

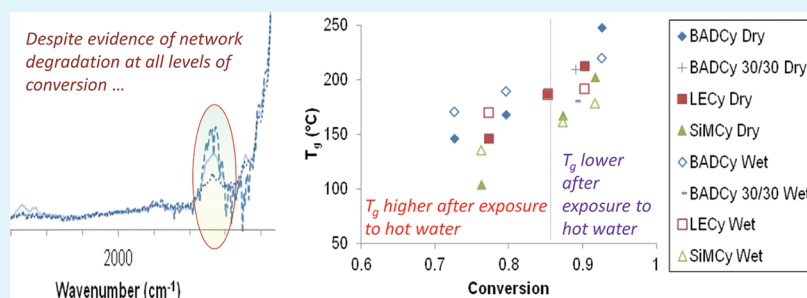
Effect of Chemical Structure and Network Formation on Physical Properties of Di(Cyanate Ester) Thermosets

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ABSTRACT: Key physical properties of three dicyanate ester monomers, bisphenol A dicyanate (BADCy), bisphenol E dicyanate (LECy), and the dicyanate of a silicon-containing analogue of bisphenol A (SiMCy) were investigated as a function of cyanurate conversion at conversions ranging from approximately 70% to greater than 90% in order to assess the range of applicability of both traditional and more unusual structure–property–process relationships known for cyanate ester resins. A more complete understanding of these relationships is essential for the continued development of cyanate ester resins and their composites for a wide variety of aerospace applications. The degree of cure in each system was determined by differential scanning calorimetry (DSC). The degree of conversion achieved at a given temperature was dependent on the structure of the repeat unit, with SiMCy displaying the highest relative ease of cure. The density at room temperature was found to decrease monotonically with increasing conversion for all monomer types studied. In contrast, the water uptake decreased with increasing cure for all three materials over most or all of the conversion range studied, but leveled off or began to increase with increasing conversion at conversions of approximately 90%. The T_g decreased after exposure to hot water in resins with greater than 85% conversion, but unexpectedly increased in samples with lower conversions. An investigation of the effect of hot water exposure on network chemistry via infrared spectroscopy indicated that carbamate formation varied with both monomer chemistry and extent of cure, but was greatest for the BADCy polycyanurates. On the other hand, the unreacted cyanate ester band tended to disappear uniformly, suggesting that reactions other than carbamate formation (such as cyclotrimerization) may also take place during exposure to hot water, possibly giving rise to the observed unusual increases in T_g upon exposure.

KEYWORDS: cyanate ester, polycyanurate, resin, cure kinetics, water uptake

1. INTRODUCTION

Cyanate ester resins^{1–3} comprise a widely recognized class of high-temperature thermosetting polymers with numerous applications in aerospace and high-performance material arenas. In aerospace structures, they are best known as composite resins in combination with glass or polyethylene reinforcements for use in radomes and antenna structures,⁴ where their unusually low dielectric constant and low moisture uptake properties provide unique performance advantages. In addition to radomes and antennae, additional aerospace applications in which cyanate esters are prized for their elevated glass transition temperature, good adhesion to metals, resistance to degradation by moisture, and excellent flame, smoke, and toxicity characteristics include pultruded brush seals for engine turbines,⁵ filament wound composite structures for airframes,⁶

heat shields for atmospheric re-entry,⁴ and metal insert molded control surfaces.⁷ Outstanding resistance to many forms of high energy radiation and the potential for very low outgassing make cyanate esters desirable for satellite and space structures,⁸ as well as in unusual applications such as magnet casings for prototype thermonuclear fusion reactors.⁹

Beyond their usefulness for a large number of applications, cyanate ester resins also represent an excellent class of thermosetting materials for studying structure–process–property relationships. Their suitability for such studies derives from the high selectivity of the cyclotrimerization reaction that

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provides cross-linking,¹⁰ as well as the ease of blending with additional monomers (for cocuring)^{11–13} or with thermoplastics (for toughening via reaction-induced phase separation).^{14,15} Although certain mechanistic details, particularly where catalysts are involved, remain disputed, the cure chemistry and kinetics of cyanate ester resins have been very well studied,^{1–3} and the physical properties over a wide range of conversions are readily understood through tools such as transformation-temperature-property diagrams.¹⁶ Moreover, the cyanate ester monomer, the triazine ring (the main product of cross-linking), and many of the intermediates and possible side products exhibit readily discernible peaks in infrared spectra. Finally, cyanate esters exhibit a very large change in dry glass transition temperature upon cure, meaning that the diBenedetto equation¹⁷ can often be used as an unusually sensitive measure of the degree of conversion. As a result, even after vitrification, insoluble polycyanurate networks are typically amenable to a range of techniques that can reveal, with useful precision and reliability, many key features of the network structure.

Despite the widespread applications and usefulness for studies of structure–process–property relationships, there have been relatively few systematic examinations of the effect of repeat unit chemical structure on cyanate ester network formation and the resultant physical properties. Although there is a great deal of information available on the most commonly used cyanate esters, such as the dicyanate ester of bisphenol A (herein and commonly referred to as “BADCy”),¹⁸ there is much less data, particularly in the form of direct comparisons performed under identical conditions, with even its closest analogs, such as the dicyanate ester of bisphenol E (“LECy”). Guenther et al.¹⁹ compared the physical properties of BADCy to a silicon-containing analog (termed “SiMCy”). However, this comparison focused only on physical properties with relatively little information about network development. Additional research has compared BADCy to more unusual monomers, such as phenolphthalein-based cyanate esters,²⁰ fluorinated cyanate esters,²¹ dicyclopentadiene dicyanate esters,²² biphenylated cyanate esters,²³ and many types of cyanate ester nanocomposite materials.^{24–27} As of yet, however, a careful comparison of BADCy with its closest analogs, including differences in network development (i.e., the effect of structure on cure kinetics, especially for catalyzed systems, and the effect of conversion on physical properties) has not been performed.

