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

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14. 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 over 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<sub>g</sub> 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<sub>g</sub> upon exposure.

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

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KEYWORDS: Cyanate Ester, Polycyanurate, Resin, Cure Kinetics, Water Uptake.
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 over 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.
1. Introduction

Cyanate ester resins\textsuperscript{1-3} comprise a widely recognized class of high-temperature thermosetting polymers with numerous applications in aerospace and other high performance areas. In aerospace structures, they are best known as composite resins in combination with glass or polyethylene reinforcements for use in radomes and antenna structures\textsuperscript{4}, where their unusually low dielectric constant and low moisture uptake provide unique performance advantages. In addition to radomes and antennas, other 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\textsuperscript{5}, filament wound composite structures for airframes\textsuperscript{6}, heat shields for atmospheric re-entry\textsuperscript{4}, and metal insert molded control surfaces\textsuperscript{7}. Outstanding resistance to many forms of high energy radiation and the potential for very low out-gassing make cyanate esters desirable for satellite and other space structures\textsuperscript{8}, as well as in unusual applications such as magnet casings for prototype thermonuclear fusion reactors\textsuperscript{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 provides cross-linking\textsuperscript{10}, as well as the ease of blending with other monomers (for co-curing)\textsuperscript{11-13} or with thermoplastics (for toughening via reaction-induced phase separation)\textsuperscript{14,15}. Although some mechanistic details, particularly where catalysts are involved, remain disputed, the cure chemistry and kinetics of cyanate ester resins have been very well studied and most of the details are well understood. 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 equation\textsuperscript{16} 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”), 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”). Guenthner et al. 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, fluorinated cyanate esters, dicyclopentadiene dicyanate esters, biphenylated cyanate esters, and many types of cyanate ester nanocomposite materials. 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.

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), 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 density, thermal expansion, glass transition temperature, and water uptake. In the case of BADCy, many of these physical properties were observed by Georjon and Galy to behave contrary to expectations for the formation of typical macromolecular networks, due to the net creation of free volume as higher conversions were obtained. Similar unusual behavior has been noted for epoxy resins as well. 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 the procedure specified in the literature.¹⁸ 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 comprised of 30 parts by weight nonylphenol to one part by weight of 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 one to two hours). These batches were retained for up to 30 days. Due to 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 de-gassed at 95 °C for 30 minutes under reduced pressure (300 mm Hg). To prepare cured
samples, silicone molds made from R2364A silicone from Silpak Inc. (mixed at 10:1 by weight with R2364B platinum-based curing agent and cured overnight at room temperature, followed by post-cure at 150 °C for 1 hour) were prepared by de-gassing for 60 minutes at 95 °C and 300 mm Hg. The uncured cyanate ester mixture was mixed and de-gassed using the method for preparing DSC samples described 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 hours 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 hour 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 minutes and 200 °C for 30 minutes. The discs were used for thermomechanical analysis (TMA) and hot water exposure tests.

**Characterization.** DSC was performed on a TA Instruments Q2000 calorimeter under 50 mL/min. of flowing nitrogen. Samples were heated to their respective cure temperatures for 12 hours and then cooled to 0 °C at 20 °C/min. The samples were then heated to 350 °C, then cooled to 25 °C and re-heated 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. The 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 °C 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°C 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 10mL 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.

3. **Results and Discussion**

Our studies of dicyanate ester cure kinetics focused on the late stages (generally post-vitrification) of cure, since 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, were used for late stage cure kinetic studies and their structures are shown in Figure 1.

![Chemical structures of the dicyanate ester monomers studied.](image)

In most cases, the monomers were brought to different degrees of cure by heating at different temperatures for 12 hours. Based on 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, a sample composed of the BADCy
monomer was cured for 30 minutes at 150 °C, then ramped 5 °C/min to 200°C and then held at 200 °C for 30 minutes.

**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 \( \Delta H_0 \) is the enthalpy of cyclotrimerization of the uncured monomer and \( \Delta H \) is the residual enthalpy of cure for the partially cured material. On a molar equivalent basis, the enthalpy of cure was 102 kJ/eq. for LECy and 98 kJ/eq. for both BADCy and SiMCy. These values are very close to the generally accepted average of 100 kJ/eq.\(^1\), although slightly higher than the 83-95 kJ/eq. previously reported\(^ {30} \) 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 minutes had a conversion of 0.89 whereas BADCy cured at 200 °C for 12 hours reached a conversion of just 0.92.

