocatalytic reaction models were fit to experimental data. As expected, the n^{th} order reaction model gives an infinite high reaction rate at beginning of reaction, while autocatalytic reaction model gives a zero initial reaction rate and a better fit with $R^2 > 0.99$. The experimental data (symbols) and model fits (solid lines) for sample A4 are shown in Figure 3-11. The cure kinetic parameters obtained from the model are listed in Table 3-4. The DSC thermograms of A2 and A3 samples have two peaks, which are hard to deconvolute into separate peaks, hence the composite peak did not yield a good fit for these two suspensions. The A1 suspension gives similar reaction orders (total reaction order of 1.9) as the BECy/silica nanoparticles samples, which are similar to the results from the isoconversional analysis. The catalytic effects of alumina nanoparticles at low loading levels and silica nanoparticles are mainly attributed to physically adsorbed water and hydroxyl groups on the surface of the nanoparticles. For the high level of loading, A4 gives a higher activation energy and a different reaction order (total reaction order of 3.6) than other samples but shift the exothermal peak to lower temperatures. This suggest that with increasing alumina loadings, the cure of BECy follows a different reaction mechanism even as the water and hydroxyl groups still affect the reaction at a smaller degree.

Table 3-4 Summary of cure kinetic parameters obtained from autocatalytic model fitting of DSC dynamic thermograms.

Vol. %		0	0.16	0.7	1.6	3.2
BECy/Alumina	Sample	Neat BECy	A1	A2	A3	A4
	E_a^* (kJ/mol)	100.5	82.4	-	-	100.2
	$\ln A$	16.7	12.5	-	-	21.0
	n	1.1	1.0	-	-	2.6
	m	0.8	0.7	-	-	1.1
BECy/Silica	Sample	-	S1	S2	S3	S4
	E_a^* (kJ/mol)	-	91.8	90.3	90.2	84.4
	$\ln A$	-	14.8	14.5	14.5	13.2
	n	-	1.0	1.1	1.1	1.1
	m	-	0.8	0.8	0.8	0.7

* from Kissinger's analysis.

By replacing $f(\alpha)$ with the autocatalytic model, conversion rate Eq. (3-7) can be rewritten as:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT_c}\right)(1-\alpha)^n \alpha^m \quad (3-9)$$

where, T_c is the isothermal cure temperature. Applying the cure kinetic parameters in Table 3-4, the isothermal cure behavior of BECy/nanoparticles can be predicted.

Figure 3-12 Predictions of BECy nanocomposites curing at isothermal conditions: (a) BECy nanocomposites with different nanoparticles loadings, isothermal cure at 180 °C; (b) BECy/Alumina, 3.2 vol.% sample isothermal cure at different temperatures.

Figure 3-12 shows the predicted isothermal cure of BECy/nanoparticles. As shown in Figure 3-12a, silica nanoparticles increase the conversion rate of BECy monomer during isothermal cure at 180 °C. The low alumina loading, i.e. 0.16 vol.%, has the similar catalytic effect as silica nanoparticles: increase the conversion rate at certain conversion, but not significantly. The high alumina loading (3.2 vol.%) has a dramatic catalytic effect on the isothermal cure of BECy. The conversion rate is 30 times higher than neat BECy, and 13 times higher than the same loading of BECy/silica nanoparticles at the maximum reaction rate. It is obvious that isothermal cure temperature affects the cure of BECy. As expected, through the whole isothermal cure, samples cured at high temperatures give higher monomer conversion rates than samples cured at low temperatures (Figure 3-12b).

3.5 Conclusions

Both alumina and silica nanoparticles contain physically adsorbed water and hydroxyl groups on the surface. The drying process at high temperature (350 °C) reduces the water content, but alumina nanoparticles are much more likely to adsorb moisture from the environment even at short exposure times. The TG results indicated that alumina nanoparticles contain about 5 times more physically adsorbed water and hydroxyl groups than the silica nanoparticles of the same size. The water and hydroxyl groups on the surface of the nanoparticles play an important role in the cure of BECy. Silica nanoparticles have a slight catalytic effect on the cure kinetics of BECy. This catalytic effect is mainly attributed to the physically adsorbed water and hydroxyl groups on the silica surface. Therefore, with higher silica nanoparticle loading, the activation energy decreased from 100.5 kJ/mol for neat BECy to 84.4 kJ/mol for the BECy with 3.2 vol.% silica nanoparticles. The catalytic effect of alumina nanoparticles was more pronounced and complex. Besides the physically adsorbed water and hydroxyl groups on the surface contributing to the cure of BECy, the electron donating character (Lewis acidity) of the γ -alumina, significantly affects the cure of BECy. DSC thermograms of BECy containing different loadings of alumina nanoparticles showed a transition from one reaction mechanism catalyzed by hydroxyl functionality (water, surface hydroxyl group, and the phenol in the BECy monomer) to another dominated by the catalytic effect of the Lewis acidity. The isoconversional analysis confirmed this trend. An

autocatalytic reaction model was successfully used to fit the experimental data obtained from DSC dynamic scans. The model fitting suggests that silica and low loadings of alumina nanoparticles have a similar cure of BECy following the same reaction mechanism with a total reaction order of 1.9; however, with increasing alumina nanoparticles, the reaction mechanism changes. The cure of BECy with high loading of alumina follows a reaction mechanism with a total reaction order of 3.7. The cure kinetic parameters were used to predict the isothermal cure of BECy without catalyst. The prediction shows that alumina nanoparticles significantly increase the BECy monomer conversion rate compared to silica nanoparticles and neat BECy.

3.6 Acknowledgement

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CHAPTER 4: RHEOLOGY AND DYNAMIC MECHANICAL ANALYSIS OF BISPHENOL E CYANATE ESTER/ALUMINA NANOCOMPOSITES

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4.1 Abstract

Alumina nanoparticles were functionalized with 3-Glycidyloxypropyl trimethoxysilane (GPS) for compatibility with a low viscosity bisphenol E cyanate ester (BECy) resin. The functionalized alumina nanoparticles were characterized with Fourier transform infrared (FTIR) and thermogravimetric (TG) analysis. The alumina nanoparticles cause an increasing viscosity in the suspension with increasing alumina loading and a concurrent catalytic effect on the cure of the BECy resin. As expected, the gelation time of the uncatalyzed suspensions at 130 °C are reduced by the addition of alumina nanoparticles. TEM micrographs reveal that most of the alumina nanoparticles are well dispersed in the BECy matrix but a small number of particles formed agglomerates. The thermal-mechanical properties of cured BECy/bare alumina and BECy/functionalized alumina nanocomposites are evaluated by dynamic mechanical analysis. The storage modulus increases with both bare and functionalized alumina loading. Although the T_g of bare and functionalized alumina/BECy nanocomposites decreases with increasing filler, the reduction in T_g is less drastic when the alumina nanoparticles are first functionalized.

4.2 Introduction

Bisphenol E cyanate ester (BECy), bis-(4-cyanatophenyl)-1,1-ethane, belongs to a family of cyanate esters, which can form high-temperature thermosetting polymers, and have excellent thermal and mechanical properties. Unlike other high-temperature thermosets that

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exist as a solid at room temperature, BECy monomer has an extremely low viscosity, 0.09-0.12 Pa s [1]. BECy is cured through the cyclotrimerization of three cyanate groups (-OCN) and results in a highly cross-linked network (Figure 4-1). The cured BECy has a high glass transition temperature (up to 270 °C) and shows excellent mechanical properties [2]. Therefore, it is an ideal candidate for use in resin-injection repair of high-temperature composites and a topic of research in our group.

Figure 4-1 Chemical structure of BECy and cyclotrimerization reaction scheme.

Polymer matrices reinforced with nano-size fillers have shown major improvements in mechanical properties, thermal stability, fire retardancy, and other engineering properties compared to the neat resin [3-6]. The overall properties of polymer nanocomposites are significantly affected the large surface-to-volume ratio of the filler. This larger surface-to-volume ratio results in a large portion of the polymer matrix being part of an interfacial region with properties and morphology which may be different from the bulk polymer network. To achieve optimum performance, the nanophase should be well dispersed, forming a nanocomposite free of agglomerates [7]. Development of new dispersion and surface treatment techniques for nanoparticles, such as using silane coupling agents to modify the surface of nanoparticles, has enabled the use of nanocomposites in a variety of applications. Surface treatment of the nanoparticles minimizes particle/particle interaction, leading to improved dispersion, and enhanced particle/matrix compatibility.

Oxide nanoparticles, such as alumina, silica, and titania, usually contain substantial amounts of hydroxyl groups on the surface. Specifically, alumina nanoparticles, which are low cost and can be easily functionalized, have been used as fillers with a broad choice of polymer matrices, such as epoxy [8], PMMA [9-12], PS and PVE (poly vinyl ester) [13]. In our previous work, fumed silica and alumina nanoparticles were used as fillers to form nanocomposites with BECy. The BECy/silica nanocomposites showed enhanced storage moduli and reduced damping behavior [14] compared to the neat resin. The alumina nanoparticles were also shown, by differential scanning calorimetry, to have a catalytic effect on the cure of BECy [15]. In this study, the alumina nanoparticles are functionalized with 3-Glycidyloxypropyl trimethoxysilane (GPS). Both bare and functionalized alumina nanoparticles are added to BECy to form polymer nanocomposite through *in-situ* polymerization. In addition, the rheological and thermal-mechanical properties of the BECy/alumina nanocomposites are investigated in detail.

4.3 Experimental

4.3.1 Materials

BECy monomer was supplied by Bryte technologies, Inc. (Morgan Hill, CA) as EX1510 resin, which was used as received, without further purification. The liquid phase organometallic-based catalyst, EX1510-B, was supplied with the resin. For the catalyzed systems, it was used at the manufacturer's suggested loading of 3 phr (parts per hundred resin). The epoxy group terminated silane, 3-Glycidyloxypropyl trimethoxysilane (GPS), was purchased from Sigma-Aldrich Inc. (St. Louis, MO) and used as received. Tetrahydrofuran (THF) was purchased from Fisher Scientific Inc. (Pittsburgh, PA) and distilled from sodium and benzophenone before use. Spherical alumina nanoparticles were supplied by Nanophase Technologies, Inc. (Romeoville, IL) as NanoTek aluminum oxide, which is γ -phase alumina (density of 3.6 g/cm³) with an average particle size (diameter) of 40 nm and a specific surface area of 44 m²/g. Before use, the nanoparticles were dried *in vacuo* at 120 °C for 24 hr.

4.3.2 Specimen preparation

Alumina nanoparticles (4 g) and glassware were dried in a convection oven at 150 °C for 4 hr. After drying, the nanoparticles were transferred into a 250 mL flask containing

150 mL of fresh distilled THF and a magnetic stirring bar, and sealed with rubber stopper. Next, the alumina nanoparticles were dispersed in THF for 2 hr in a sonicated water bath. A stoichiometric amount of silane was determined from the specific surface area of alumina, the areal density of hydroxyl groups on the alumina surface ($4\mu\text{mol}/\text{m}^2$) [16,17], and the molecular weight of the silane. An excess of GPS, 0.3 mL, (more than 10 times of the stoichiometric amount) was used to ensure complete coverage of the nanoparticles. Finally, the mixture was stirred and refluxed at 90 °C for two days under dry nitrogen. The functionalized alumina nanoparticles were then separated from the reaction mixture by centrifuging for five min at 3000 rpm. The supernatant THF, which contained excess silane, was decanted, and the nanoparticles were dispersed into fresh THF. The disperse-centrifuge wash cycle was repeated for three times to ensure the excess silane was removed. The functionalized alumina nanoparticles were dried *in vacuo* at 120 °C for 24 hr and stored in a desiccator.

To prepare the suspension of BECy/alumina, the dried alumina nanoparticles were first weighed in a vial, and then BECy monomer was added according to the desired nanoparticle loadings of 0.5, 2, 5 and 10 wt.%. The total amount of the mixture for each composition was c.a. 10 g. The mixture was sealed with a lid, and then subjected to ultrasonic treatment in a water bath for 2 hr. To further disperse the particles, the suspension was processed using a Fisher Model 100 Sonic Dismembrator (Fisher Scientific Inc., Pittsburgh, PA) with 3.2 mm diameter probe tip for a total of 30 s at a frequency of 23 kHz. The power output ranged between 16 and 18 W during sonication. For each composition, a portion (1 g) of the dispersed suspension was set aside for rheological evaluation. For the remaining materials (9 g), catalyst was added to the suspension at a level of 3 phr and mixed with a magnetic stir bar. Again, a portion (1 g) of the catalyzed suspension was immediately sealed and stored in a freezer at -13 °C for subsequent rheokinetic testing.

The remaining catalyzed suspensions, approximately 8 g for each composition, were poured into high-temperature silicone rubber molds ($27\times 48\times 8\text{ mm}^3$) and degassed at room temperature for 1 hr *in vacuo* at 23.4 mmHg. Then, the suspensions were cured in a programmable convection oven with the following cure schedule: (1) heat from room temperature to 180 °C at a rate of 1 °C/min; (2) isothermally cure at 180 °C for 2 hr; (3) heat

to 250 °C at 1 °C/min and isothermally cure for another 2 hr; (4) cool down to room temperature at a cooling rate of about 2 °C/min. The cured samples for dynamic mechanical analysis (DMA) were machined from the solid block of material using a diamond blade saw (TechCut 5TM Precision Sectioning Machine with Diamond Wafering Blade, Allied High Tech Products, Inc., Rancho Dominguez, CA). Samples were machined to 30×5×0.5 mm and stored in a desiccator. The neat BECy control samples without any nanoparticles were also prepared in the same manner as above.

4.3.3 Experimental procedure

Nanoparticles were characterized by a Fourier transform infrared (FTIR) spectrometer (VERTEX 70, Bruker Inc., Billerica, MA). The nanoparticles were mixed with KBr powder at an approximate ratio of 1:100, ground and compressed into a pellet. FTIR spectra were recorded in transmission mode with a spectrum range from 4000-400 cm⁻¹ at resolution of 4 cm⁻¹ under vacuum.

The amount of silanes immobilized on the surface of the alumina nanoparticles was determined by thermogravimetric analysis (TG, model Q50 TA Instruments, Inc., New Castle, DE). About 10 mg of nanoparticles were placed in a platinum pan, and heated at a rate of 20 °C/min from 25 °C to 800 °C under dry air purge at 60 mL/min.

Uncatalyzed BECy/alumina nanoparticle suspensions were tested for rheological properties using a TA Instruments AR2000ex stress-controlled rheometer with a Peltier temperature control stage, utilizing a cone/plate geometry (45 mm diameter cone with 1° angle). A sample volume of 0.30 mL was transferred to the rheometer using a 1-mL syringe. A continuous flow test was conducted for each sample from shear rates of 0.1 to 100 s⁻¹ (5 points per decade) at 25 °C.