Of particular importance for aerospace applications is the effect of the exposure to water on the performance of cyanate ester resins and composites. Cyanate ester monomers, particularly when catalyzed, may react with adventitious moisture to form carbamates. When subsequently heated, these can liberate CO₂ to form blisters or voids, critically weakening structural components.^{28,29} Although polycyanurates are known for their low coefficient of hygroscopic expansion and stability when exposed to cold water, they can undergo hydrolysis when exposed to hot water or under basic conditions,³⁰ via mechanisms that are specific to cyanurate linkages.³¹ The long-term degradation in physical properties caused by such hydrolysis is perhaps the dominant concern for many potential aerospace applications of polycyanurates, hence an understanding of the effects of moisture on polycyanurates as a function of network structure is of particular importance.

In what follows, we present a comparison of three different, but closely related, di(cyanate ester) monomers, BADCy, LECy and the aforementioned SiMCy (structures shown in Figure 1),

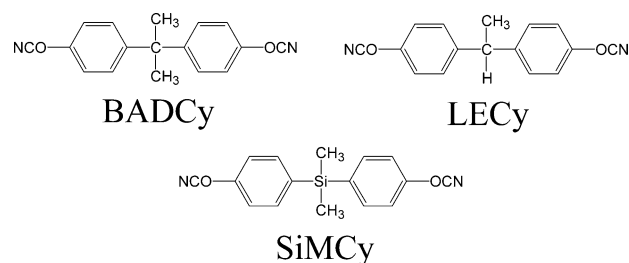


Figure 1. Chemical structures of the dicyanate ester monomers studied.

at conversions ranging from approximately 70 to above 90%. The cure conditions required to achieve a given level of conversion are compared, as are physical properties, such as glass transition temperatures before and after exposure to hot water, water uptake, density, and coefficient of thermal expansion. In the case of BADCy, many of these physical properties were observed by Georjon and Galy³² to behave contrary to expectations for the formation of typical macromolecular networks, because of the net creation of free volume as higher conversions were obtained.³³ A similar net creation of free volume with increasing conversion has been noted for certain high-temperature epoxy resins as well (see, for instance, the reports listed by Gupta and Brahatheeswaran).³⁴ The systematic study of these properties will shed important light on the relationships between network formation and physical properties, with potential application to a wide range of high-performance thermosetting resins. These relationships will not only help to provide a means for systematic optimization of physical properties of thermosetting polymers, but also provide valuable insight into how monomer chemistry shapes the physical process of network formation, a key remaining challenge in the field of thermosetting polymers.

2. EXPERIMENTAL SECTION

Materials. The dicyanate esters of bisphenol A (Primaset BADCy) and bisphenol E (Primaset LECy) were purchased from Lonza and used as received. “SiMCy”, a silicon-containing analog of Primaset BADCy, was synthesized according to a procedure which has been recently published,³⁵ and which closely follows earlier published procedures.^{19,36} Nonylphenol (technical grade) was purchased from Aldrich, and copper(II) acetylacetonate was purchased from ROC/RIC; both were used as received.

Sample Preparation. Batches of catalyst comprising 30 parts by weight nonylphenol to one part by weight copper(II) acetylacetonate were prepared by mixing the ingredients in a vial and heating to 60 °C while stirring vigorously until complete dissolution took place (typically 1–2 h). These batches were retained for up to 30 days. Because of the low humidity ambient environment, the only precautions taken when storing the Primaset BADCy and LECy resins were the use of tightly sealed containers and avoidance of exposure to high humidity environments. However, for the novel material SiMCy, for which the stability data are unknown, the sample was stored at or below 4 °C as an added precaution.

Uncured samples for differential scanning calorimetry (DSC) analysis were prepared by mixing monomer with 2 parts per hundred by weight of catalyst at 95 °C, following which the mixture was partially degassed at 95 °C for 30 min under reduced pressure (300 mmHg). To prepare cured samples, we prepared silicone molds made from R2364A silicone from Silpak Inc. (mixed at 10:1 by weight with R2364B platinum-based curing agent, degassed for 60 min at 25 °C and cured overnight at room temperature, followed by postcure at 150 °C for 1 h). The uncured cyanate ester mixture was mixed and degassed using the method for preparing DSC samples described