The values of conversion obtained for each cure temperature using the above equation are plotted in Figure 2. The 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
Table 1. Enthalpies of cyclotrimerization for pure dicyanate monomers and residual cyclotrimerization enthalpies for partially cured dicyanates.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Final Cure Temp. (°C)</th>
<th>ΔH (J/g)</th>
<th>ΔH₀ (J/g)</th>
<th>χ</th>
</tr>
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<tbody>
<tr>
<td>BADCy</td>
<td>Not Cured</td>
<td>-</td>
<td>700</td>
<td>-</td>
</tr>
<tr>
<td>LECy</td>
<td>Not Cured</td>
<td>-</td>
<td>770</td>
<td>-</td>
</tr>
<tr>
<td>SiMCy</td>
<td>Not Cured</td>
<td>-</td>
<td>670</td>
<td>-</td>
</tr>
<tr>
<td>BADCy</td>
<td>125</td>
<td>180</td>
<td>-</td>
<td>0.74</td>
</tr>
<tr>
<td>BADCy</td>
<td>150</td>
<td>140</td>
<td>-</td>
<td>0.80</td>
</tr>
<tr>
<td>BADCy</td>
<td>200</td>
<td>60</td>
<td>-</td>
<td>0.92</td>
</tr>
<tr>
<td>LECy</td>
<td>125</td>
<td>190</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>LECy</td>
<td>150</td>
<td>110</td>
<td>-</td>
<td>0.86</td>
</tr>
<tr>
<td>LECy</td>
<td>170</td>
<td>70</td>
<td>-</td>
<td>0.91</td>
</tr>
<tr>
<td>SiMCy</td>
<td>100</td>
<td>150</td>
<td>-</td>
<td>0.78</td>
</tr>
<tr>
<td>SiMCy</td>
<td>125</td>
<td>100</td>
<td>-</td>
<td>0.85</td>
</tr>
<tr>
<td>SiMCy</td>
<td>150</td>
<td>50</td>
<td>-</td>
<td>0.93</td>
</tr>
<tr>
<td>BADCy 30/30</td>
<td>200</td>
<td>80</td>
<td>-</td>
<td>0.89</td>
</tr>
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</table>

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. 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, due to the longer Si-C bonds.
that feature a lower deformation energy, followed by the LECy, which is somewhat more flexible than the BADCy, due to lower steric hindrance around the core bonds. The relative core flexibilities are reflected in the fully cured $T_g$ values for the monomers, which increase in the order SiMCy (274 °C), LECy (291 °C), BADCy (298 °C). 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. 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 ($\chi$) and is accurately described by the diBenedetto equation,

$$\frac{T_g-T_{g0}}{T_{g\infty}-T_{g0}} = \frac{\lambda \chi}{1-(1-\lambda)\chi}$$
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 separately by DSC. A diBenedetto plot of BADCy, LECy, and SiMCy as shown in Figure 3 was then used to calculate the experimental parameter $\lambda$ (the non-normalized values are shown in Figure 7). Values for $\lambda$ of 0.44, 0.39 and 0.27 were obtained for BADCy, LECy and SiMCy respectively. These values are similar to those obtained by Sheng et al.\textsuperscript{32} for the commercial resin EX-1510, which is described as being quite similar to LECy. Because, in theory, the value of $\lambda$ depends on differences in heat capacity in the cured and uncured network, it should be quite similar for all three materials.

![Figure 3. diBenedetto plot of BADCy, LECy and SiMCy polycyanurates.](image)

The densities of the polycyanurate networks at different conversions are plotted in Figure 4. As the degree of cure of each polycyanurate system increased, the density of the partly cured resin decreased. Within experimental error, the magnitude of the density decreases appeared to be the same for BADCy and LECy, with perhaps a smaller decrease for SiMCy. Note also that the magnitude of the decrease observed for BADCy was similar to that observed by Georjon and Galy.\textsuperscript{28} It should also be noted that, because the coefficient of thermal expansion also decreases with increasing cure (see the discussion below), a decrease in the density at room temperature with increasing conversion does not
necessarily imply that the network expands during cure, only that more of the unoccupied volume of the network is “locked in” at higher conversions.

![Density vs conversion of BADCy, LECy and SiMCy polycyanurates.](image)