Rheokinetic tests (oscillatory) for catalyzed suspensions were conducted at isotherms of 110, 130, 140 and 150 °C, using AR2000ex rheometer in stress control mode at an amplitude of 1000 Pa and 1 Hz, with 25-mm diameter disposable parallel plates and a 0.5 mm gap. The suspension (0.25 mL) was applied to the geometry using a 1-mL syringe. The sample was held for two minutes to reach equilibrium temperature before commencing the measurements. The rheokinetic tests for the uncatalyzed suspensions were conducted in the same manner as mentioned above, but with longer holding periods before the oscillatory

experiment started, 10 hr and 20 hr for 10 and 5 wt.% BECy/alumina suspensions, respectively.

The thermal-mechanical properties of cured BECy/alumina nanocomposites were evaluated by a TA Instruments DMA Q800 (dynamic mechanical analysis) equipped with a liquid nitrogen cooling accessory (GCA). All samples were tested with a tension film fixture in a temperature sweep mode from 30 to 330 °C at a heating rate of 3 °C/min. A constant oscillating strain of 0.025% at 1 Hz was applied throughout the test, with a static load tracking at 125% of the dynamic force.

The BECy nanocomposites for transmission electron microscope (TEM) were prepared using a Leica ultracut microtome. Multiple sections with the thickness of 100 nm were cut and floated onto a 300 mesh copper grid with a thin carbon support film. The samples were obtained on a JEOL (Tokyo, Japan) 1200EX scanning/transmission electron microscope (STEM) at an accelerating voltage of 80 kV.

4.4 Results and discussion

4.4.1 Functionalization of alumina nanoparticles

Surface functionalization of nanoparticles is utilized to improve dispersion of particles in the BECy monomer and to strengthen the interfacial bonds between the particles and the polymer matrix. 3-Glycidyloxypropyl trimethoxysilane (GPS) was immobilized on the surface of alumina nanoparticles, and Figure 4-2 shows the functionalization reaction scheme. GPS contains a terminal epoxy groups which can covalent bond with the BECy network during cure.

Figure 4-2 Reaction scheme of functionalization reaction of alumina nanoparticles with GPS silane.

Gravimetric thermograms of dried alumina-GPS (Al-GPS) and bare alumina nanoparticles (Al) were compared to determine the amount of silane immobilized on the surface (see Figure 4-3). For the Al nanoparticles, the weight loss is due to desorption of physically adsorbed gas and water, and dehydroxylation of adjacent $-OH$ groups on the surface. For the Al-GPS nanoparticles, the mass loss due to evaporation of the physically adsorbed water is less than the bare alumina (below $200^{\circ}C$), presumably because the physically adsorbed water and surface hydroxyl groups reacted with GPS during the functionalization reaction in dry THF [13]. Above $200^{\circ}C$, the weight loss of Al-GPS nanoparticles is attributed to the condensation of adjacent GPS on the surface (Figure 4-2), and decomposition of GPS, which is indicated by a color change from white to grey after the TG test. By comparing the mass loss of bare alumina and Al-GPS nanoparticles, the graft density of GPS was estimated to be 2 molecule/ nm^2 . Since the surface density of hydroxyl group for alumina was reported to be $4-7 \mu mol/m^2$ for Al_2O_3 [16,17] (2.5-4 molecule/ nm^2), the estimated graft density of GPS is close to the maximum value which can be obtained to accommodate the cross-section of the GPS molecule.

Figure 4-3 TG test results of bare and GPS functionalized alumina nanoparticles.

Figure 4-4 shows the FTIR spectra of bare alumina and Al-GPS. Both samples show large -OH stretching bands at $\sim 3500\text{ cm}^{-1}$. The peak at 1630 cm^{-1} is assigned as inter- or intra-nanoparticle surface hydrogen bonding [18], and the sharp peak at 1380 cm^{-1} is not common but Ref.[10] suggests that this peak is due to physically adsorbed water. The spectrum of Al-GPS shows the alkyl C-H stretching at 2929 and 2868 cm^{-1} (which are not present in the spectrum of bare alumina), the Si- CH_2 stretching at 1280 cm^{-1} , and the Si-O at 1097 cm^{-1} as a shoulder. Since the Al-GPS was washed with fresh THF and is absent of excess free GPS, it must be successfully immobilized on the surface of the alumina nanoparticles.

Figure 4-4 FTIR spectra of bare and GPS functionalized alumina nanoparticles.

4.4.2 Suspension rheology

Figure 4-5 shows the plot of viscosity vs. shear rate for uncatalyzed BECy/alumina suspensions (0, 0.5, 2 and 10 wt.%) at $25\text{ }^{\circ}\text{C}$. In our previous work, BECy/fumed silica suspensions showed pseudo-plastic or “shear thinning” behavior, while the neat BECy monomer exhibited near Newtonian flow [19]. For shear rates between 0.1 and 20 s^{-1} , all BECy/alumina suspensions show similar “shear thinning” behavior. However, such “shear thinning” behavior is much less pronounced than in the BECy/fumed silica suspensions. The primary mechanism for the pseudo-plastic or “shear thinning” behavior is well known, and is attributed to the formation of hydrogen bonds between hydroxyl groups of neighboring

particles [20]. The hydrogen bonds form under low shear and are broken under high applied shear. Additionally, physical entanglement and agglomeration of nanoparticles also contribute to this phenomenon. Consequently, “shear thinning” behavior is more pronounced at higher solid loadings, in which the distance between particles is reduced and particles are more likely to agglomerate [19]. Unlike fumed silica, which yields mostly aggregates, the alumina nanoparticles are mostly in the form of individual particles with a broad size distribution. Hence, the alumina exhibits less physical entanglement and agglomeration in BECy at similar loading level than the silica, and the “shear thinning” behavior of the BECy/alumina suspensions is much less pronounced. With addition of alumina nanoparticles, the viscosities of the suspensions increase. Compared to neat BECy monomer, the viscosity of 10 wt.% BECy/alumina suspensions increases two fold, but is still much lower than other high temperature resins.

Figure 4-5 Viscosity vs. shear rate for bare alumina suspensions and neat BECy monomer.

Einstein’s equation for the viscosity of a suspension of rigid spherical particles reads [21]:

$$\eta = \eta_m(1 + k_E\phi_f) \quad (4-1)$$

where, η and η_m are the viscosity of the suspension, and suspending matrix liquid, respectively, and ϕ_f is the volume fraction of the filler. If the particles are rigid spheres that

agglomerate to give strong clusters which are roughly spherical in shape, the Einstein coefficient k_E is given by:

$$k_E = \frac{2.5(V_S + V_L)}{V_S} = 2.5 + \frac{V_L}{V_S} \quad (4-2)$$

where, V_S is the actual volume of the spheres in a typical agglomerate, and V_L is the volume of the matrix fluid that is entrapped within the agglomerate or on its surface. Thus, agglomerations increase the Einstein coefficient, k_E , and, hence, increase the suspension viscosity. The Einstein equation only holds for rigid particles in extremely low concentrations.

Many modifications to Einstein's equation have been proposed to express the viscosity of suspensions, with the Roscoe and Mooney equations being among the most useful. The Roscoe equation is expressed as:

$$\eta = \eta_m \left(1 - \frac{\phi_f}{\phi_{max}}\right)^{-2.5} \quad (4-3)$$

where, ϕ_{max} is the maximum volume fraction possible. The value of ϕ_{max} is the critical packing density which depends on the packing geometry and can range from 0.37, for random close packing (agglomerated), to 0.74, for hexagonal close packing.

The Mooney equation holds for the viscosity of many kinds of suspensions over the entire concentration range. The Mooney equation is expressed as:

$$\eta = \eta_m \exp \left(\frac{k_E \phi_f}{1 - \phi_f / \phi_{max}} \right) \quad (4-4)$$

For suspensions of polydisperse particles, the Mooney equation can describe the results well, but only if completely unrealistic parameters are used to fit the experimental data.

The viscosity at a shear rate of 100 s^{-1} of BECy/alumina suspensions for each composition is shown in Figure 4-6. The lines represent the Roscoe and Mooney models with an assumption of either random close packing ($\phi_{max} = 0.37$) or random loose packing of nonagglomerated spheres ($\phi_{max} = 0.601$) [21]. The experimental viscosity of BECy/alumina suspensions is much higher than that predicted by the Roscoe model (Eq. (4-3)). The best fit is given by the Mooney model (Eq. (4-4)) with ϕ_{max} of 0.37 and k_E of 16.4. As mentioned before, the Einstein coefficient k_E is related to the level of agglomeration, with larger values of k_E corresponding to higher level of agglomeration. Additionally, the strong interactions between the alumina surface and the BECy monomer contribute to the increased viscosity.

BECy monomer contains polar cyanate groups, which may form hydrogen bonds with the hydroxyl groups on the alumina surface [22]. According to Eq. (4-2), a large k_E value of suggests that significant liquid is entrapped within the agglomerates or on its surface, which may also be attributed to strong interfacial connections between the BECy monomer and the alumina nanoparticles.

Figure 4-6 Viscosity at a shear rate of 100 s^{-1} vs. volume fraction of nanoparticles. Lines represent the different theoretical models.

4.4.3 TEM micrographs

The degree of dispersion is one of the most critical parameters in determining whether nanocomposites are successfully processed and is often evaluated by transmission electron microscopy (TEM). The cured BECy/alumina nanocomposites were microtomed into thin sections for TEM observation. TEM micrographs of the BECy nanocomposites with 0.5 and 10 wt.% are shown in Figure 4-7. The as-received alumina has an average size of 40 nm in diameter with a broad size distribution, ranging from several nm to 150 nm. Obviously, the smaller alumina particles form agglomerates more easily, affecting the rheology and thermal-mechanical properties of the BECy as discussed before. Overall, the alumina nanoparticles, especially the larger particles, are well dispersed in BECy for all

solids loading levels studied in this work and the size of any agglomerates is mostly less than 200 nm.

Figure 4-7 TEM micrographs (at the same scale) of BECy/Alumina nanocomposites: (a) 0.5 wt.% and (b) 10 wt.%.

4.4.4 Rheokinetic evaluation

Dynamic oscillatory rheology was used to monitor changes in rheological properties during isothermal cure. Figure 4-8 shows dynamic rheological properties of catalyzed

BECy/alumina suspensions (10 wt.%) at isothermal temperatures of 110, 130, 140 and 150 °C. Gelation is associated with a dramatic increase in viscosity [23]. The gelation point was taken where the storage shear modulus, G' , is equal to the loss shear modulus, G'' , ($G' \times G''$ crossover), which is often taken as the time when the monomer first forms a percolating cross-linked network and the macroscopic viscoelastic response of the material is dominated by its elastic behavior [24,25,26]. As shown in Figure 4-8, as isothermal cure temperature is increased from 110 to 150 °C, the time to reach gelation (gel time) is reduced dramatically.

Figure 4-8 Rheological properties of BECy/alumina (10 wt.%) nanocomposites during isothermal cure at different temperatures.

The apparent activation energy for gelation can be calculated from the gel time (t_{gel}) at different temperatures. Since the network structure is a unique function of conversion, α , the conversion at gel point may be considered constant and independent of isothermal cure temperature [27], and the gel time and cure temperature can be assumed to follow an Arrhenius relationship:

$$\ln t_{gel} = \ln A' + \frac{E_a}{RT} \quad (4-5)$$

where, A' is a constant related to the reaction model, R is the universal gas constant, and E_a is the apparent activation energy for gelation. Therefore, a plot of $\ln t_{gel}$ vs. $1/T$ (Figure 4-9) gives a slope proportional to the activation energy. The E_a for catalyzed BECy/alumina

(10 wt.%) nanocomposite is calculated as 90.0 kJ/mol, which is much higher than the value for the activation energy for the cure of the same system (60.3 kJ/mol) obtained by using dynamic scanning calorimetry (DSC) [15]. As discussed in the previous section, the alumina nanoparticles have a significant effect on the rheological properties of the BECy/alumina suspension. The dynamic oscillatory experiments not only monitor the formation of the cross-linked network, but also the effect of the alumina nanoparticles on the suspension.

Figure 4-9 Arrhenius plot of $\ln t_{gel}$ vs. $1/T$ for 10 wt.% alumina in BECy. Symbol: experimental data. Solid line: best linear fit line.

The catalyzed BECy/alumina suspensions containing, 2 and 5 wt.% alumina, were also tested at 130 °C. The gel time does not show any significant change with the loading of alumina nanoparticles. To further evaluate the effect of alumina on BECy curing under dynamic oscillatory conditions, additional BECy/alumina suspensions were prepared without catalyst and tested at 130 °C. The results are illustrated in Figure 4-10. The gel time is reduced from 23.5 to 13.8 hr, for suspensions containing 5 and 10 wt.% alumina, respectively. As a control sample, uncatalyzed neat BECy was isothermally cured at 130 °C for a week. The viscosity of neat BECy increased slightly but never gelled. The catalytic effect of alumina is believed to be due to the surface hydroxyl groups and physically adsorbed water, which can act as a catalyst to initiate the cross-linking of cyanate ester [2].

The catalytic effect of alumina nanoparticles are evaluated and discussed in detail in a separate paper [15].

Figure 4-10 Rheological properties of 5 wt.% and 10 wt.% BECy/alumina nanocomposites (without catalyst) during isothermal cure at 130 °C.

4.4.5 Dynamic mechanical properties

In dynamic mechanical analysis, a sinusoidal force is applied to a sample and the material's response to that force is recorded. The storage modulus, E' , represents the material's ability elastically store energy. The loss modulus, E'' , is proportional to dissipative and viscous losses that occur in the materials under cyclic loading. The viscoelastic behavior of the material causes the deformation to lag behind the applied force by a phase angle δ , which is used to define the damping as:

$$\tan \delta = E''/E' \quad (4-6)$$

A typical DMA curves is shown in Figure 4-11a for the BECy nanocomposite with 10 wt.% alumina. The glass transition temperature (T_g) can be determined from the onset of the storage modulus, E' , drop, the peak of the loss modulus, E'' , or the peak of $\tan \delta$. In this study, the peak of E'' is used for assigning T_g values.

Figure 4-11 (a) Typical DMA curves for BECy/Al-GPS nanocomposites, 10 wt.%; (b) Storage modulus vs. temperature for BECy/Al-GPS nanocomposites with different compositions.