Table 1. Summary of DSC Data for Individual Dicyanate Monomers and Partially Cured Polycyanurates

monomer	final cure temp. (°C)	ΔH (J/g)	ΔH_0 (J/g)	χ	T_g (1st heating, °C)	T_g (2nd heating, °C)
BADCy	not cured		700 ± 30		-38 ± 1	300 ± 3
LECy	not cured		770 ± 30		-47 ± 1	288 ± 5
SiMCy	not cured		670 ± 30		-46 ± 1	262 ± 16
BADCy	125	182 ± 10		0.74 ± 0.02	134 ± 2	
BADCy	150	140 ± 1		0.80 ± 0.01	168 ± 1	
BADCy	200	56 ± 5		0.92 ± 0.01	244 ± 2	
LECy	125	192 ± 1		0.75 ± 0.01	142 ± 1	
LECy	150	108 ± 13		0.86 ± 0.02	183 ± 2	
LECy	170	69 ± 3		0.91 ± 0.01	213 ± 3	
SiMCy	100	154 ± 14		0.78 ± 0.02	91 ± 2	
SiMCy	125	101 ± 2		0.85 ± 0.01	152 ± 1	
SiMCy	150	47 ± 7		0.93 ± 0.01	186 ± 3	
BADCy 30/30	200	77 ± 8		0.89 ± 0.01	213 ± 3	

above, and then poured into the prepared mold (no release agent was used). The open mold and sample were then placed under flowing nitrogen at 25 °C and ramped 5 °C/min to the corresponding cure temperature and held at that temperature for 12 h to produce void-free discs measuring approximately 11.5–13.5 mm in diameter by 1–3 mm thick and weighing 200–400 mg. BADCy samples with a final cure temperature of 200 °C were first brought to 150 °C for 1 h before being ramped to 200 °C, in order to avoid excess vaporization of monomer. The material labeled “BADCy 30/30” was cured at 150 °C for 30 min and 200 °C for 30 min. The discs were used for thermomechanical analysis (TMA) and hot water exposure tests.

Characterization. DSC was performed on a TA Instruments Q200 calorimeter under 50 mL/min of flowing nitrogen. Samples were heated to their respective cure temperatures for 12 h and then cooled to 0 at 20 °C/min. The samples were then heated to 350 °C, then cooled to 25 °C and reheated to 350 °C, all at 10 °C/min. Oscillatory TMA was conducted with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. Partially cured discs were held in place via a 0.2 N initial compressive force with the standard ~5 mm diameter flat cylindrical probe while the probe force was modulated at 0.05 Hz over an amplitude of 0.1 N (with a mean compressive force of 0.1 N) and the temperature was ramped to 350 °C followed by two heating and cooling cycles between 100 and 200 °C (to determine thermal lag), all at 20 °C/min. Discs that were exposed to water were cycled between -50 and 50 °C to determine thermal lag before ramping the temperature to 350 at 20 °C/min to determine T_g . Linear coefficients of thermal expansion (CTEs) were determined from the dimension change of the cylindrical sample with respect to temperature. All values are reported in ppm/°C at 75 °C. Density of the cured samples was determined using solutions of calcium chloride in deionized water. Discs of the partially cured polycyanurates were placed in a vessel and two solutions, at different concentrations, were combined until a neutrally buoyant solution was obtained. The density of the neutral solution was measured by weighing a 10 mL aliquot of the solution using a volumetric flask. This value was compared to the expected density of a calcium chloride solution at the known concentration and ambient conditions. Fourier Transform Infrared Spectroscopy (FT-IR) was carried out using a Thermo Corporation Nicolet 6700 FT-IR Spectrometer in attenuated total reflectance mode with a resolution of 4 cm⁻¹. Spectra were collected by averaging 32 scans.

Moisture uptake experiments were performed using cured discs of uniform 11.7 mm diameter and 3 mm thickness. Prior to measurement, each disk was placed in a vacuum oven and weighed periodically until the weight stabilized to within 0.0001 g. After stabilization, each disk was placed into ~300 mL of deionized water maintained at a temperature of 85 °C. At periodic intervals after immersion, each sample was removed from the water, gently patted dry with a paper towel, and weighed a minimum of three times (all weights agreed to within 0.0003 g). Following the weighing procedures, which generally took less than 15 min, the samples were

reimmersed in the hot water. As a consequence of degradation, some samples became opaque, starting at corners, then spreading through the sample. After approximately 500 h, one of the opaque samples began to exhibit chalking during handling; at this point the experiment was halted. A separate batch of samples prepared in an identical manner was exposed to the 85 °C water for 96 h (enough time for equilibration when chemical degradation occurs much more slowly), then removed and tested via oscillatory TMA to measure “wet” glass transition temperatures.

3. RESULTS AND DISCUSSION

Our studies of dicyanate ester cure kinetics focused on the late stages (generally postvitrification) of cure because much kinetic data on the earlier stages is already available. Additionally, it is during the later stages of cure that the more unusual structure–property relationships have been observed. Three different dicyanate esters, Primaset LECy, Primaset BADCy, and SiMCy, a silicon-containing analogue of BADCy first synthesized by Wright,³⁶ were used for late stage cure kinetic studies, and their structures are shown in Figure 1.

In most cases, the monomers were brought to different degrees of cure by heating at different temperatures for 12 h. On the basis of the results of DSC experiments, cure temperatures were selected that gave approximate conversions of 0.7, 0.8, and 0.9 for each material, and can be seen in Table 1. To investigate the difference in polycyanurate properties, not only as a function of conversion but also as a function of cure schedule used to reach a given conversion, we cured a sample composed of the BADCy monomer for 30 min at 150 °C, then ramped it at 5 °C/min to 200 °C, and then held it at 200 °C for 30 min. These “BADCy 30/30” samples were used only for key physical property tests.