**Figure 4.** Density vs conversion of BADCy, LECy and SiMCy polycyanurates.

As mentioned previously, a greater extent of conversion resulted in a resin with a lower CTE (see Figure 5). Interestingly, the effect appears to be significantly greater for SiMCy, followed by LECy, then BADCy. The effect also appears to be greatest at lower conversions for SiMCy, and to a lesser extent, LECy. These results, at 75 °C, were likely strongly influenced by the proximity of the glass transition, which is closest to the measurement temperature for SiMCy, then BADCy, at the lowest conversion studied.
To examine water uptake, plots of weight gain on immersion versus $t^{1/2}/h$, in which $t$ is the immersion time, and $h$ the sample thickness, and for which the slope near the origin is related to the diffusion coefficient, are shown in Figure 6 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, some 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 hours 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. It was found that an increase in the degree of cure was accompanied by an increase in water absorption. This effect was attributed to an experimentally determined increase in free volume with increasing conversion. However, the materials in this study showed mainly a decrease in water uptake with increasing conversion despite an increase in apparent
Figure 6. Weight gain vs $t^{1/2}/h$ for (a) BADCy, (b) LECy and (c) SiMCy with different extents of cure.
free volume. An important difference, though, is that this study covered a conversion range of 70-90%, and included cases in which the $T_g$ of the partly cured resin was only modestly higher than the exposure temperature, whereas the work of Georjon and Galy covered a conversion range of 85-100% and involved much higher values of $T_g$ relative to the exposure temperature. Thus, the results reported herein appear to be driven primarily by plasticization and network degradation, 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 – 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.

A more detailed analysis results in the same general conclusion. At lower conversions, the water uptake increases in the order BADCy < LECy < SiMCy, in accordance with the relative dry glass transition temperature (see Figure 7), with the lowest dry $T_g$ resulting in the highest uptake at longer times. Also, at these low conversions, the weight gain curves tend to increase continually. At higher conversions, though, the relative performance of the materials change, 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. The early segment is thus dominated by physical ingress of water, while the later weight gain primarily reflects chemical degradation of the network. 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, while 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. Moreover, according to the results of Georjon and Galy, it is free volume associated
with the formation of cyanurate groups that provides for increased water uptake.\textsuperscript{28} The data reported herein show that SiMCy has both 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), as well as perhaps the least decrease in density (and presumably therefore, the least extent of free volume creation) associated with the formation of cyanurate groups during the late stage 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.

We have previously reported 96 hour 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.\textsuperscript{30} Moreover, from the data reported herein, it is clear that the water uptake drops rapidly with increasing conversion at conversions 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.\textsuperscript{28} Thus, taken together, the data of Georjon and Galy along with our previously reported data and the presently reported data, seem to indicate water uptake passing through a minimum at a conversion of about 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 results to date on these catalyzed BADCy, LECy, and SiMCy systems is available.

Of all the physical properties studied, the “wet” T_g of cyanate esters is perhaps the most important, since it is often used as the key determinant of maximum use temperature, yet it provided
perhaps the most unusual of the results reported herein. In Figure 7, the $T_g$s of partially cured polycyanurates as measured by oscillatory thermomechanical analysis (OTMA) before and after immersion in hot water are illustrated. 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, while 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 Galy\textsuperscript{28} and earlier reported by us for fully cured samples.\textsuperscript{30}

![Figure 7. Dry and “Wet” $T_g$s for BADCy, LECy and SiMCy with different extents of cure.](image)

In order to investigate these matters more fully, the FT-IR spectra of partially cured cyanate esters was compared before and after exposure. The spectra of the SiMCy sample at 78% conversion, which showed the greatest extent of degradation, for example (Figure 8), showed a decrease in the bands at 2240-2280 cm$^{-1}$ corresponding to cyanate ester groups and the appearance of bands at 1750 cm$^{-1}$ 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 9) and SiMCy samples after immersion (Figure 10) 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 11). Moreover, although 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.33
Figure 9. IR spectra of BADCy cured for 12 hours at 125 °C, 150 °C and 200 °C after immersion in hot water.

Figure 10. IR spectra of SiMCy cured for 12 hours at 100 °C, 125 °C and 150 °C after immersion in hot water.

Figure 11. Conversion of cyanate ester to carbamate.
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 about 160 °C, even while further degradation of the network continued. 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 12). We further speculate that the creation of phenol

![Figure 12. Hydrolysis of polycyanurate network.](image)

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 8-10. It would also explain the differences in carbamate formation among repeat unit chemistries. Since 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 ageing data generated from hot water exposure to long-term predictions of performance in humid environments at lower temperatures.

4. Conclusions

The cure characteristics and corresponding physical properties of three similar bisphenol dicyanate ester monomers have been examined over conversions ranging from around 0.75 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 of the partially cured polycyanurates decreased with increasing conversion with the exception of BADCy cured at 200 °C with a short cure time (30 minutes). This water uptake data, coupled with that reported previously for partially cured BADCy reveal that as conversion of a polycyanurate increases the water absorption also decreases initially, then increases with further conversion. This minimum in water absorption occurs at approximately 85-90% conversion for BADCy. Polycyanurates with high degrees of conversion reached a plateau in water uptake, while polycyanurates with low conversions did not reach a plateau and water uptake continued to increase at long times, presumably due to 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 had a decrease in T<sub>g</sub>. 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<sub>g</sub> may be due to formation 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<sub>g</sub> of the material, while also accounting for the observed differences in carbamate formation.

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