The storage modulus vs. temperature for BECy/Al-GPS nanocomposites is shown in Figure 4-11b. With an increase in Al-GPS nanoparticle loading, the storage modulus increases in the glassy region, and slightly increases in the rubbery region. For the BECy nanocomposites with bare alumina nanoparticles, there is a similar increase in storage modulus with increasing nanoparticle loading (not shown).

Figure 4-12 Summary of DMA test results: (a) storage modulus E' at 35 °C vs. nanoparticles loading; (b) glass transition temperature vs. nanoparticles loading. The dash lines indicate the corresponding values of neat BECy.

Figure 4-12a shows the storage modulus at 35 °C as a function of nanoparticle loading. As expected, the largest increase in modulus is for the samples at the highest loading levels (10 wt.%). At 10 wt.% nanoparticle loading, the BECy/Al-GPS nanocomposite has a larger storage modulus than the corresponding nanocomposite reinforced with bare alumina. However, Al-GPS does not show a significant difference from bare alumina nanoparticles in the improvement of storage modulus for BECy resin.

The elastic modulus of the composites is often estimated from various theoretical models. Two simple models, isostress and isostrain models, give the lower and higher bound modulus, respectively. The isostress model, sometimes called the inverse rule of mixtures, assumes that the matrix and filler are stressed equally, giving a lower bound composite modulus E_c , as:

$$E_c = \left(\frac{\phi_f}{E_f} + \frac{\phi_m}{E_m} \right)^{-1} \quad (4-7)$$

where, E_f is the modulus of the filler (393 GPa for alumina¹), E_m is the modulus of the matrix (2.5 GPa for neat BECy), ϕ_f and ϕ_m are the volume fractions of the filler and the matrix, respectively. Assuming the strain is constant in each of the phases, an isostrain model, also known as the rule of mixtures, gives the upper bound for the composite modulus as:

$$E_c = E_f \phi_f + E_m \phi_m \quad (4-8)$$

The well-known Halpin-Tsai equation is more suitable for prediction of composite modulus because it includes a factor ζ to describe the influence of the geometry of the fillers. For spherical particles, the factor ζ is equal to 2. The Halpin-Tsai equation is expressed as:

$$E_c = E_m \left(\frac{1 + \zeta \eta \phi_f}{1 - \eta \phi_f} \right) \quad (4-9)$$

where,

$$\eta = \frac{E_f/E_m - 1}{E_f/E_m + \zeta} \quad (4-10)$$

For polymers containing nearly spherical particles, with each phase having an distinct modulus, the Kerner equation can be used to calculate the modulus of a composite [21]. Lewis and Nielson present the Kerner equation in the following generalized form.

$$E_c = E_m \left(\frac{1 + AB \phi_f}{1 - B \psi \phi_f} \right) \quad (4-11)$$

where, A is a constant related to the filler geometry and the Poisson's ratio, ν , of the matrix:

$$A = \frac{7 - 5\nu}{8 - 10\nu} \quad (4-12)$$

The constant B has a similar form to η in the Halpin-Tsai equation:

$$B = \frac{E_f/E_m - 1}{E_f/E_m + A} \quad (4-13)$$

Its value is equal to 1 for very large ratios of E_f/E_m . The factor ψ depends on the maximum packing fraction ϕ_{max} , as defined above in the discussion of suspension rheology. If the

modulus of the filler is much larger than that of the polymer matrix, and if the Einstein coefficient is much larger than 1, the factor ψ is given by:

$$\psi = 1 + \frac{\phi_m}{\phi_{max}} [\phi_{max}\phi_f + (1 - \phi_{max})\phi_m] \quad (4-14)$$

The experimentally measured storage moduli of BECy/alumina and BECy/Al-GPS nanocomposites are plotted with these various models in Figure 4-13. For the Kerner model, a matrix Poisson's ratio of 0.35 which results in a value of 1.167 for A . For all volume fractions, the isostress, Halpin-Tsai and Kerner equations underestimate the modulus of the nanocomposites. For traditional composites reinforced with conventional fillers, a dispersed particle is in the range of micrometers, and the interfacial region is not often taken into account [28]. For the nano-size fillers, the specific surface area is very large, causing the volume fraction of the interfacial region to be significant, comparable with or even larger than that of the dispersed phase. Correspondingly, the mobility of polymer chains nearby the filler is restricted. Therefore, traditional micromechanical models may under-predict for the modulus for nanocomposites because they fail to account for the significant interphase region. Since the epoxy groups in GPS are immobilized on the surface of the alumina, it can react with BECy to form covalent bonds with the polymer network. In a similar way, surface hydroxyl groups (on the bare alumina) have also been shown to form covalent bonds with curing cyanate ester resins [2]. The polymer chains near the interface are more confined and restricted, which results in a higher storage modulus than would be expected.

Figure 4-12b shows the glass transition temperatures for the BECy/alumina and BECy/Al-GPS nanocomposites. The addition of alumina nanoparticles, bare or functionalized, decreases the T_g of the BECy nanocomposites. This behavior was also reported for PMMA/alumina nanoparticle composites, where the authors suggested that the nanoparticles actually increase the polymer mobility in the nanocomposites [29]. If the nanoparticles are not sufficiently wet by the polymer it can act like a nanosize voids in the polymer matrix and decrease the T_g due to the increased free surface. However, according to the previous discussion, the increase of storage modulus of BECy nanocomposites over tradition micromechanical models is due to the restricted mobility of the polymer chains. The decrease of T_g must be caused by other reasons.

Figure 4-13 Storage modulus at 35 °C vs. volume fraction of nanoparticles. Lines represent the fittings from different models.

First, our parallel study on alumina nanoparticles suggested that the alumina nanoparticles contained trace amounts of physically adsorbed water on the surface and easy to absorb moisture from the environment after drying [15]. The water on the surface of the alumina nanoparticles may act as a contaminant during cure by chemically obstructing the formation of triazine rings in the network structure and reducing the polymer's overall crosslink density. As a comparison, fumed silica contains much less physically adsorbed water, as a result the T_g of BECy/silica nanocomposites remains nearly constant with the addition of silica nanoparticles [14]. The addition of Al-GPS also decreases the T_g of the nanocomposites. However, T_g of BECy/Al-GPS nanocomposites is slightly higher than that of the BECy/bare alumina nanocomposites at similar loading levels. The GPS groups on the surface make the alumina nanoparticles more compatible with the BECy matrix, and the epoxy groups on the immobilized silane may react with the BECy during cure. A strong interfacial bond between the nanoparticles and BECy matrix is formed, contributing to a higher T_g than the corresponding bare alumina nanocomposites. Additionally, the TG results (Figure 4-3) indicated that Al-GPS nanoparticles contained less physically absorbed water

than bare alumina. As a result, the mobility of polymer is more limited and shows a slower reduction in T_g with filler loading.

Second, the nanoparticles may interrupt the formation of the cross-linked network during the curing process. The addition of nanoparticles actually decreases the cross-linking density, which results a decrease in T_g of BECy nanocomposites. In neat resins, the cross-linking density can be estimated from the storage modulus in the rubbery plateau, with storage modulus being proportional to the crosslink density. However, the relationship between cross-linking density and loading of nanoparticles is still unclear, it is likely a combination of reinforcement effects from the filler and reduction of crosslink density. Additionally, the $\tan \delta$ curves (damping) for both BECy/Al and BECy/Al-GPS nanocomposites show an increase with nanoparticle loading (not shown here). The increase of composite damping is usually, but not always, related to the presence of new damping mechanisms, such as changes in polymer conformation and morphology introduced by fillers [30], which may also contribute to the decrease of the BECy nanocomposite T_g .

4.5 Conclusions

Bare alumina nanoparticles were successfully functionalized with GPS. The BECy suspensions containing bare alumina show “shear thinning” behavior, which was more pronounced for high alumina nanoparticle loadings. With addition of alumina nanoparticles, the viscosity of the BECy suspensions is increased. Comparison of the experimental data and viscosity models suggests that the increase of viscosity is influenced by the presence of agglomerations of alumina and hydrogen bonding between agglomerates and the polar BECy monomer. However, TEM micrographs showed that alumina nanoparticles were relatively well dispersed in the BECy matrix, though a small number of alumina nanoparticles formed agglomerates with diameter measuring less than 200 nm. Rheokinetic evaluation of the catalyzed BECy/alumina suspensions gave an activation energy of gelation of 90 kJ/mol. Rheokinetic results of uncatalyzed samples showed that alumina nanoparticles had a catalytic effect on the cure of BECy, and increasing the alumina content reduces the gel time. Both Al and Al-GPS nanoparticles increased the storage modulus of BECy nanocomposites. Isostress, isostrain, Halpin-Tsai and Kerner models were compared to the storage moduli of the

nanocomposites. The results suggest that the presence of a large interphase region with properties different from the bulk matrix. With the addition of the nanoparticles, the T_g decreased. The BECy/Al-GPS showed less reduction in T_g than the bare Al systems which is attributed to the stronger interfacial bonding between the Al-GPS nanoparticles with the BECy matrix and the lower quantities of adsorbed water on the nanoparticle surfaces.

4.6 References

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CHAPTER 5: CREEP BEHAVIOR OF BISPHENOL E CYANATE ESTER/ALUMINA NANOCOMPOSITES

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5.1 Abstract

The creep behavior of neat bisphenol E cyanate ester (BECy) and a BECy/alumina nanocomposite was studied through tensile creep testing by dynamic mechanical analysis (DMA). The tensile creep compliance was measured at isothermal conditions between 190 and 320 °C at 10 °C intervals. The long-term creep behavior in a high temperature environment was predicted by time-temperature superposition (TTS). The frequency dependent dynamic properties of neat BECy and the BECy/alumina nanocomposite were also evaluated at the same isothermal conditions as the creep experiments. Based on the frequency-time transformation method, the frequency dependent dynamic data was transformed into time-domain creep compliance data. The transformed creep compliance data shows much lower creep compliance than experimental tensile creep data at temperatures above the glass transition. However, the transformed creep compliance data is useful for the prediction of long-term creep behavior because the frequency dependent dynamic test eliminates the possible physical and/or chemical aging of the material due to the aggressive testing conditions.

5.2 Introduction

Unlike other high-temperature thermosetting polymers, such as bismaleimides, polyimides, and other cyanate esters, the bisphenol E cyanate ester, bis(4-cyanatophenyl)-1,1-ethane (BECy), is a unique thermoset forming monomer because it is a super-cooled

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liquid at room temperature with an extremely low viscosity, 0.09-0.12 Pa s [1]. As shown in Figure 5-1, the BECy monomer forms into a cross-linked network through the formation of triazine rings at the intersection of three cyanate groups. The low viscosity of the monomer and the excellent mechanical properties of the cured polymer with a high glass transition temperature ($\sim 270^\circ\text{C}$) make BECy an excellent candidate for many applications [2-4]. We are trying to develop a repair resin system based on BECy for the resin-injection repair of high-temperature polymer composites. In this application, the processing characteristics and mechanical properties at elevated temperatures are the most crucial factors.

Figure 5-1 Chemical structure of BECy and cyclotrimerization reaction scheme.

To alter the processing characteristics of the prepolymer and the thermal-mechanical properties of the cured product, the polymers are often modified with fillers. In recent years, nano-size fillers, such as nanoclay, nanotubes, and ceramic nanoparticles, have generated enormous interest in science and engineering. Polymers reinforced with nano-fillers often show improvements in mechanical and barrier properties, flame retardancy, and dimensional stability [5,6]. Oxide nanoparticles, such as silica and alumina, are often used as nano-fillers with a broad range of polymers because of their low cost and ability to be functionalized. In our previous study, both silica and alumina were used as fillers to tailor the properties of BECy. The BECy/silica nanocomposites containing 27 vol.% fumed silica (with an average diameter of 40 nm) showed a 75% increase in storage modulus in the glassy region [4]. The addition of alumina nanoparticles showed similar improvements in storage modulus;

however, the alumina had a deleterious effect on the glass transition temperature, which decreased monotonically with alumina loading [7]. Subsequently, the alumina was functionalized with 3-Glycidyloxypropyl trimethoxysilane (GPS) to improve the nanoparticle dispersion and compatibility with the polymer matrix. The epoxide moiety on the GPS can react with the BECy resin during cure and form strong covalent bonds at the BECy/alumina interface (see Figure 5-2). These BECy/GPS functionalized alumina (Al-GPS) nanocomposites show an even higher increase in storage modulus with filler loading, but still exhibit a decrease in T_g compared to the neat BECy. However, the T_g suppression is not as severe as it is with composites containing the unfunctionalized alumina [8]. Figure 5-3 shows the storage modulus and damping behavior versus temperature for the neat BECy and the BECy/Al-GPS (10 wt.%) composite, illustrating the higher glassy modulus but lower glass transition temperature for the reinforced system.

Figure 5-2 Functionalization of alumina nanoparticles with GPS and formation of covalent bonds with cross-linked BECy network.

BECy and BECy matrix composites have high glass transition temperatures and show excellent mechanical properties in short term testing. In the application of resin-injection repair of high-temperature composites, the long term durability of cured repair agents under constant load at high temperature is crucially important. When subjected to external loads, polymer composites are subject to creep deformation, a slow and continuous increase of strain. The slow deformation of the composites may lead to catastrophic failure after long times at elevated temperatures if adequate design margins are not used.

Figure 5-3 DMA data for neat BECy and BECy/Al-GPS composite. Frequency: 1Hz.

In this work, the long-term creep behavior of neat BECy and BECy/Al-GPS nanocomposites is evaluated by short-term tensile creep experiments at various elevated temperature isotherms. Creep compliance master curves are generated using both manual shift factors and shift factors calculated from the activation energy of the glass transition relaxation. The short term creep behaviors are fitted by the Burger and the discrete retardation spectrum models. The fitting parameters obtained from these models are used to understand the creep mechanism and predict long term performance. Additionally, dynamic frequency sweep experiments are performed at the same isothermal temperatures to obtain frequency-domain dynamic data which is then transformed into time-domain creep compliance data using an inverse fast Fourier transform technique.