Late Stage Cure Kinetics of Di(Cyanate ester)s. The cyclotrimerization exotherm of unreacted cyanate groups was used to determine the extent of cure using the equation

$$\chi = \frac{(\Delta H_0 - \Delta H)}{\Delta H_0}$$

where ΔH_0 is the enthalpy of cyclotrimerization of the uncured monomer and ΔH is the residual enthalpy of cure for the partially cured material. On a molar equivalent basis, the enthalpy of cure was 102 kJ/equiv. for LECy and 98 kJ/equiv. for both BADCy and SiMCy. These values are very close to the generally accepted average of 100 kJ/equiv.,³⁷ although slightly higher than the 83–95 kJ/equiv. previously reported³⁸ for these catalyzed monomers (Table 1). For the later stages of cure, it

was found that the final cure temperature, rather than time, was by far the most significant factor in reaching a given degree of conversion. The BADCy material cured at 200 °C for 30 min had a conversion of 0.89, whereas BADCy cured at 200 °C for 12 h reached a conversion of just 0.92, illustrating the dramatic but very well-known effect of vitrification.

The values of conversion obtained for each cure temperature using the above equation are plotted in Figure 2. The

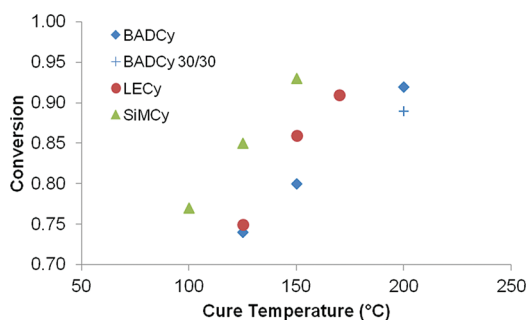


Figure 2. Conversion at 12 h vs cure temperature of BADCy, LECy, and SiMCy polycyanurates; conversion at 30 min vs final cure temperature for BADCy 30/30. The uncertainties in the conversions are approximately the size of the symbols, and are listed in Table 1.

temperatures required to reach a particular degree of conversion reflect the relative ease of late stage cure for the different monomers, with SiMCy being easiest, followed by LECy, and then BADCy (hence the relative horizontal displacement of each data set). In addition, a careful examination of Figure 2 reveals that, despite some scatter in the data, the data points for a given material tend to fall along a straight line, with the slope of the line connecting the data points for SiMCy being steeper than for BADCy, and the slope for LECy falling between the two. Thus, as expected, a small increase in cure temperature is most efficient at inducing further cure in SiMCy, while being least efficient in BADCy. Interestingly, the apparent linearity of the data implies that achieving additional conversion via increased cure temperature does not become significantly more difficult until almost complete conversion is attained (theoretically, the curves must become flat as they approach full conversion, but no flattening was clearly detectable over the selected range of conversions).

These observed differences in late stage cure behavior were somewhat surprising given the similarity in monomer molecular structure and peak cure exotherm temperatures, as well as the enthalpies of cyclotrimerization.³⁸ On the other hand, if the cyanate ester monomers are viewed as consisting of aryl cyanate arms attached to a “core” of variable molecular bond flexibility, then the SiMCy monomer would be expected to exhibit the greatest core flexibility, because of the longer Si–C bonds that feature a lower deformation energy, followed by the LECy, which is somewhat more flexible than the BADCy, because of lower steric hindrance around the core bonds. The relative core flexibilities are reflected in the fully cured T_g values for the monomers (Table 1), which increase in the order SiMCy < LECy < BADCy. When viewed from the standpoint of core flexibility, the most flexible core corresponds to the greatest ease of cure, a result previously observed for tricyanate esters as well.³⁹ These data suggest that the late stage cure kinetics may be determined principally by the need to significantly deform the segments of the network to accommodate further cyclotrimerization.

Properties of Partially Cured Polycyanurates. In cyanate esters, the glass transition temperature is not only a key physical property, it also provides a highly useful indication of the degree of conversion. The T_g of polycyanurate systems has been shown to follow a unique relationship with the extent of conversion (χ) and is accurately described by the diBenedetto equation¹⁷

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\chi}{1 - (1 - \lambda)\chi}$$

where T_{g0} and $T_{g\infty}$ are the monomer T_g and the T_g of the fully cured material, respectively, and were determined by DSC. Although the parameter λ may be calculated from experimental thermodynamic data such as the change in heat capacity at the glass transition, in general, as in this work, it is treated simply as an adjustable parameter. Using the values of T_{g0} and $T_{g\infty}$ shown in Table 1 for the appropriate monomer, a value for λ was calculated by solving the above equation for each individual sample. To calculate an overall value for λ , the values were combined in a weighted average, using the inverse of the calculated variance (determined through propagation of uncertainty) as the weighting factor. Values for λ of 0.38 ± 0.04 , 0.41 ± 0.06 , and 0.25 ± 0.07 were obtained for BADCy, LECy, and SiMCy, respectively. These values are similar to those obtained by Sheng et al.⁴⁰ for the commercial resin EX-1510, which is described as being quite similar to LECy. The diBenedetto plot can be seen in Figure 3.

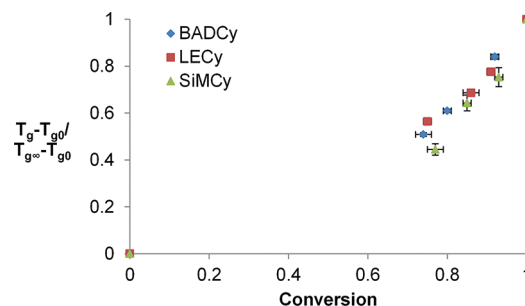


Figure 3. diBenedetto plot of BADCy, LECy, and SiMCy polycyanurates. Note that in some cases the uncertainties are smaller than the size of the symbols.