5.2.1 Theory

In a creep experiment, stress, σ , is maintained at a constant value and the time dependence of the strain, $\varepsilon(t)$, is measured. Generally, polymers are viscoelastic, or time dependent: their deformation behavior is a combination of viscous and elastic responses to external forces. In order to compare creep data at different loads, the creep strain is normalized with respect to the applied stress as the creep compliance, $J(t)$:

$$J(t) = \frac{\varepsilon(t)}{\sigma} \quad (5-1)$$

Numerous creep models have been proposed and applied to describe the creep behavior of viscoelastic materials [9-11]. The simplest models for stress relaxation and creep are the Maxwell and Voigt models, in which a dashpot (with viscosity of η) and a spring (with modulus of E) are arranged in series and parallel, respectively. By combining Maxwell and Voigt models in a series, a new four-element Burger model is generated (Figure 5-4), where the total strain is given by

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (5-2)$$

$$\varepsilon = \frac{\sigma}{E_1} + \frac{\sigma}{E_2} (1 - e^{-t/\tau}) + \frac{\sigma}{\eta_1} t \quad (5-3)$$

where σ is the applied stress, t is the creep time and the retardation time τ is defined by

$$\tau = \frac{\eta_2}{E_2} \quad (5-4)$$

By normalizing with respect to applied stress, the creep compliance can be expressed as:

$$J = J_1 + J_2(1 - e^{-t/\tau}) + \frac{t}{\eta_1} \quad (5-5)$$

Figure 5-4 The 4-element Burger model used to represent viscoelastic behavior.

The Burger model can be expanded to a more general case consisting of n number of Maxwell and Voigt models. As a result, the complex creep behavior of real polymers can be characterized by the generalized discrete retardation spectra [12]:

$$J(t) = J_0 + \frac{t}{\eta_0} + \sum_{i=1}^n J(i) (1 - e^{-t/\tau_i}) \quad (5-6)$$

where, J_0 and η_0 is the initial creep compliance and viscosity, respectively.

5.2.2 Time-temperature superposition principle (TTS)

Structural materials are often designed to have long lifetimes, often tens of years. It is impractical in most cases to conduct long-time creep testing for the entire service lifetime. Therefore, it is necessary to use accelerated procedures to characterize the viscoelastic behavior of composites. Among these procedures, the time-temperature superposition principle is widely accepted and used in creep testing of composites at elevated temperatures to determine their long term creep behavior [13]. By the principle of TTS, the effect of elevated temperature is assumed to be equivalent to stretching the real time of the creep response by a certain shift factor a_T . The creep compliance is assumed to be a function of time and temperature:

$$J = J(t, T) \quad (5-7)$$

and temperature dependent shift factor, a_T , is given by

$$\log a_T = \log \frac{t}{t_r} \quad (5-8)$$

where, t is the actual test time and t_r is the reduced time, which is the expanded time scale for the creep master curve at an isothermal reference temperature.

Through this method, short term creep tests at a range of temperatures can be used to generate a transient long term creep compliance master curve. Since the master curve spans a much longer time than the individual short term curves, the long term creep behavior of materials can be predicted at any reference temperature.

5.2.3 Frequency-time transformation

Tensile creep testing at elevated temperatures makes the prediction of long term creep behavior of materials possible in a much short time. However, the aggressive environmental conditions, such as testing temperatures above T_g , may cause physical and/or chemical aging in the materials [13]. Therefore, other alternative methods for characterizing the long term performance of materials have been developed. One of them is frequency-time transformation [14-16]. By using inverse fast Fourier transformation (IFFT) and numerical

integration, frequency-domain dynamic data can be transformed into time-domain creep compliance data:

$$J(t) = J_0 + \int_0^t F^{-1}[J^*(f)]dt \quad (5-9)$$

where, F^{-1} is the inverse Fourier transform, $J^*(f)$ is the frequency domain complex compliance:

$$J^*(f) = 1/E^*(f) \quad (5-10)$$

and

$$E^*(f) = E'(f) + iE''(f) \quad (5-11)$$

where, E' and E'' are storage and loss modules, respectively.

5.3 Experimental

5.3.1 Materials

BECy monomer was supplied by BRYTE technologies, Inc. (Morgan Hill, CA) as EX1510 resin, which was used as received without further purification. The liquid phase organometallic-based polymerization catalyst (BRYTE technologies, Inc.) was supplied with the resin. For the catalyzed systems, it was used at the manufacturer's suggested loading of 3 phr (parts per hundred resin). 3-Glycidyloxypropyl trimethoxysilane (GPS) was purchased from Sigma-Aldrich Inc. (St. Louis, MO) and used as received. Tetrahydrofuran (THF) was purchased from Fisher Scientific Inc. It was distilled from sodium and benzophenone before use. Alumina nanoparticles were supplied by Nanophase Technologies, Inc. (Romeoville, IL) as NanoTek aluminum oxide, which is γ -phase alumina with an average particle size (diameter) of 40 nm and a specific surface area of 44 m²/g. Before use, the nanoparticles were dried *in vacuo* at 120 °C for 24 hr.

The functionalization of alumina with GPS is described in detail elsewhere [8]. In brief, alumina nanoparticles were dispersed into dry THF by ultrasonication and then GPS was added into the suspension. The suspension was refluxing at 90 °C for 2 days before the functionalized alumina nanoparticles were isolated by centrifuge. After several washing cycles, dispersion in fresh THF by ultrasonication, and then isolation centrifuge, the GPS functionalized alumina nanoparticles (Al-GPS) were again dried *in vacuo* at 120 °C for 24 hr. The Al-GPS were characterized by Fourier transform infrared (FTIR) spectrometry and

thermogravimetric analysis (TG). The grafting density was estimated from TG as 2 GPS molecules/nm².

5.3.2 Specimen preparation

The dried nanoparticles were first weighed in a vial. Then, BECy monomer was added according to the desired nanoparticle loading (10 wt.%). The total weight of the mixture was c.a. 8 g. The vial containing the mixture of BECy and nanoparticles was sealed with a lid, and then subjected to ultrasonic treatment in a water bath for two hr. To further disperse the particles, the mixture was sonicated with a high intensity ultrasonic tip (Fisher Model 100 Sonic Dismembrator, Fisher Scientific Inc., Pittsburgh, PA) intermittently for a total of 30 seconds to prevent excessive temperature rise. The power output ranged between 16 and 18 W at a frequency of 23 kHz during sonication. After the BECy/nanoparticle suspension was well dispersed, the catalyst was added at a loading of 3 phr and mixed with a with magnetic stir bar. Then, the suspension was poured into a high-temperature silicone rubber mold (27×48×8 mm) and degassed at room temperature for 1 hr under vacuum at 23.4 mmHg. Finally, the suspension was cured in the programmable convection oven by following the curing schedule: (1) heat from room temperature to 180 °C at a heating rate of 1 °C/min; (2) isothermally cure at 180 °C for 2 hr; (3) heat to 250 °C at 1 °C/min and isothermally cure for another 2 hr; (4) cool down to room temperature at a cooling rate of 2 °C/min. The neat BECy cured samples were prepared following the same procedure sans nanoparticles.

Samples were machined from the solid block of material using a diamond blade saw (TechCut 5TM Precision Sectioning Machine with diamond wafering blade, Allied High Tech Products, Inc., Rancho Dominguez, CA). Samples for dynamic mechanical analysis (DMA) were machined to 30×5×0.5 mm and stored in a desiccator.

5.3.3 Experimental procedure

Samples were tested using a TA Instruments (New Castle, DE) dynamic mechanical analyzer (DMA) Q800 with liquid nitrogen gas cooling accessory (GCA) from 30 to 330 °C at a heating rate of 3 °C/min. A constant amplitude of 0.025% strain at 1 Hz was applied throughout the test, with a static load tracking at 125% of the dynamic force unless otherwise stated. A tension film fixture with a length of 20 mm was utilized for each test.

Creep and creep recovery cycles were conducted at isotherms between 190 and 320 °C in intervals of 10 °C, an equilibrium time of 5 min was allowed for each interval before the load was applied. For each isotherm, a constant stress of 0.4 MPa was applied for 30 min, followed by a 30 min recovery period.

Frequency sweep tests were conducted at isotherms between 180 and 300 °C in intervals of 10 °C, an equilibrium time of 5 min was allowed for each interval before commencing the frequency sweep. For each isotherm, a constant amplitude of 0.025% strain was applied at eight different frequencies ranged from 0.1 to 20 Hz with a static load tracking of 125% of the dynamic force. At the completion of the experiment, a storage modulus vs. frequency master curve is generated by the TTS principle and a frequency-time transformation is performed to transform the data into long term creep compliance using Eq. (5-9).

5.4 Results and discussion

The neat BECy samples were tested at different frequencies by DMA to evaluate the glass transition temperature and their response to frequency. The activation energy of the glass transition relaxation represents the energy barrier that must be overcome for the occurrence of molecular motions causing the transition, and can be estimated from the frequency dependence of T_g measured through DMA [17].

Figure 5-5a shows the $\tan \delta$ (equal to E''/E') curves for a series of test frequencies at a heating rate of 3 °C/min. The T_g 's are determined by the peak of the $\tan \delta$ curves. Then, the activation energy of the glass transition relaxation is calculated from the slope of a plot of $\ln(f)$ vs. $1/T_g$ as [18]:

$$\Delta E = -R \frac{d(\ln(f))}{d(1/T_g)} \quad (5-12)$$

where, R is universal gas constant (8.314 J/K mol) and f is frequency. Figure 5-5b shows this plot for neat BECy; ΔE is calculated as 763.3 kJ/mol. Similarly, the activation energy of the glass transition for the BECy/Al-GPS nanocomposite is estimated as 760.0 kJ/mol (the plot is not shown here).

Figure 5-5 (a) $\tan \delta$ curves for different frequencies for the neat BECy and (b) variation of T_g as measured by the $\tan \delta$ peak with the test frequency.

Typical strain response to creep and recovery at 250°C is showed in Figure 5-6, with results from both neat BECy and BECy/Al-GPS nanocomposites plotted. Generally, when a constant stress is applied, a deformation occurs instantaneously, which is related to the elastic character of the materials. And then, a delayed and continuous increase of strain occurs at a decreasing rate, in which the viscous character of the materials is more involved. When the

stress is removed, a continuously decreasing strain follows an initial elastic recovery. The strain cannot recover completely even after remove the applied load for a long period of time, it is due to the viscous character of the materials and a permanent deformation occurs. The two viscosities, η_1 and η_2 (shown in Figure 5-4), describe the viscous characters of the materials and depend strongly on temperature. BECy/Al-GPS nanocomposite has a T_g just above 250 °C, and shows a greater deformation occurred for BECy/Al-GPS than neat BECy, which has a T_g of 10 °C higher than BECy/Al-GPS.

Figure 5-6 Strain response to creep and recovery cycle at 250 °C for neat BECy and BECy/Al-GPS nanocomposite.

Figure 5-7 shows the creep compliance vs. actual test time for the entire test of neat BECy. The breaks in the data correspond to the recovery periods and equilibrium time for reaching the isotherm temperatures. Figure 5-8 shows the shifted data with a reference temperature of 200 °C on a log time scale for the neat BECy sample. The reduced time, t_r , is the expanded time scale for the creep master curve at an isothermal reference temperature as defined by Eq. (5-8). For the temperatures higher than the reference temperature (T_{ref}), the curve is shifted to the right with a negative shift factor ($\log a_T < 0$) and for the temperatures lower than T_{ref} , the curve is shifted to the left with a positive shift factor ($\log a_T > 0$). In Figure 5-8, the shift factors are chosen by hand so that the isothermal curves overlap to

generate a smooth master curve. The creep testing data of the BECy/Al-GPS nanocomposite is shifted similarly. The master curves of the neat BECy and the BECy/Al-GPS nanocomposite are showed in Figure 5-9 for a reference temperature of 200 °C.

Figure 5-7 Creep compliance vs. actual test time. The symbols represent data obtained at each isotherm.

Figure 5-8 Manually shifted compliance data for neat BECy at a reference temperature of 200 °C (the data of 260 °C is unshifted).

Figure 5-9 The master curves generated from manually shifted data for neat BECy and BECy/Al-GPS nanocomposite.

Table 5-1 Static and creep modulus at different temperatures and times.

Sample		E' at 40 °C (GPa)	E' at 200 °C (GPa)	1 year reduced E' (MPa)	5 year reduced E' (MPa)
Experimental Creep	Neat BECy	2.5	2.0	86	49
	BECy/Al-GPS	3.3	2.4	42	26
Transformed Creep	Neat BECy	-	-	1300	1100
	BECy/Al-GPS	-	-	770	540

The lines showing service times of 1, 10 and 100 years at 200 °C are plotted in Figure 5-9. As measured in the temperature-sweep DMA test in Figure 5-3, the BECy/Al-GPS (10 wt.%) has a much higher storage modulus of 3.3 GPa than neat BECy (2.5 GPa) at 40 °C (Table 5-1). At 200 °C, the storage moduli are reduced to 2.4 and 2.0 GPa for BECy/Al-GPS and neat BECy, respectively. The predictions show that the modulus (inverse of creep compliance) of both neat BECy and BECy/Al-GPS are dramatically reduced after long times at elevated temperature. The T_g of the materials play an important role in the creep

behavior, especially when the use temperature is close to the T_g . The T_g of neat BECy, 263 °C as measured from the onset drop of the storage modulus or 286 °C as measured from the $\tan \delta$ peak, is about 10 °C higher than the T_g of the BECy/Al-GPS nanocomposite. Therefore, while the initial modulus at 200 °C is slightly higher for the composite, the neat BECy has a lower predicted long term creep compliance because of its higher T_g .

Figure 5-10 Master curve for neat BECy, $T_{ref} = 200^\circ\text{C}$: (a) manually shifted and (b) shifted by using shift factors estimated from activation energy.

The master curves in Figure 5-9 are generated by manually shifting experimental data. Alternatively, the shift factors can be estimated from the activation energy of the glass transition relaxation, which, as discussed above, was found to be 763.0 and 760.0 kJ/mol for neat BECy and BECy/Al-GPS nanocomposite, respectively (Figure 5-5b). Assuming the activation energy is constant, the shift factors are given by [19,20]:

$$\log a_T = \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \log e \quad (5-13)$$

which is derived from the Arrhenius relationship. Eq. (5-13) holds for temperatures below T_g of the polymer, where the Williams-Landel-Ferry (WLF) equation is not applicable. For a reference temperature of 200 °C, the shift factors are estimated from Eq. (5-13) and the master curve is shown in Figure 5-10 for neat BECy at temperatures below T_g . The master curves generated by activation energy shift factors do not overlap well. Figure 5-11 shows the relationship of shift factors with temperatures. The constant activation energy assumption gives a linear relationship for $\log a_T$ vs. $1/T$. For both the neat BECy and the BECy/Al-GPS nanocomposite, the manual shift factors do not follow the linear activation energy shift factors, indicating that the activation energy of relaxation is not constant and has a complex relationship with temperature.

Figure 5-11 Shift factors vs. $1/T$ for manual shift and estimated from constant activation energy: (a) the neat BECy and (b) BECy/Al-GPS nanocomposite. For calculated shift factors, the open symbols represent the temperatures above T_g .