Of all the physical properties studied, the “wet” T_g of cyanate esters is perhaps the most important. This is because it is often used as the key determinant of maximum use temperature, and it provided perhaps the most unusual of the results reported herein. In Figure 4, the T_g s of partially cured polycyanurates as

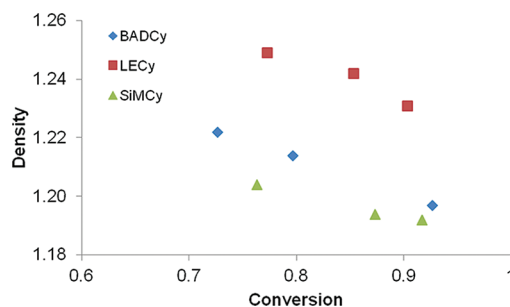


Figure 4. Dry and “wet” T_g s for BADCy, LECy, and SiMCy with different extents of cure prior to immersion.

measured by oscillatory thermomechanical analysis (OTMA) before and after immersion in hot water are illustrated. Note that the “dry” T_g values measured by OTMA on cured discs were higher than the corresponding T_g values obtained by in situ cure of melted monomer in the DSC by 8 ± 7 °C, which is not significant considering that the typical reproducibility of OTMA T_g measurements has been determined by us to be ± 9 °C.³⁵

The polycyanurates with the highest degree of conversion showed a decrease in the T_g on exposure to hot water. However, samples with a conversion below 85% experienced an increase in T_g after exposure to a hot/wet environment, whereas LECy at 85% conversion exhibited identical dry and wet T_g values. The increase in T_g after exposure to water of the polycyanurates with the lower degrees of cure is especially surprising because these materials displayed evidence of degradation, and the close adherence of cyanate esters to the diBenedetto equation suggests that degradation of the network should lead to significant reductions in T_g , as was observed by Georjon and Galy³³ and earlier reported by us for fully cured samples.³⁸

To investigate these matters more fully, we compared the FT-IR spectra of partially cured cyanate esters before and after exposure. The spectra of the SiMCy sample at 78% conversion, which showed the greatest extent of degradation, for example (Figure 5), showed a decrease in the bands at 2240–2280 cm^{-1}

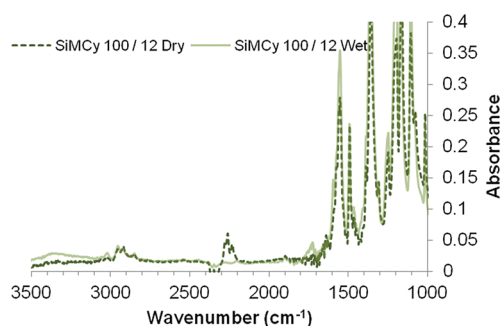


Figure 5. IR spectra of SiMCy cured at 100 °C for 12 h before and after immersion in hot water.

corresponding to cyanate ester groups and the appearance of bands at 1750 and 3400 cm^{-1} , indicative of carbamate C–O stretch and N–H stretch, respectively. However, a comparison between the spectra of BADCy samples after immersion (Figure 6) and SiMCy samples after immersion (Figure 7)

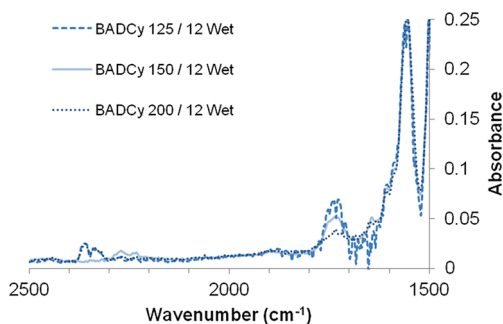


Figure 6. IR spectra of BADCy cured for 12 h at 125 °C, 150, and 200 °C after immersion in hot water.

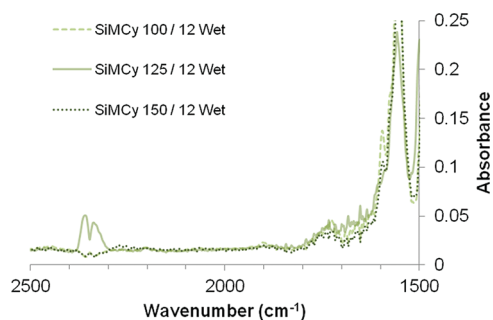


Figure 7. IR spectra of SiMCy cured for 12 h at 100 °C, 125, and 150 °C after immersion in hot water.

reveals that the characteristic bands for carbamate formation are present to a much greater extent in BADCy, despite the fact the BADCy showed the least amount of long-term weight gain associated with hydrolysis. On the other hand, carbamate formation was always more pronounced in less cured samples, as it should be, because only uncured cyanate esters should generate carbamate groups (Figure 8). Moreover, although