As discussed in the introduction, numerous creep models have been proposed and applied to describe the creep behavior of viscoelastic materials. The simple four-element

Burger model (Eq. (5-5)) and more general discrete retardation spectra (Eq. (5-6)) are used to fit the experimental creep test data in this study. Figure 5-12 shows the creep response of the neat BECy and the BECy/Al-GPS nanocomposite at 250 °C with applied constant stress of 0.4 MPa for 30 min. Symbols represent the experimental data, and lines, solid and dash, represent the model fit by the discrete retardation spectrum and the Burger model, respectively. Since the BECy/Al-GPS nanocomposite is closed to glass transition at this temperature, the creep compliance at such conditions is higher than neat BECy. Both the discrete retardation spectrum and the Burger model give a good fit with correlation coefficient $R > 0.99$.

Figure 5-12 Creep compliance in 30 min creep period at 250 °C and model fittings: Solid lines for Burger model, dash lines for discrete retardation spectra model.

The Burger model is simpler and more straightforward compared to the discrete retardation spectrum. Hence it used to fit the experimental data at different temperatures. The Burger model fitting results are shown in Figure 5-13 as solid lines. Since the BECy is polymerized into a permanent cross-linked network, it does not show accelerated viscoelastic flow behavior at temperatures above T_g . Therefore, Figure 5-13 only shows the fitting results at temperatures below T_g , which are in agreement with the experimental data (correlation coefficient $R > 0.99$ except the data measured at 200 °C). In the Burger model, the initial

deformation comes from the spring elastic element (E_1 , Figure 5-3), and later time-dependent deformation comes from the parallel spring (E_2) and dashpot (η_2), and from the viscous dashpot flow (η_1 in Eq. (5-5)). All of these parameters can be obtained from model fittings of experimental creep data and are listed in Table 5-2, in which the retardation time τ is defined by Eq. (5-4).

Figure 5-13 Strain response to creep at different temperatures below T_g : (a) the neat BECy and (b) BECy/Al-GPS nanocomposite.

As expected, for both the neat BECy and the BECy/Al-GPS nanocomposite, with increasing creep temperature the modulus, E_1 , decreases, indicating that the materials soften at elevated temperatures. The viscosity η_1 also decreases with increasing temperature and higher flow occurs in the dashpot, which increases the permanent deformation. The parallel (Voigt) unit in the model is used to describe the retarded elastic strain of the materials. Similar to E_1 and η_1 in series (Maxwell) unit, E_2 and η_2 (η_2 is calculated by Eq. (5-4)) decreases with increasing temperature, which give a delayed deformation at longer creep times. Because of reinforcement from functionalized alumina nanoparticles, the BECy/Al-GPS nanocomposite has a higher short-term tensile storage modulus than neat BECy. Similarly, the initial modulus, E_1 , of the BECy/Al-GPS nanocomposite is higher than the neat BECy in the glassy region, but E_1 decreases more with increasing temperature than neat BECy, which is attributed to the lower T_g of the BECy/Al-GPS nanocomposite.

Table 5-2 Parameters obtained from Burger model.

Sample	Temperature (°C)	E_1 (GPa)	E_2 (GPa)	τ (s)	η_1 ($\times 10^{14}$ Pa·s)
neat BECy	190	1.9	10.1	120	9.3
	200	1.9	7.2	156	1.4
	210	1.8	5.4	170	0.2
	220	1.8	4.5	154	0.1
	230	1.7	3.5	162	0.07
	240	1.5	2.5	147	0.04
	250	1.2	1.4	144	0.01
	260	0.7	0.3	206	0.002
BECy/Al-GPS Nanocomposite	190	2.1	9.5	89	2.8
	200	2.0	6.3	157	1.5
	210	1.9	4.6	158	0.2
	220	1.8	3.4	174	0.1
	230	1.6	2.4	168	0.04
	240	1.3	1.3	152	0.01
	250	0.6	0.2	234	0.001
	260	0.2	0.06	163	0.0009

Alternatively, the viscoelastic response of polymer materials can be obtained by measuring the tensile modulus as a function of frequency. The frequency dependent dynamic data can be transformed into time domain creep compliance data by using the inverse fast Fourier transformation (IFFT). Frequency sweep tests were conducted at isotherms between 180 and 300 °C in intervals of 10 °C with a frequency range of from 0.1 to 20 Hz.

Figure 5-14 Frequency sweep data for neat BECy: (a) Storage modulus vs. frequency. The symbols represent data obtained at each isotherm, range of from 180 to 290 °C at intervals of 10 °C. (b) Master curve at a reference temperature of 200 °C.

An unshifted modulus vs. frequency plot is shown in Figure 5-14a, and Figure 5-14b shows a manually shifted master curve obtained by time temperature superposition for the neat BECy data. In contrast to the time-domain creep test, for temperatures higher than the reference temperature ($T_{ref} = 200\text{ }^{\circ}\text{C}$), the curve is shifted to the left with a positive shift factor ($\log a_T > 0$), and for temperatures lower than T_{ref} , the curve is shifted to the right with a negative shift factor ($\log a_T < 0$).

Figure 5-15 The frequency dependent master curves generated from manually shifted data for neat BECy and BECy/Al-GPS nanocomposite.

By the TTS principle, the modulus response to frequency can be expanded to much broader frequency ranges, where real experiments are not possible. Figure 5-15 shows master curves of tensile storage modulus vs. frequency generated from manually shifted data with a reference temperature of $200\text{ }^{\circ}\text{C}$ for both the neat BECy and the composite. At high frequencies, the nanocomposite has a higher storage modulus than the neat BECy, which is attributed to the reinforcement of from the alumina nanoparticles. With decreasing frequency, the composite's storage modulus decreases and is lower than neat BECy below a certain value ($\log f \sim 3.5 \log(\text{Hz})$). The low frequency allows long range polymer chain motion to take place, which is limited at short time scale (high frequency). Hence, the size of the conformational changes increases, ultimately resulting in a decreasing storage modulus.

Since T_g (264 °C, determined by onset of E' drop) of the BECy/Al-GPS nanocomposite is close to the reference temperature and lower than the neat BECy T_g , the molecular mobility is higher at such temperatures. At very low frequencies (long time scales), large scale polymer chain motions are inhibited by cross-links in the BECy, and the storage modulus reaches the rubbery plateau without further decrease.

Figure 5-16 The master creep compliance curves transformed from frequency dependent dynamic data for neat BECy and BECy/Al-GPS nanocomposite.

By using the inverse fast Fourier transformation (IFFT), the frequency-domain dynamic data can be transformed into time-domain creep compliance data. The transformed creep compliance master curves are shown in Figure 5-16. The overall trend for transformed creep compliance master curves are similar to the experimental ones: the modulus (inverse of creep compliance) of both neat BECy and BECy/Al-GPS are dramatically reduced after long times at high temperature, and the modulus of the composite decreases more rapidly because of its lower T_g . However, the transformed creep compliance obtained from the frequency-domain dynamic data is lower than that obtained from the creep testing, and the differences between the two sets of creep compliance data increases at longer time. The values of creep compliance predicted from these two methods are listed in Table 5-1. One possible reason is that physical/chemical aging occurred during the creep tests at the higher temperature conditions. As a result of chemical aging, such as chain scission and devitrification at the

temperatures above T_g and oxidation at the surface of the samples, the apparent storage modulus increases, and the creep behavior at such temperatures is far away from the real creep behavior at relatively low reference temperatures. Compared to experimental creep tests, the frequency sweep tests were less impacted by the physical/chemical aging effects, especially for the high frequency range because of shorter testing time at high temperatures, resulting in lower creep compliance.

5.5 Conclusions

The DMA temperature sweep tests performed at different frequencies showed that addition of functionalized alumina nanoparticles did not significantly change the activation energy of the glass transition relaxation for the BECy matrix. Creep testing performed at elevated temperatures accelerated characterization of creep behavior for neat BECy and BECy/Al-GPS nanocomposite. By using the principle of TTS, long term creep behavior of neat BECy and BECy/Al-GPS nanocomposite were predicted. At 200 °C, BECy/Al-GPS nanocomposite can maintain their mechanical properties for several hundred hours. The neat BECy has a lower modulus at the same temperature, but can maintain its mechanical properties for an even longer time due to its higher T_g . Master creep compliance curves were generated by shifting the data by hand and also using shift factors estimated from the activation energy of glass transition relaxation. However, the shift factors estimated from constant activation energy of the glass transition did not give satisfactory results. Both Burger and discrete retardation spectrum models were used to fit the creep data at elevated temperatures, which is helpful for understanding the creep mechanism. The frequency sweep tests were conducted to evaluate the thermal-mechanical properties of the neat BECy and the BECy/Al-GPS nanocomposite response to frequency. This data was used to generate master curves of storage modulus vs. frequency using TTS. The frequency-domain dynamic data was transformed into time-domain creep compliance data by IFFT. The transformed creep compliance data showed similar trends as the experimental creep compliance but had significantly lower magnitudes. The differences between the two methods are attributed to the possible physical/chemical aging during the testing at aggressive elevated temperatures.

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CHAPTER 6: GENERAL CONCLUSIONS

6.1 General discussions

BECy has low viscosity at room temperature and can polymerize into a thermosetting polymer with a high glass transition temperature and good thermal stability. Fully cured BECy has a T_g of 274 °C and reaches the highest rate of decomposition at 446 °C in air. The relationship of conversion vs. time at different isothermal cure temperatures shows how increasing the curing temperature increases the reaction rate and a post-cure process above 250 °C is needed to fully cure the resin. The kinetic parameters are calculated by applying an autocatalytic model to fit the isothermal cure data. The analysis gives an activation energy of 60.3 kJ/mol and a total reaction order around 2.4. Isothermal curing experiments also shows a one-to-one relationship between the T_g of partially cured BECy and conversion. Multi-heating rate scans were analyzed by Kissinger's and Ozawa's approaches. The overall activation energy calculated from Kissinger's approaches is 66.7 kJ/mol, which is higher than the value obtained from the isothermal cure method. Ozawa and Friedman analysis give a relationship of activation energy vs. conversion, and an average value of 61.2, 56.8 kJ/mol, respectively.

Both alumina and silica nanoparticles contain physically adsorbed water and hydroxyl groups on the surface. The drying process at high temperature (350 °C) reduces the water content, but alumina nanoparticles are much more likely to adsorb moisture from the environment even at short exposure times. The TG results indicated that alumina nanoparticles contain about 5 times more physically adsorbed water and hydroxyl groups than the silica nanoparticles of the same size. The water and hydroxyl groups on the surface of the nanoparticles play an important role in the cure of BECy. Silica nanoparticles have a slight catalytic effect on the cure kinetics of BECy. This catalytic effect is mainly attributed to the physically adsorbed water and hydroxyl groups on the silica surface. Therefore, with higher silica nanoparticle loading, the activation energy decreased from 100.5 kJ/mol for neat BECy to 84.4 kJ/mol for the BECy with 3.2 vol.% silica nanoparticles. The catalytic effect of alumina nanoparticles was more pronounced and complex. Besides the physically adsorbed water and hydroxyl groups on the surface contributing to the cure of BECy, the electron

donating character (Lewis acidity) of the γ -alumina, significantly affects the cure of BECy. DSC thermograms of BECy containing different loadings of alumina nanoparticles showed a transition from one reaction mechanism catalyzed by hydroxyl functionality (water, surface hydroxyl group, and the phenol in the BECy monomer) to another dominated by the catalytic effect of the Lewis acidity. The isoconversional analysis confirmed this trend. An autocatalytic reaction model was successfully used to fit the experimental data obtained from DSC dynamic scans. The model fitting suggests that silica and low loadings of alumina nanoparticles have a similar cure of BECy following the same reaction mechanism with a total reaction order of 1.9; however, with increasing alumina nanoparticles, the reaction mechanism changes. The cure of BECy with high loading of alumina follows a reaction mechanism with a total reaction order of 3.7. The cure kinetic parameters were used to predict the isothermal cure of BECy without catalyst. The prediction shows that alumina nanoparticles significantly increase the BECy monomer conversion rate compared to silica nanoparticles and neat BECy.

Bare alumina nanoparticles were successfully functionalized with GPS. The BECy suspensions containing bare alumina show “shear thinning” behavior, which was more pronounced for high alumina nanoparticle loadings. With addition of alumina nanoparticles, the viscosity of the BECy suspensions are increased. Comparison of the experimental data and viscosity models suggests that the increase of viscosity is influenced by the presence of agglomerations of alumina and hydrogen bonding between agglomerates and the polar BECy monomer. However, TEM micrographs showed that alumina nanoparticles were relatively well dispersed in the BECy matrix, though a small number of alumina nanoparticles formed agglomerates with diameter measuring less than 200 nm. Rheokinetic evaluation of the catalyzed BECy/alumina suspensions gave an activation energy of gelation of 90 kJ/mol. Rheokinetic results of uncatalyzed samples showed that alumina nanoparticles had a catalytic effect on the cure of BECy, and increasing the alumina content reduces the gel time. Both Al and Al-GPS nanoparticles increased the storage modulus of BECy nanocomposites. Isostress, isostrain, Halpin-Tsai and Kerner models were compared to the storage moduli of the nanocomposites. The results suggest that the presence of a large interphase region with properties different from the bulk matrix. With the addition of the nanoparticles, the T_g

decreased. The BECy/Al-GPS showed less reduction in T_g than the bare Al systems which is attributed to the stronger interfacial bonding between the Al-GPS nanoparticles with the BECy matrix and the lower quantities of adsorbed water on the nanoparticle surfaces.

The DMA temperature sweep tests performed at different frequencies showed that addition of functionalized alumina nanoparticles did not significantly change the activation energy of the glass transition relaxation for the BECy matrix. Creep testing performed at elevated temperatures accelerated characterization of creep behavior for neat BECy and BECy/Al-GPS nanocomposite. By using the principle of TTS, long term creep behavior of neat BECy and BECy/Al-GPS nanocomposite were predicted. At 200 °C, BECy/Al-GPS nanocomposite can maintain their mechanical properties for several hundred hours. The neat BECy has a lower modulus at the same temperature, but can maintain its mechanical properties for an even longer time due to its higher T_g . Master creep compliance curves were generated by shifting the data by hand and also using shift factors estimated from the activation energy of glass transition relaxation. However, the shift factors estimated from constant activation energy of the glass transition did not give satisfactory results. Both Burger and discrete retardation spectrum models were used to fit the creep data at elevated temperatures, which is helpful for understanding the creep mechanism. The frequency sweep tests were conducted to evaluate the thermal-mechanical properties of the neat BECy and the BECy/Al-GPS nanocomposite response to frequency. This data was used to generate master curves of storage modulus vs. frequency using TTS. The frequency-domain dynamic data was transformed into time-domain creep compliance data by IFFT. The transformed creep compliance data showed similar trends as the experimental creep compliance but had significantly lower magnitudes. The differences between the two methods are attributed to the possible physical/chemical aging during the testing at aggressive elevated temperatures.