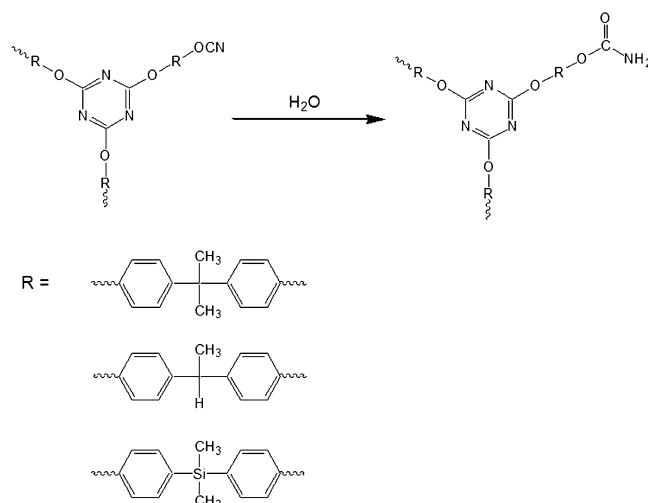


Figure 8. Conversion of cyanate ester to carbamate.

carbamate formation should result in some permanent weight gain, hydrolysis of the more prevalent cyanurate rings should account for the majority of the weight gain, and, unfortunately, the products of cyanurate hydrolysis, consisting of phenolic species, are difficult to detect unambiguously in FT-IR spectra, though they can be seen via near-IR spectroscopy.³¹

Thus, although FT-IR did confirm that at least some of the expected reactions indeed take place, by itself, it did not provide sufficient evidence to explain the unusual changes in T_g observed on exposure to hot water. It should be noted that, in the study of the hydrolysis of novolac type cyanate esters reported by Marella et al., the “wet” T_g was observed to stabilize at approximately 160 °C, even while further degradation of the network continued.³¹ We speculate that perhaps hydrolysis, which is expected to lead to the formation of two phenol groups in place of the attachment to the cyanurate cross-linking site, facilitates the formation of two hydrogen bonds in place of the covalent attachment, and thus, rather than destroying the network completely, simply substitutes a hydrogen bonded network for a covalent network, preserving a relatively high T_g (Figure 9).

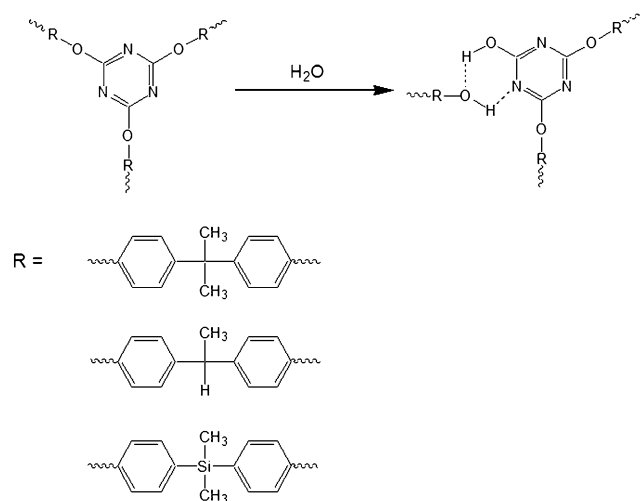


Figure 9. Hydrolysis of polycyanurate network.

We further speculate that the creation of phenol groups may actually catalyze further cyclotrimerization, and that at low conversions, the increase in T_g caused by the cyclotrimerization can outweigh the mitigated decrease in T_g caused by substitution of the covalent network bonding by hydrogen bonding. The proposed reaction would explain the apparent lack of cyanate ester peaks in the spectra of the supposedly partly cured samples shown in Figures 5–7. A careful examination of Figure 5 also shows an increase in the intensity of the peak corresponding to cyanurate formation near 1550 cm^{-1} , relative to the reference peak associated with phenyl groups near 1500 cm^{-1} , and similar increases were seen in the comparative spectra of BADCy and LECy as well. Cyclotrimerization would also explain the differences in carbamate formation among repeat unit chemistries. Because SiMCy cures the most readily at lower temperatures, it would be reasonable to expect that, in a scenario in which carbamate formation competes with cyclotrimerization, cyclotrimerization would be most favored in SiMCy while carbamate formation would be most favored in BADCy. Such speculation at least provides a plausible starting point for what is likely to be extensive further investigation needed to clarify this interesting, but highly important, phenomenon. In particular, the presence of competing chemical reactions during exposure to hot water implies that a simple time–temperature superposition (such as an Arrhenius relationship) may not be sufficient to relate accelerated aging data generated from hot water exposure to long-term predictions of performance in humid environments at lower temperatures in cyanate esters.

Closely related to “wet” T_g in importance for cyanate esters is the extent of water uptake. To examine water uptake, plots of weight gain on immersion at 85 °C versus $t^{1/2}/h$, in which t is the immersion time, and h the sample thickness (3 mm in this case), and for which the slope near the origin is related to the diffusion coefficient, are shown in Figure 10 for the three materials studied. As would be expected for networks of similar chemical composition, the diffusion coefficient for water appears similar for all three materials. However, over longer periods of time, certain trends begin to emerge. The water uptake for all three materials decreases with increasing conversion, except for BADCy, in which the water uptake is least at 89% conversion, then is slightly higher at 93% conversion. It should also be noted that at approximately 100

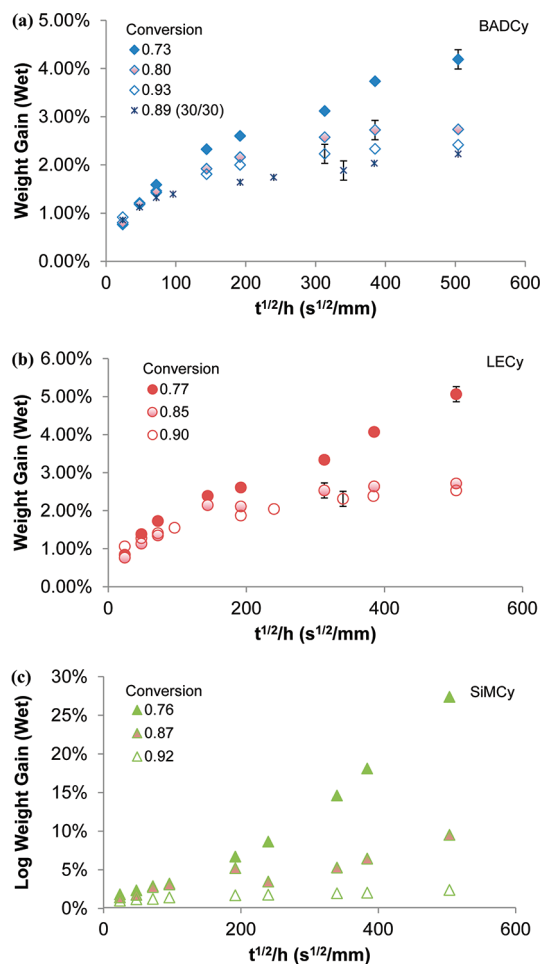


Figure 10. Weight gain vs $t^{1/2}/h$ for (a) BADCy, (b) LECy, and (c) SiMCy with different extents of cure, on immersion in 85 °C water. Note that the uncertainties (0.2%) are smaller than the symbols in c.

h of water exposure, the SiMCy polycyanurate with the lowest degree of cure became opaque white in color, possibly due to degradation of the resin network, which was accompanied by a large increase in moisture uptake.

The water uptake behavior of uncatalyzed and catalyzed BADCy as a function of conversion has been reported by Georjon and Galy,³³ with separate but very similar results published for BADCy with a different catalyst system by Hayashi.⁴¹ It was found that an increase in the degree of cure was accompanied by an increase in water absorption over conversion ranges of 82–100%. This effect was attributed to an experimentally determined increase in free volume with increasing conversion. We also recently published results³⁵ for water uptake of catalyzed BADCy, LECy, and SiMCy at conversions of 95–100% in which a positive correlation (significant at 94% confidence) between water uptake and conversion was observed, along with a negative correlation (also significant at 94% confidence) between density at room temperature and conversion.

Shimp and various co-workers^{42,43} studied the physical properties as a function of conversion for BADCy and LECy, and the dicyanate ester of bisphenol M (RTX366) using a zinc naphthenate catalyst (as opposed to the copper(II) acetylacetonate catalyst used for the results reported herein). Their results showed decreasing water uptake after immersion at 100 °C over conversion ranges of 73–82% for BADCy and 76–

88% for LECy. For the bisphenol M-based dicyanate ester, the water uptake was lowest at 89% conversion, slightly higher at 99% conversion, and moderately higher at 83% conversion. Combining these previous results, it thus appears that moisture uptake in cyanate esters tends to exhibit a minimum at 80–90% conversion, in agreement with the observations reported herein.

On the basis of the shape of the uptake curves seen in Figure 10, it appears that over the longer term, plasticization and network degradation play a significant role in water uptake, particularly at lower conversions. In fact, for the SiMCy sample cured at 100 °C, for which the measured dry T_g values ranged from 90 to 105 °C, it seems plausible that plasticization by hot water would eventually drive the T_g below the exposure temperature, resulting in a large increase in water uptake, as was observed experimentally. At lower conversions, the water uptake increases in the order BADCy < LECy < SiMCy, in accordance with the relative dry glass transition temperature (see Figure 4), with the lowest dry T_g resulting in the highest uptake at longer times. In these conversions, the weight gain curves tend to increase continually. At higher conversions, though, the relative performance of the materials changes, with SiMCy having the lowest uptake, followed by BADCy, then LECy, and with the curves flattening significantly with increasing time. Previous studies of moisture uptake have shown that the weight gain curve may be divided into an early segment in which almost all of the weight gain is reversible upon drying, and a later segment in which almost all of the weight gain is permanently retained even after drying.³¹ The early segment is thus dominated by physical ingress of water, whereas the later weight gain primarily reflects chemical degradation of the network.⁴⁴ Adopting this model for the data reported herein reveals that SiMCy appears to have the lowest capacity for water absorption, but the highest level of degradation, whereas LECy has the highest capacity for water absorption and BADCy has the least degradation.

In previously reported work, we noted that the water uptake of cyanate esters appears to depend on the density of cyanurate groups, with the highest density producing the highest water uptake at short exposure times.^{35,38} Moreover, according to the results of Georjon and Galy³³ and Hayashi,⁴¹ it is free volume associated with the formation of cyanurate groups that provides increased water uptake. The data reported herein show that SiMCy has the lowest concentration of cyanurate groups for a given conversion based on its density and equivalent weight, and confirmed by DSC measurements of the enthalpy of cure. Thus, the model of Georjon and Galy implies that it should have the least capacity for water absorption, as indeed it does. Examining the same data for BADCy and LECy would imply a slightly higher water absorption for LECy, as indeed is also the case. Comparisons of water uptake among the three monomers at conversions greater than 95% have confirmed these trends.³⁵