6.2 Recommendations for future research

There are several additional types of research work that would be beneficial for determining the suitability of the BECy/alumina nanocomposites for high-temperature structural repair applications.

Surface functionalization of alumina nanoparticles is an important factor to reduce agglomeration and improve the thermal mechanical properties of BECy nanocomposites. Many types of silanes, which contain the different functional groups, can be immobilized on the surface of alumina nanoparticles. It's expected that the functionalized alumina nanoparticles containing different surface functional groups would affect the properties of BECy nanocomposites in different ways. The further comparing characterization would be useful to determine the effects of functional groups on the surface of alumina.

Since the alumina showed catalytic effect on the cure of BECy, a full cure kinetic model would be beneficial for determining cure schedules for BECy/alumina nanocomposites. Some parameters, such as the monomer conversion at gel point in rheokinetic experiments, are needed to be evaluated. As a result, a time-temperature transformation (TTT) diagram for BECy/alumina nanocomposites can be developed.

It was found that the storage modulus of the BECy nanocomposites increased and T_g decreased through the long time storage. This may be caused by the aging of the material, which is an important concern if this material is transferred to a commercial product and given a shelf life. The further characterization should be performed to determine aging effects (physical/chemical) of the BECy/alumina nanocomposites at different conditions, such as long time service at elevated temperatures.

The cured BECy polymers are brittle and there is a large scattering in tensile testing results, such as tensile strength, maximum elongation. Changing the content of alumina, and surface functionalities may make it possible to further tailor the properties of the composites. The alumina functionalized with GPS showed improvement in tensile strength, and further research work should be conducted to improve the toughness of BECy nanocomposites.

For the resin-inject repair applications, adhesion is obviously an important property so that surface tension measurements and lap shear testing (or other adhesive test method) are recommended. For resin-inject repair of composites, the substrate would be an aerospace structural composite (carbon/epoxy or BMI/epoxy panels). Other mechanical characterizations, such as tensile testing, fracture testing, impact testing, and real creep testing, would be beneficial. The effect of environmental factors, such as humidity and the

presence of contaminants, on properties would also be useful for determining properties for materials used in less than ideal conditions.

CTE (coefficients of thermal expansion) describes the thermal expansion behavior of materials and is another important concern for the resin-inject repair applications. The mismatches in CTE will cause thermal stresses when temperatures fluctuate. The characterization of BECy nanocomposite CTE will be beneficial.

Full-scale testing of the repair should be conducted in order to determine the feasibility of making repairs with such materials before it is transferred to a commercial product. The composition of BECy nanocomposites should be changed according to the test results. Finally, the materials should have an optimized combination of properties for actual applications.

APPENDIX A: THE INFLUENCE OF CROSS-LINKING AGENTS ON RING-OPENING METATHESIS POLYMERIZED THERMOSETS

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A.1 Abstract

The addition of suitable cross-linking agents with norbornene-based monomers has significant effects on the thermal properties of the resulting polymers formed by olefin metathesis. Ethylidenenorbornene (ENB) and endo-dicyclopentadiene (endo-DCPD) were mixed separately with various loadings of three different cross-linking agents and then polymerized with the addition of Grubbs' catalyst. The polymerization kinetics and resulting glass transition temperature (T_g) of the systems were evaluated by differential scanning calorimetry (DSC). The addition of the first cross-linking agent, norbornadiene (CL-1), to both endo-DCPD and ENB resulted in decreasing glass transition temperatures with increasing concentrations. In contrast, the addition of the other two cross-linking agents (CL-2 and CL-3), which were both custom synthesized bifunctional norbornyl systems, to both endo-DCPD and ENB resulted in a monotonic increases in T_g with cross-linker concentration. By tailoring the loading of these custom cross-linking agents, the properties of these polymer systems can be controlled for various applications, including self-healing composites.

Keywords: cross-linking agent, dicyclopentadiene, ROMP, glass transition temperature

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A.2 Introduction

Transition-metal-catalyzed ring-opening metathesis polymerization (ROMP) is a powerful reaction for the synthesis of various polymers from cyclic alkenes [1]. In the last decade, significant advances have been made in ROMP initiators and resulting homopolymers and copolymers. Ruthenium-based catalysts developed by Grubbs [2] exhibit remarkable tolerance toward oxygen, moisture and numerous functionalities. With the advances in catalysts for ROMP reactions, applications of ROMP have been widened to various fields. For structural applications, ROMP is often used to polymerize low viscosity monomers in reaction injection molding (RIM) techniques. ROMP was also used in recently developed self-healing composite materials, where self-healing is accomplished by incorporating a microencapsulated norbornene-based healing agent and a catalytic chemical trigger within a polymer matrix [3]. In this application, as in RIM, the addition of multifunctional cross-linking agents to the ROMP monomers affects the cross-linking density and thermo-mechanical properties of the resulting polymer.

Figure A-1 ROMP monomers and cross-linking agents.

Norbornene-based monomers (see Figure A-1), *endo*-dicyclopentadiene (DCPD) **1** and *exo*-DCPD **2**, polymerize, with the addition of ruthenium-based Grubbs catalyst, to form cross-linked polymers of high toughness. Recent studies showed that *exo*-DCPD is more reactive than *endo*-DCPD for ROMP primarily for steric reasons [4]. Only *endo*-DCPD is commercially available and it is necessary to synthesize *exo*-DCPD from *endo*-DCPD.

Another ROMP monomer for structural and self-healing applications is ethylenenorbornene (ENB) **3**, which has higher ROMP reactivity but polymerizes into a linear polymer. However, ENB can be blended with DCPD or added with cross-linking agents to form a cross-linked network. The addition of suitable cross-linking agents with any of these monomers has significant effects on the thermal properties of the resulting polymer.

Several norbornene based ROMP cross-linking agents (**CL-1** to **CL-3**) with varying degrees of complexity (shown in Figure A-1) were purchased or synthesized in our laboratory to meet different application requirements [5-7]. By adding the cross-linking agents at varying concentrations to the ROMP monomers, the cross-linking density of polymerized system is changed, resulting in controlled properties for various applications, including self-healing composites. In addition to the tailored cross-linking density that may be obtained by adding cross-linking agents to the monomers, the cross-linking agents may also accelerate the ROMP reaction, especially when mixed with the sterically hindered *endo*-DCPD monomer.

Figure A-2 ROMP mechanism for *endo*-DCPD system contained cross-linking agent (CL-3).

The ROM polymerization, initiated by Bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (Grubbs' 1st generation catalyst), both DCPD and ENB are highly exothermic because of the relief of ring strain energy [8]. The first step of this process

involves dissociation of a phosphineligand from the precatalyst. Then, the resulting 14-electron complex undergoes a [2+2] cycloaddition with monomer to give metallacyclobutane intermediate **4**, which rapidly undergoes a [2+2] cycloreversion to produce the ring-opened product **5**. Intermediate **5** contains a catalytically active Ru-alkylidene, and undergoes further chain growth reactions until monomer is completely consumed. For DCPD, the remaining double bond may be polymerized in a similar way to form a cross-linked poly-DCPD network. Figure A-2 illustrates the ROMP mechanism for the *endo*-DCPD/CL-3 system. With cross-linking agent CL-3, a highly cross-linked poly-DCPD network is formed.

In this paper, we report on the use of differential scanning calorimetry (DSC) to evaluate the polymerization of *endo*-DCPD, *exo*-DCPD and ENB. Three kinds of cross-linking agents, CL-1, 2 and 3, were mixed with *endo*-DCPD and ENB separately, and then polymerized. The glass transition temperatures (T_g) of cured samples were investigated in detail by DSC.

A.3 Experimental

All reagents were obtained from commercial suppliers and used without further purification unless otherwise stated. All reactions were carried out in oven-dried glassware under a dry nitrogen atmosphere at ambient temperature unless otherwise stated. Flash column chromatography was carried out on MP silica gel 60, grade 32-63 μm .

A.3.1 Preparation of *exo*-dicyclopentadiene

exo-DCPD was synthesized from the *endo*-isomer by a slight modification of literature method [9]. Hydrobromic acid aqueous solution (48%, 172.8 g) was added to fresh distilled *endo*-DCPD (70.2 g, 0.53 mol) by addition funnel. The reaction was carried out at 75 °C for 12 hr and was cooled to room temperature. After the addition of water (100 mL), 5% sodium bicarbonate solution was added to neutralize the reaction mixture. Subsequently, the mixture was extracted with Et₂O (3×200 mL). The combined extract was dried with anhydrous sodium sulfate. After removal of Et₂O by rotavapor, reduced pressure distillation gave a colorless liquid, hydrogen bromine adduct (b.p. 86~88 °C /0.1 mmHg). A solution (4.82 mol/L) containing potassium hydroxide (63.1 g) in 95% ethanol (233.5 mL) was added to hydrogen bromine adduct (79.4 g, 0.37 mol) by addition funnel. The mixture was heated

under refluxing for 24 hr. After the addition of water (100 mL), the mixture was extracted with Et₂O (3×200 mL). The combined extract was dried with anhydrous sodium sulfate. After removal of Et₂O by rotavapor, reduced pressure distillation gave the dehydrohalogenation product contained 10% *endo*-DCPD. Dehydrohalogenation product was re-distilled at 190 °C; *endo*-DCPD was decomposed and distilled out. Reduced pressure distillation of residue gave *exo*-DCPD (b.p. 60 °C/0.2 mmHg, 31.7 g, overall yield 45.1%). ¹H NMR (400MHz, CDCl₃) δ 6.08 (m, 2H), 5.75 (m, 1H), 5.54 (m, 1H), 2.66 (s, 1H), 2.57 (s, 2H), 2.50 (m, 1H), 2.21 (m, 1H), 1.89 (m, 1H), 1.48 (m, 1H), 1.31 (m, 1H).

A.3.2 Preparation of CL-2 and CL-3

Norbornene-based cross-linking agents (CL-2 and 3) were synthesized by following reported methods [7,10].

Cross-linking agent CL-2, the mixture of 1,4,4a,5,8,8a-Hexahydro-1,4,5,8-*exo*,-*endo*-dimethanonaphthalene (CL-2a) and 1,4,4a,5,8,8a-Hexahydro-1,4,5,8-*endo*,-*endo*-dimethanonaphthalene (CL-2b), was prepared by adding bicyclo[2.2.1]hepta-2,5-diene (8.6g, 93.3mmol) and hydroquinone (13 mg, 0.12 mmol) to dicyclopentadiene (6.2 g, 46.9 mmol). The reaction was carried out in hard-glass pressure vessel at 190 °C for 18 h. The resulting mixture was subjected to reduced pressure fractional distillation and gave cross-linking agent CL-2 (7.8 g 52.9%), which is the mixture of *exo*,-*endo*-isomer CL-2a (83%) and *endo*,-*endo*-isomer CL-2b. ¹H NMR for CL-2a (300MHz, CDCl₃) δ 6.20 (m, 2H), 6.03 (m, 2H), 2.67 (m, 2H), 2.60 (m, 1H), 2.47 (m, 2H), 2.19 (m, 2H), 1.62 (m, 1H), 1.49 (m, 1H), 0.96 (m, 1H). ¹H NMR for CL-2a (300MHz, CDCl₃) δ 5.30 (m, 4H), 2.70 (m, 2H), 2.59 (m, 4H), 1.48 (m, 4H).

Cross-linking agent CL-3, 1,4-Di-(*exo*-bicyclo[2.2.1]hept-5-en-2-yl)benzene, was prepared by first adding bicyclo[2.2.1]hepta-2,5-diene (5.00 g, 5.43 mmol), DMF (dimethylformamide 5 mL), 1,4-diiodobenzene (1.40 g, 4.22 mmol) and piperidine (2.2 mL, 22.22 mmol) and bubbling with dry nitrogen. Bis(triphenylphosphine)palladium(II) acetate(0.324 g, 0.43 mmol) was added to the mixture and bubbled with nitrogen until it was completely dissolved. The mixture was cooled to 0 °C. Subsequently, formic acid (0.86 mL, 22.79 mmol) was added slowly. On completion of the addition of formic acid, the temperature was warmed up to room temperature over 2 hr. The reaction mixture was heated

to 60 °C for 4h and was cooled to room temperature. After the addition of water (100 mL), the mixture was extracted with Et₂O (3×100 mL). The combined extracts was dried with anhydrous sodium sulfate and concentrated by rotavapor. Chromatography (hexanes) of the residue gave cross-linking agent CL-3 (0.866 g, 78%). ¹H NMR (400MHz, CDCl₃) δ 7.21 (s, 4H), 6.26 (m, 2H), 6.16 (m, 2H), 2.96 (s, 2H), 2.88 (s, 2H), 2.70 (m, 2H), 1.57 (m, 6H), 1.42 (m, 2H).

A.3.3 Differential scanning calorimetry

Bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (Grubbs' 1st generation catalyst) was purchased from Sigma-Aldrich Inc. (St. Louis, MO) as a purple powder. First, 10 mg Grubbs' catalyst was dissolved in 10 mL of methylene chloride. The required amount of catalyst solution (to obtain a 2.0 mg/mL catalyst concentration in samples) was added to vials using a syringe. Methylene chloride was removed by dry nitrogen flow and the catalyst formed much smaller, more soluble crystals than the crystalline form of the "as-received" catalyst [11]. Then, monomer was added to the vial and the vial was vigorously mixed for less than 10 seconds to dissolve the catalyst powder, forming a homogeneous solution. Because of high reactivity, ENB monomer was mixed with catalyst at 0 °C or low temperature dry ice bath (water/ethanol = 50/50, volume ratio). The solution was dropped into liquid nitrogen to create small frozen droplets of catalyzed monomer. Finally, small frozen beads of catalyzed monomer was placed into aluminum DSC sample pans and loaded into the DSC chamber at a standby temperature of -50 °C.

To investigate how the concentration of cross-linking agents influence the cure kinetics and resulting glass transition relaxation properties of the systems, two series of samples were prepared each containing the cross-linking agents mixed with either *endo*-DCPD or ENB. For each series, cross-linking agents CL-1, CL-2 and CL-3 were added with various loading. Isothermally cured samples were prepared in order to measure the final glass transition temperature by dissolving cross-linking agents into *endo*-DCPD or ENB at varying monomer/cross-linking agent ratio. This solution was then added to required amount of re-crystallized catalyst. After catalyst was completely dissolved, catalyzed monomer/cross-linking agent solution were dropped into DSC sample pans and fully cured isothermally in a programmable oven at presetting temperature of 70 °C for 1 hr, then 170 °C for 30 min.