We have previously reported 96 h water uptake values for BADCy, LECy, and SiMCy at close to complete conversion; and in all cases, they are higher than the comparable values reported herein for systems at 90% conversion.^{35,38} Moreover, from the data reported herein, it is clear that the water uptake drops rapidly with increasing conversion at values of 70–80%, then stabilizes at higher conversions, whereas in the data of Georjon and Galy, the water uptake is relatively flat at conversions of 85–95%, then increases rapidly.³³ Thus, taken together, the data of Georjon and Galy along with our previously reported data and the presently reported data of Shimp and Ising,⁴² all indicate water uptake passing through a

minimum at a conversion of approximately 85–90% for BADCy and LECy, and perhaps at somewhat higher conversions for SiMCy. These results are readily explained as being due to competition between a self-reinforcing plasticization and degradation, which dominates at lower conversions, and free volume creation, which dominates at higher conversions. As the T_g of the resin approaches the exposure temperature, degradation becomes even more important, and dominates the results at even higher conversions, leading to the somewhat different water uptake behavior for SiMCy. Thus a relatively straightforward picture that explains all of the water uptake results to date on these catalyzed BADCy, LECy, and SiMCy systems is available.

Because of the potential importance of density in determining water uptake properties, we measured the densities of the polycyanurate networks at room temperature just prior to immersion in water. The results are plotted in Figure 11. As

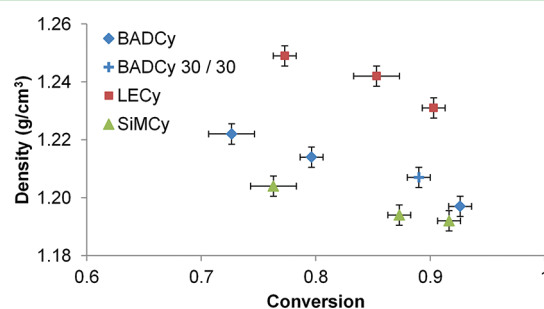


Figure 11. Density at room temperature vs conversion of BADCy, LECy, and SiMCy polycyanurates.

the degree of cure of each polycyanurate system increased, the density of the partly cured resin generally decreased. The most important aspect of the density data in terms of its connection with water uptake is the fact that the two variables do not correlate well. The minimum in water uptake does not correspond to a maximum in density, as might be expected based on arguments that water uptake in cyanate esters is controlled by free volume. Alternatively, at the conversions studied, it is clear that additional factors, such as the ease of plasticizing the network, primarily determine the water uptake.

Previous work on BADCy³³ and BADCy blends with LECy and SiMCy³⁵ at high conversions has shown that the coefficient of thermal expansion (CTE) tends to exhibit a small decrease with increasing conversion, although related recent work on polycyanurates has shown that high levels of free chain ends (which should disappear as conversion increases) in the network do not affect the CTE greatly.³⁶ Linear CTE data at 75 °C for the partially cured polycyanurate systems considered herein (Figure 12) appears to exhibit a slight decrease in CTE with increasing conversion, mainly at low conversions for SiMCy, and to a lesser extent, for LECy. However, not only are the experimental errors for these particular CTE measurements larger than normal due to the need to avoid in situ cure while performing oscillatory TMA, but the results at 75 °C were likely strongly influenced by the proximity of the glass transition, which is closest to the measurement temperature for SiMCy at the lowest conversion studied. Thus, whether the small trends in glassy-state CTE for polycyanurates seen at higher conversions also apply at lower conversions remains an unanswered question.

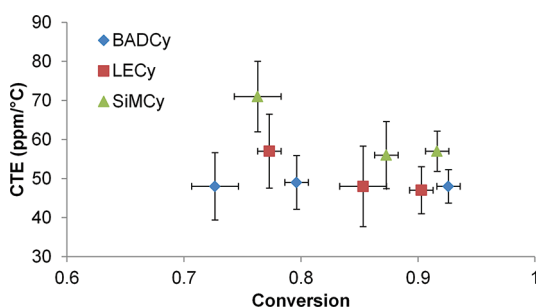


Figure 12. CTE at 75 °C vs conversion of BADCy, LECy and SiMCy polycyanurates.

4. CONCLUSIONS

The cure characteristics and corresponding physical properties of three similar bisphenol dicyanate ester monomers have been examined over conversions ranging from around 0.7 to 0.9. For all three monomers, the extent of cure depended much more on cure temperature than cure time. The degree of conversion achieved for a given cure temperature was greatest for the SiMCy dicyanate. The greater relative ease of cure of the SiMCy monomer may be attributed to the longer Si–C bonds, which may impart greater flexibility, allowing more cyanate groups to cyclotrimerize at high degrees of cure. The water uptake data, coupled with previously reported results for similar systems, reveal that as conversion of a polycyanurate increases the water absorption tends to pass through a minimum at 80–90% conversion. The water uptake in polycyanurates with high degrees of conversion reached a stable value at long times, whereas at low conversions the water uptake increased continually, presumably because of hydrolysis of the resin network. Surprisingly, polycyanurates with a low degree of conversion displayed an increase in T_g after exposure to hot water while the polycyanurates with a high degree of cure showed a decrease in T_g . The IR spectra of all polycyanurates exposed to hot water showed evidence of carbamate formation. The relative intensity of peaks corresponding to the carbamate functionality was greatest for BADCy and the least intense for SiMCy. For materials with the lowest degree of cure, the increase in T_g may be due to the formation of phenolic moieties resulting from hydrolysis of the polycyanurate network which are able to hydrogen bond and/or catalyze cyclotrimerization of unreacted cyanate groups, both of which would result in an increase in the T_g of the material, while also accounting for the observed differences in carbamate formation.

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