Finally, the sample pans containing the fully cured samples were loaded into the DSC chamber at a standby temperature of 25 °C.

The concentration of cross-linking agents in the mixtures ranged from 2.6 wt.% to 24.8 wt.% while the catalyst concentration was fixed at 2.0 mg/mL for all samples. DSC measurements were performed with a Perkin Elmer Pyris 1 DSC system (Perkin Elmer Inc., Waltham, MA). The DSC cell was swept by a constant flow of nitrogen at 20 mL/min. Tests were performed in a dynamic mode at heating rates of 10 °C/min (unless otherwise stated) over a temperature range of -50–200 °C for evaluation of polymerization of monomers and 25–200 °C for measurement of glass transition temperature.

A.4 Results and discussion

Typical DSC scan for the three ROMP monomers is shown in Figure A-3. The polymerization of *endo*-DCPD, *exo*-DCPD and ENB are highly exothermic because of the relief of ring strain energy. The location and form of the exothermic peaks indicate that ENB has the highest reaction activity among these three norbornene-based monomers [12,13]. Additionally, because of the low melting point (-80 °C), polymerization of ENB was started at as low as temperature of -20 °C. Therefore, it is necessary to prepare samples contained ENB monomer at very low temperature.

Figure A-3 Typical DSC dynamic scan at 10 °C/min (catalyst concentration: 2 mg/mL).

Evaluations of polymerization were performed in a dynamic mode at various heating rates by DSC. T_g measurements of fully cured samples were performed at a fixed heating rate of 10 °C/min. Figure A-4 illustrated the DSC scans at different heating rates for the polymerization of ENB/CL-2 systems. There was no difference between ENB with 4.8 wt.% CL-2 (solid line) and ENB with 9.2 wt.% CL-2 (dot line with symbol) thermograms. This indicates that extra cross-linking agents added to the systems do not have a significant effect on cure kinetics for ENB system (though the same cannot be said for the sterically inhibited *endo*-DCPD systems). But, as expected, the glass transition temperature of the resulting networks increases with increasing loadings of cross-linking agents.

Figure A-4 DSC dynamic scan at different heating rate for the ENB samples with different loading of CL-2 (catalyst concentration: 2 mg/mL).

The results of T_g measurements of fully cured samples are shown in Figure A-5. These T_g values were determined from the inflection point of the stepwise transition during dynamic temperature scans at 10 °C/min. As expected, the glass transition temperature of the resulting networks increases with increasing loadings of cross-linking agents. Since the molecular weights of the cross-linking agents vary significantly, the cross-linking agent loadings are plotted on both a wt.% and mole.% in Figure A-5.

While the addition of CL-2 and CL-3 results in a monotonic increase in the glass transition temperature for both ENB (Figure A-5a and b) and *endo*-DCPD (Figure A-5c and d); the addition of CL-1 causes a reduction in T_g with increasing loading levels for both systems. Obviously, CL-1 is not an effective cross-linking agent. After incorporation of CL-1 into the polymer structure, it becomes a disubstituted cyclopentadiene, similar to the cyclopentene group in poly-DCPD, and is less reactive [14]. The DSC scan curves for each ENB/CL-1 sample showed only one T_g . Therefore, ENB/CL-1 systems are polymerized to form random copolymers. The T_g of ENB/CL-1 system can be calculated by the Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (\text{A-1})$$

where T_{g1} and T_{g2} represent the glass transition of the component polymers and w_1 and w_2 are the weight fractions.

Figure A-5 Effect of cross-linking agents on the glass transition temperature of the thermosets.

The T_g of poly-ENB was measured as 110 °C and T_g of poly-norbornadiene (CL-1) was reported as 35 °C [15]. The calculated results match very closely with the experimentally measured glass transitions and are shown for each weight fraction in Table A-1 below. The residue cyclopentene groups of the polymerized CL-1 are more stable to olefin metathesis than the norbornene ring and fail to form a cross-linking network with poly-ENB. The similar results are observed in *endo*-DCPD/CL-1 system: with the increasing loadings of CL-1, the glass transition temperatures of the systems decrease. The only difference is that T_g does not have a linear relationship with CL-1 loadings because *endo*-DCPD can homogeneously polymerize as a cross-linked network without any cross-linking agents. As with the ENB/CL-1 system, the reduction in T_g indicates that CL-1 does not increase the degree of cross-linking in *endo*-DCPD/CL-1 system.

Table A-1 Calculated T_g of ENB/CL-1 system.

Wt. %	Mol. %	Measured T_g (°C)	Calculated T_g (°C)
0	0	110	110
4.8	6.2	106	106
9.2	11.6	102	102
12.9	16.2	99	98
16.7	20.7	94	95
21.3	26.1	92	91

In great contrast, as the CL-2 and CL-3 loadings increase, the T_g of the ENB and *endo*-DCPD systems also increase. This increase of T_g is a clear indication of the increasing degree of cross-linking in these systems. Both CL-2 and CL-3 have two norbornene rings, each with equal metathesis reactivity that is similar to the reactivity of the norbornene ring of ENB. Once one of two norbornene rings of CL-2 and CL-3 polymerized, the other norbornene rings will undergo further reactions without a decrease of reactivity. From the chemical structure, the two norbornene rings of CL-3 are separated by a benzene ring and are independent each other. Therefore, the remained norbornene ring is less affected by the other ring being incorporated into a growing polymer network and has more space to move, and a greater chance of reacting with other norbornene rings of monomer, cross-linking agents and polymer chains. Compared with CL-2, similar loading of CL-3 increase the system T_g more

as shown in Figure A-5b (the weight fraction loading of cross-linking agents were converted to mole fraction based on the molecule weight of monomer and cross-linking agents). For example, with 10.8% (mole fraction) loading of CL-2, the T_g of ENB/CL-2 system is 131 °C; with almost the same loading of CL-3 (10.6%), the T_g of ENB/CL-3 system is increased to 147 °C.

Because *endo*-DCPD can form a cross-linked network without addition of cross-linking agents, the influence of cross-linking agents is more complicated. For the *endo*-DCPD/CL-2 system, once ROM polymerization is initiated by Grubbs' catalyst, a poly-DCPD network forms even at low degree of cross-linking. The formed network limits the motion of cross-linking agents and un-reacted norbornene rings of the cross-linking agents and polymer chains. As shown in Figure A-5c, although T_g is increased with increasing of CL-2 loading, the rate of increase with CL-2 loading decrease at higher weight fraction.

As mentioned before, the two norbornene rings of CL-3 are separated by a benzene ring and independent each other. CL-3 shows very different effects on the glass transition of the *endo*-DCPD system. In this case, the rate of T_g increase with CL-3 loading increases. At higher CL-3 loadings there may be a plateau, with T_g only increasing slightly with higher cross-linking loadings. However, to date, there is no experimental data to prove this trend because of difficulties in sample preparation. It's hard to dissolve solid CL-3 (m.p. 71.0 °C) in *endo*-DCPD.

A.5 Conclusions

The reactivity of monomers, *endo*-DCPD, *exo*-DCPD and ENB was evaluated by exothermic peak locations at various heating rates by DSC measurements. The results showed that ENB has highest ROMP reaction activity. Polymerization kinetics of ENB mixtures with custom cross-linking agents (CL-2) were also evaluated by DSC. Cross-linking agents have no obvious effects on polymerization kinetics of ENB/CL-2 system, because both monomer and cross-linking agents have similar reaction groups.

The influence of cross-linking agents on the glass transition of *endo*-DCPD and ENB was investigated in details. With increasing loading of cross-linking agent CL-1, both *endo*-DCPD and ENB system showed decreased glass transition temperatures. However, with the

addition of CL-2 and CL-3, both *endo*-DCPD and ENB systems showed monotonic increases in T_g . Because of different chemical structures, CL-2 and CL-3 have different effects. At similar mole fraction loading, CL-3 is more efficient to increase the degree of cross-linking.

We are currently working on additional cross-linking agents (CL-4 and CL-5 in Figure A-6). CL-4 will allow investigation of homologous series of cross-linking agents to determine the influence of cross-linker length on T_g enhancement. CL-5 differs from previous cross-linking agents by being tri-functional rather than bi-functional and should result in even high levels of cross-linking at lower loading levels. More experiments are also proceeding, such as swelling tests to determine the degree of cross-linking and Dynamic Mechanical Analysis (DMA) for physical properties of monomer/cross-linking agent systems.

Figure A-6 Additional cross-linking agents to be investigated.

A.6 Acknowledgements

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APPENDIX B: INFLUENCE OF CROSS-LINK DENSITY ON THE PROPERTIES OF ROMP THERMOSETS

A paper to be submitted to an academic journal

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B.1 Abstract

A norbornene-based cross-linker (CL) was synthesized and mixed at different loadings with two separate monomers for self-healing polymer applications: 5-ethylidene-2-norbornene (ENB) and *endo*-dicyclopentadiene (*endo*-DCPD). The monomer/cross-linker systems were polymerized by ring-opening metathesis polymerization (ROMP) with Grubbs' catalyst. The thermal-mechanical properties of the polymerized networks were evaluated by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) and the curing process was monitored by parallel plate oscillatory rheometry. The viscosities of the pre-polymer blends are shown to be adequately low for self-healing, and exhibit a high ROMP reactivity to form cross-linked networks with enhanced thermal-mechanical properties. The addition of cross-linker increases the glass transition temperature (T_g) and the storage modulus both above and below T_g . The storage modulus increase above T_g is used to estimate the molecular weight (M_c) between entanglements or cross-link sites for both ENB and *endo*-DCPD-based networks. The cross-linker also greatly accelerates network formation as defined by the gelation time.

B.2 Introduction

Self-healing polymers represent a new paradigm in materials design [1,2]. In these materials, which are inspired by biological systems where damage triggers an autonomic healing response, self-healing is accomplished by embedding liquid healing agent filled

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microcapsules within a polymer matrix. When damage occurs, microcracks rupture the embedded capsules, release healing agent into the crack plane. There the released healing agent it contacts an embedded chemical trigger (catalyst) and polymerizes, bonding the crack faces back together.

There are several requirements for successful healing agents: 1) the healing agent should polymerize at room temperature to produce a very strong thermoset with good thermomechanical properties and adhesive strength; 2) the catalyst loading should be as low as possible to eliminate its deleterious effect on the virgin mechanical properties of the polymer matrix and to reduce overall cost; 3) the self-healing agent should have a very low viscosity and low surface energy to completely fill the microcracks before polymerization occurs.

Endo-dicyclopentadiene (*endo*-DCPD) has been used extensively as the healing agent in self-healing composites with good results [3-10]. In these works, the Grubbs' first generation catalyst was used as the embedded trigger to initiate ring-opening metathesis polymerization (ROMP). *Endo*-DCPD is capable of forming a cross-linked structure with high toughness and strength. However, it has a relatively slow in situ polymerization rate and requires high loadings of catalyst, which is undesirable for self-healing applications. Low temperature self-healing applications are also limited because *endo*-DCPD has a melting point just below room temperature [5].

Figure B-1 Chemical structures of *endo*-DCPD and ENB monomers.

Another norbornene-based monomer (Figure B-1), 5-ethylidene-2-norbornene (ENB) has a very low melting point of -80 °C, and much higher ROM reactivity than DCPD [11,12]. However, ENB forms a linear polymer through ROMP. Also, the modulus and glass

transition temperature (T_g) for poly-ENB are both lower than the cross-linked poly-DCPD. ENB can be blended with *endo*-DCPD or with other cross-linking agents (or cross-linkers) to form a cross-linked network and improve its thermal-mechanical properties. Liu *et al.* [13] reported that blends of ENB and DCPD polymerize much faster than neat DCPD, even at lower catalyst loadings, with increasing ENB content. The ENB/DCPD also shows increased rigidity after cure compare to pure ENB. In our previous work [14], norbornene-based cross-linkers (CL-2 and CL-3) with varying degrees of complexity were synthesized from norbornadiene (CL-1) (Figure B-2). By adding the cross-linker at varying concentrations to the ROMP monomers, the properties of the resulting polymers can be tailored. With addition of CL-2 and CL-3, the glass transition temperature (T_g) of both ENB and *endo*-DCPD systems increases, while the addition of CL-1 decreases T_g for both systems.

Figure B-2 Chemical structures of cross-linking agents. CL-2 (CL) is a mixture of *exo*-, *endo*-isomer and *exo*-, *exo*-isomer.

In this study, we first investigate the influence of CL-2 and CL-3 on the viscosity of the DCPD and ENB healing agents. Based on these results we then select the most promising crosslinker as CL-2 (hence forth referred to as CL) and investigate its effect on gelation kinetics by parallel plate oscillatory rheology. The thermal-mechanical properties of cured ENB/CL and DCPD/CL systems are characterized by using DMA and DSC.

B.3 Experimental

Dicyclopentadiene (*endo*-DCPD, 95%, Acros Oragnics, Belgium), 5-ethylidene-2-norbornene (ENB, 99%, Sigma-Aldrich Inc., St. Louis, MO) were used as received without

further purification. Grubbs' 1st generation catalyst, bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (Sigma-Aldrich Inc.) was first dissolved in methylene chloride and then recrystallized under dry nitrogen flow to form much smaller, more soluble crystals [15]. Synthesis of CL (CL-2) and CL-3 was reported in our previous work [14], CL is a mixture of *exo*, *endo*-isomer (83 mol.%) and *exo*, *exo*-isomer (17 mol.%).

The mixtures of cross-linker/monomer were prepared at the different cross-linker loading, ranging from 2.6 to 20.3 wt.%. The catalyst concentration used in this study was 1.0 mg/mL and 2.0 mg/mL for ENB and *endo*-DCPD systems, respectively, unless otherwise stated. To make a fully cured sample, the recrystallized catalyst was added to the cross-linker/monomer mixtures and stirred for 10 s in a vial at room temperature for the DCPD systems and at 0 °C for the ENB samples. Next, the catalyzed mixture was poured into glass molds (1×10×80 mm). The DCPD-based samples were cured isothermally in a programmable oven at 70 °C for 2 hr, followed by a post-cure at 170 °C for 1.5 hr. For the ENB-based systems, the samples were polymerized with the following cure schedule: 5 °C for 5 h, then 30 °C for 1 hr, 70 °C for 1 hr, and finally 170 °C for 1 hr. After the sample was slowly cooled down to room temperature in the oven, it was removed from the glass mold for subsequent DMA and DSC testing.

The viscosity of an uncatalyzed mixture of ENB/CL and *endo*-DCPD/CL was measured with a cone (0.45 °, 15.11 mm radius) and plate viscometer (High Shear CAP-2000+, Brookfield Engineering, Inc., Middleboro, MA). The experiment was conducted at 20 °C with shear rate of 13333 s⁻¹ (1000 rpm).

Isothermal cure characterization of catalyzed ENB/CL and *endo*-DCPD/CL systems was monitored with a parallel plate rheometer (ARES parallel plate rheometer, Rheometric Scientific Inc., USA) by applying a small oscillating strain to the sample and measuring the response stress. All experiments were performed at 23 °C, using stress control mode at an amplitude of 6% strain and 1 Hz, with the 25-mm diameter disposable parallel plates and 0.6 mm gap.

Differential scanning calorimetry (DSC Q20, TA instruments, Inc., New Castle, DE) was used to measure the glass transition temperature (T_g) of fully cured samples. Tests were

performed at a heating rate of 10 °C/min from 40–200 °C under dry nitrogen purge at 50 mL/min.

The thermal-mechanical properties of ENB/CL and DCPD/CL were evaluated by dynamic mechanical analysis (DMA Q800, TA instruments). All samples were tested in the thin film tension mode at an oscillating strain of 5 μ m and frequency of 1 Hz, using a sample size of 1×5×35 mm. The experiments were performed at a heating rate of 3 °C/min from 30 °C to 230 °C under a nitrogen atmosphere.

B.4 Results and discussion

In functional self-healing materials, the healing agent must have a low viscosity and low surface energy to wick into matrix microcracks before it polymerizes. The viscosity of *endo*-DCPD with various loadings of CL and CL-3 is shown in Figure B-3. The viscosity of ENB is too low to measure with our experimental set-up and is not reported here. While both CL and CL-3 increase the viscosity of *endo*-DCPD systems, the addition of CL-3 increases the viscosity more than CL at same the loading levels. A simple rule of mixtures was used to fit the experimental data:

$$\eta_m = \eta_1 w_1 + \eta_2 w_2 \quad (\text{B-1})$$

where η_m , η_1 , and η_2 is the viscosity of the mixture, component 1, and component 2, respectively, and w_1 and w_2 are the weight fractions of the components.

Figure B-3 Viscosity of *endo*-DCPD with different loadings of cross-linking agents.

Viscosity of pure *endo*-DCPD and CL is measured as 1.91×10^{-3} Pa·s and 7.25×10^{-3} Pa·s, respectively, at a shear rate of 13333 s^{-1} . The fitting results are shown in Figure B-3 as dashed lines. At low loadings, the simple rule of mixtures fits the measured data well for both *endo*-DCPD/CL and *endo*-DCPD/CL-3, while at high loadings, the *endo*-DCPD/CL-3 blend deviates from linearity. Because cross-linker CL-3 is solid at room temperature, its viscosity cannot be measured directly. From the simple rule of mixtures for low loadings of CL-3, the effective viscosity of CL-3 at room temperature is estimated as 0.4 Pa·s, which is much higher than CL. For self-healing applications, the low viscosity system is more favorable. Hence, the most promising crosslinker, CL, was selected and the *endo*-DCPD/CL blend was further characterized.

Figure B-4 Reaction scheme for ENB/CL and *endo*-DCPD/CL polymerized through ROMP to form cross-linked structures.

ENB monomer can be polymerized in a linear structure through ROMP. With addition of the cross-linker, the ENB/CL blend is expected to form a random cross-linked network (Figure B-4, top). For *endo*-DCPD monomer, which itself polymerizes into a cross-linked network through the additional ring-opening metathesis of the less reactive cyclopentenyl double bond (Figure B-4, bottom), additional cross-linker is expected to increase the overall cross-linking density of the resulting thermoset. A swelling test was performed to qualitatively evaluate the cross-link density. Fully cured ENB/CL and *endo*-DCPD/CL samples were cut into small rectangular pieces ($1 \times 10 \times 20$ mm) with initial weights of $W_{initial}$. Next, the weighed samples were soaked in toluene at room temperature for 72 h.

Finally, the samples were taken out and weighed to determine the weight of the sample, W_{final} , which includes the mass of the solvent absorbed. Swelling percentage is calculated by Eq. (B-2) below and plotted vs. cross-linker loading in Figure B-5:

$$Swelling (\%) = \frac{W_{final} - W_{initial}}{W_{initial}} \times 100\% \quad (B-2)$$

Because ENB (0 wt.% CL) is polymerized into a linear polymer, poly-ENB can dissolve in toluene completely so that W_{final} is undefined. With increasing loadings of CL, the swelling decreases substantially for both ENB and DCPD-based systems, indicating the formation of more highly cross-linked networks. Compared to the ENB/CL system, the *endo*-DCPD/CL polymer swells less in toluene at the same CL loading due to its higher cross-linking density resulting from the additional ROMP active cyclopentenyl ring in the DCPD monomer.

Figure B-5 Swelling test results of fully cured samples.

The thermal-mechanical properties, as well as the cross-linking densities, of the copolymers were investigated by dynamic mechanical analysis (DMA). A tension fixture was used to conduct tests, in which small oscillating strain is the long-axis of the sample and the stress response is measured. Storage modulus (E') and loss modulus (E'') are determined from the in phase and out of phase response of the materials to the applied strain. The storage modulus relates to the ability of materials to store energy, while the loss modulus is attributed

to dissipative and viscous losses in the materials. The ratio of E'' to E' is the mechanical damping ($\tan \delta$). In this work, both onset of storage modulus E' drop and peak of loss modulus E'' are used to mark the glass transition temperature (T_g) of networks. The T_g was also measured by DSC as determined from the step change in the heat capacity (midpoint calculation method). The DMA curves for ENB/CL and *endo*-DCPD/CL are shown in Figure B-6 (a-d).

Figure B-6 Temperature dependence of viscoelastic properties from DMA experiments: (a) storage modulus for ENB/CL system; (b) loss modulus for ENB/CL system; (c) storage modulus for *endo*-DCPD/CL system; (d) loss modulus for *endo*-DCPD/CL system.

The cross-linking density can be described by M_c , the molecular weight between entanglements or cross-link sites [16]. The value of the storage modulus in the rubbery

plateau region is inversely proportional to the chain length between entanglements, M_c , and is given by [17]:

$$M_c = \frac{3qdRT}{E'_{T_g+50K}} \quad (\text{B-3})$$

where, q is the front factor, usually equal to 1; d , the density of the material (0.93 g/cm³ and 1.0 g/cm³ for polymerized ENB and *endo*-DCPD systems, respectively.); R , the universal gas constant (8.314 J·K⁻¹·mol⁻¹); T is equal to $T_g + 50$ K; E'_{T_g+50K} is the storage modulus at temperature of $T_g + 50$ K. The values of M_c obtained from Eq. (B-3) can be used for comparing the cross-linking density of the all the samples investigated in this study. Table B-1 lists the results obtained from both DMA and DSC experiments.

Table B-1 Experimental data obtained from DMA and DSC tests.

	CL loading (wt.%)	T_g (DSC) (°C)	T_g (E'' peak) (°C)	E' at 35°C (MPa)	E' at $T_g+50^\circ\text{C}$ (MPa)	M_c (g/mol)
ENB/CL	0	111.4	114.9	1852	10.5	954
	5.7	115.6	119.7	1903	15.2	665
	10.3	117.3	121.9	1993	16.6	614
	14.8	121.1	125.1	2020	20.4	501
	19.6	122.3	126.4	2083	28.3	362
DCPD/CL	0	140.0	150.0	1930	22.5	469
	5.2	151.7	157.1	1989	31.7	338
	9.9	157.4	162.7	2063	37.0	294
	15.1	162.2	167.8	2121	37.9	290
	20.3	164.4	168.8	2167	46.0	240

As shown in Table B-1, increasing CL loading slightly increases storage modulus, E' , in the glassy region (below T_g). The storage modulus increases about 12% for both ENB/CL and *endo*-DCPD/CL systems with CL loading increasing from 0 to 20 wt.%. The T_g determined by the peak in the loss modulus also increases with the addition of CL, in agreement with our previous DSC results [14]. For the *Endo*-DCPD, the efficiency of the cross-linker decreased above 10 wt.% CL (with M_c dropping only 18% from 10 to 20 wt.% CL versus a 37% reduction from 0 to 10 wt.%). This is presumably because of the already

high crosslink density in the DCPD system caused by the additional strained cyclic olefin in the monomer. As a result of the higher crosslink density, T_g increases with increasing CL.

Figure B-7 Tan delta curves for (a) ENB/CL and (b) *endo*-DCPD/CL systems.

This effect is more pronounced at low loadings of CL. For example, there is a 7.1 °C increase in T_g with the addition of 5 wt.% CL, while the T_g only increases by 1.1 °C when the CL loading increases from 15 to 20 wt.%. One possible reason is that CL has a higher ROMP reactivity than *endo*-DCPD (*endo*-DCPD has been shown to be significantly less reactive for

ROMP than its *exo*-isomer, primarily for steric reasons [18]). At high loadings, the CL molecules tend to react first, forming a microphase heterogeneity and property gradients throughout the network structure as the DCPD monomer is consumed later. This hypothesis is supported by the broader glass transition region on the DSC curves for *endo*-DCPD samples containing the higher loadings of CL. Our recent research on the ROMP of modified linseed oil (modified with norbornene functionality) copolymerized with CL shows similar phase-separation phenomena: cured samples changed from transparent to cloudy with increasing CL loading [19]. This lack of homogenous copolymerization with increasing CL loading, reduces the overall cross-linking efficiency.

While ENB monomer polymerized into a linear polymer, physical entanglements still contribute to a rubber plateau above T_g and an apparent M_c of 954 g/mol. With addition of CL, a chemical cross-linked network is formed and M_c decreases. The decrease of M_c indicates a reduction of chain mobility due to the increasing number of chemical cross-links provided by the additional cross-linker. The formation of the more highly cross-linked networks is also apparent by the temperature dependence of $\tan \delta$. The $\tan \delta$ curve for poly-ENB shows a small peak around 200 °C in the rubbery region above T_g (Figure B-7a). This transition is attributed to movement of coordinated segments in the amorphous polymer that relate to viscous flow [20]. With addition of cross-linker, the cross-linked network prevents the chains from slipping past each other (viscous flow) and this secondary peak in the $\tan \delta$ curve is eliminated.

While addition of CL increases the glass transition temperature and cross-link density for both ENB and *endo*-DCPD systems, it also effects the cure behavior of the blends. Gelation time is an important parameter for processing of thermosetting resins in general and for the healing agents in self-healing polymers. For self-healing applications, the gelation time of the healing agent is a lower bound for the healing time, the period when the monomer is able to wick into the damage zone before polymerizing after contacting the embedded catalyst. Generally, gelation is associated with a dramatic increase in viscosity. Gelation time can be determined rheologically by measuring the time between the beginning of the reaction and the attainment of an asymptotic viscosity increase or when the storage shear modulus, G' , exceeds the loss shear modulus, G'' . Parallel plate oscillatory rheometer was used to

measure the time dependence of G' and G'' for the ENB/CL and *endo*-DCPD/CL systems. During the polymerization, both G' and G'' increased with reaction time. The crossover of G' and G'' , where $\tan \delta$ equals 1, is recorded to determine the gel point of the blend. The beginning of the reaction is defined as the moment when the catalyst is added and mixed with the blends, so the gel point includes the time used to load the sample into the parallel plate apparatus.

Figure B-8 Evolution of storage modulus, loss modulus, and $\tan \delta$ during the reaction of the co-monomer blend. Shown here is *endo*-DCPD/CL (25.1 wt.%) curing at room temperature.

Figure B-8 shows the rheological results of the *endo*-DCPD system containing 25.1 wt.% CL. The gelation time of *endo*-DCPD/CL (25.1 wt.%) is measured as 219 s at these experimental conditions. Since ENB has a much higher ROMP reactivity than the *endo*-DCPD, a low catalyst concentration of 0.2 mg/mL is used (versus the 2.0 mg/mL for *endo*-DCPD). The gelation times from the rheology experiments for catalyzed ENB/CL and *endo*-DCPD/CL samples are shown in Figure B-9.

The addition of CL reduces the gelation time for both the ENB and *endo*-DCPD systems. The addition of CL is so effective that 5 wt.% loading of CL decreases the gelation time of ENB and *endo*-DCPD by half, from 418 to 218s and from 1456 to 735 s, respectively. For the ENB/CL system, the highest cross-linker loading (24.8 wt.%) reduces

the gelation time to 104 s, which is 4 times shorter than pure ENB without any cross-linker. For the *endo*-DCPD/CL system, the effect of cross-linker on gelation time is even more remarkable: at a CL loading of 25.1 wt.% the gelation time decreased 7 fold to 219 s.

Figure B-9 Effect of CL loading on gel times for (a) ENB and (b) *endo*-DCPD

The CL provides additional cross-linking sites for ENB and *endo*-DCPD. The gelation time is the time when a cross-linked network is first formed to develop a percolating giant macromolecule throughout the system; and the extra cross-linking sites lower the conversion necessary to form the percolating network structure. As a result, addition of CL makes the whole monomer/cross-linker system reach the gel point more quickly. In addition, since the CL is more reactive towards ROMP than *endo*-DCPD, the gel point is further reduced by the increasing cure rate of the CL blended systems. This increase in the effective cure kinetics for the *endo*-DCPD is responsible for the greater reduction in gelation time in the DCPD/CL systems than in the ENB/CL systems. The ability of self-healing agents to gel rapidly at room and/or sub ambient temperatures is favorable for reducing the required healing times in self-healing polymer composites.

B.5 Conclusions

CL can be used to modify the properties of norbornene-based monomers, ENB and *endo*-DCPD, with application for self-healing polymers. Samples of ENB and *endo*-DCPD containing different loadings of CL were prepared through ROMP. Swelling tests revealed

that addition of CL contributes to the formation of a more highly cross-linked network structure. Quantitative characterization is performed by both DMA and DSC. DMA results show that the storage modulus below the glass transition temperature increases with increasing CL loading. The storage modulus in the rubbery plateau region is used to evaluate the molecular weight between cross-links, M_c . Decreasing of M_c with CL loading confirms the formation of highly cross-linked networks for both ENB and *endo*-DCPD systems. Rheological results of catalyzed ENB/CL and *endo*-DCPD/CL show that CL greatly decreases the gelation time. ENB/CL system is more reactive in ROMP reaction than *endo*-DCPD/CL and reaches gel point quickly at lower catalyst concentrations. Future work is aimed at demonstrating improved healing efficiencies with these ENB/CL based healing agents.

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B.7 Reference

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