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INSIGHTS INTO MOISTURE UPTAKE AND PROCESSABILITY FROM NEW CYANATE ESTER MONOMER AND BLEND STUDIES

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ABSTRACT

Two major limiting factors in the use of cyanate ester resins for high-temperature aerospace applications are durability in hot/wet environments and the trade-off between obtainable glass transition temperatures and ease of processing. In order to understand how the molecular-level structure of cyanate ester resins relates to both of these issues, studies of cyanate ester monomers with novel chemical structures as well as studies of monomer blends are underway at the Air Force Research Laboratory. In particular, new tricyanate ester monomers containing mixtures of stereochemical isomers have exhibited significantly improved processability, while studies of ternary monomer blends provide a unique means of testing various mechanisms of moisture uptake.

1. INTRODUCTION

Polycyanurates (also known as “cyanate ester resins”) have emerged as an important class of thermosetting polymer composite resins in both current and developmental air and space applications [1-3]. Examples of current or previously proposed structures employing cyanate ester resins include nose radomes on the BAC-111 test bed aircraft [4], heat shields on Mars mission vehicles [5], solar panel support structures on the MESSENGER spacecraft [6], and airframe structures on supersonic missiles [7]. Polycyanurates are valued for their inherent fire resistance, low moisture uptake, stability in cold water, and maximum use temperatures that significantly exceed those of epoxy resins with corresponding temperature-dependent monomer viscosity characteristics [8]. In addition, cyanate ester monomers exhibit low toxicity, very little shrinkage or out-gassing upon cyclotrimerization, and, particularly for systems that are liquids at room temperature, favorable solubility and viscosity characteristics for the addition of co-monomers [9] or toughening agents [10]. Herein we report on our most recent research efforts both to develop novel cyanate esters with improved moisture resistance and processability, as well as to understand the mechanisms of moisture uptake in cyanate ester resins. In so doing, we present new data on the laboratory-scale synthesis and physical characterization of new cyanate ester monomers, comparable commercially available materials, and co-monomer blends.

There are several means by which the absorption of moisture negatively impacts the physical properties and processing of cyanate ester resins. First, ambient moisture can react with the uncured monomer to produce carbamates, particularly in the presence of transition metal-containing catalysts [11]. When heated to above 200°C, these liberate CO₂, resulting in blisters

and porosity. Secondly, prolonged exposure to heat and humidity or hot water will result in depolymerization and reversion of cyanate ester groups to phenol groups, thereby lowering the glass transition (and hence, maximum use) temperatures significantly [12]. Finally, ambient moisture absorbed in a cured polycyanurate can vaporize during rapid heating, leading to delamination or bubble formation, a process that has been documented for other high-temperature resins [13]. Although engineering controls can be employed to limit exposure to moisture, the development of cyanate ester formulations with reduced moisture uptake represents a more robust and potentially more affordable approach to decreasing or eliminating these negative impacts.

2. EXPERIMENTATION

2.1 Materials

The dicyanate esters of Bisphenol A (Primaset® BADCy) and Bisphenol E (Primaset® LECy) were purchased from Lonza and used as received. Two additional cyanate ester resins were also investigated. “SiMCy”, a silicon-containing analog of Primaset® BADCy, was synthesized according to the procedure specified in the literature [8]. Racemic 1,3,5-Tris(1-(4-cyanatophenyl)ethyl)benzene, herein designated as “RTCy”, a room-temperature liquid tricyanate ester whose synthesis is reported elsewhere [14], was synthesized at NAWCWD China Lake and provided to AFRL for evaluation. Nonylphenol (technical grade) was purchased from Aldrich, and Copper (II) acetylacetonate was purchased from ROC/RIC; both were used as received.

2.2 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 materials, SiMCy and RTCy, for which the stability data are unknown, the samples were stored at or below 4°C as an added precaution.

Uncured samples for differential scanning calorimetry (DSC) analysis were prepared by mixing monomer(s) and catalyst (if needed) 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 for 1 hour at 150°C followed by 24 hours at 210°C to produce void-free discs measuring approximately 11.5-13.5 mm in diameter by 1-3 mm thick and weighing 200-400 mg. The temperature ramp rate during cure was 5°C/min. Small samples weighing 5-10 mg were removed from the discs for further DSC analysis, while the discs themselves were used for density determination, thermomechanical analysis (TMA), and hot water exposure tests.

2.3 Characterization Techniques

DSC was performed on a TA Instruments Q2000 calorimeter under 50 mL/min. of flowing nitrogen. Samples were heated to 350 °C, then cooled to 100 °C and re-heated to 350 °C, all at 10 °C/min. When used to determine the melting point, an initial program consisting of alternate heating and cooling steps at 5°C/min. between 0°C and 100°C was included prior to the first heating at 10°C/min. Dynamic 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 mean 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 and the temperature was ramped twice (heating and cooling) between 100 °C and 200 °C (to determine thermal lag) with a final heating to 350 °C, all at 10 °C/min. For samples previously exposed to hot water, the heating rate was increased to 20 °C/min and the segments were run in reverse order to minimize drying before determination of the glass transition temperature.

Dynamic TMA works in much the same way as the more familiar DMTA (dynamic mechanical thermal analysis) with two key exceptions. First, the oscillatory force applied to the sample is superimposed on a mean compressive load, so that the sample is always under (time-varying) compression. Secondly, the entire sample is not placed under load. Although a thin layer of oil can be used to ensure complete contact between probe and sample, when high temperatures (such as those used in the experiments reported herein) are employed, this practice is usually avoided due to thermochemical stability concerns. As a result, not only does the probe itself cover just part of the sample, but even parts of the sample directly under the probe may not be in full contact. Thus, quantification of the compressive modulus is not reliable (except on a relative basis within the same run).

The density was determined by placing discs in solutions of CaCl₂ (as the dihydrate) and deionized water and varying the CaCl₂ concentration until neutral buoyancy was observed on bubble-free samples over a period of several minutes. The density of the neutrally buoyant solution was determined by placing 10.00 mL in a volumetric flask (calibrated with deionized water at 20 °C) and weighing, and checked against the predicted density of the solution at ambient temperature based on the known concentration of CaCl₂. Prior to thermomechanical analysis, some discs were also placed in approximately 300 mL of deionized water at 85 °C for 96 hours, with sample dimensions and weight measured before and after exposure.

2.4 Analysis Techniques

Enthalpies of polymerization were determined from DSC using the measured heat flow rates calibrated against a sapphire standard, with the subsequent heating run used as the baseline. Glass transition temperatures from DSC analysis were based on the mid-point of the transition, as identified by the TA Universal Analysis software package. Glass transition temperatures from dynamic TMA analysis were based on the peak value of either the loss modulus (E'') or $\tan \delta$ (if these peak occurred in conjunction with an approximate mid-point of the drop in storage modulus), and were corrected for thermal lag. Thermal lag was an issue in the dynamic TMA measurements due to the relatively high heating rate used (10 °C/min or 20 °C/min). These heating rates, which were higher than those normally employed during dynamic mechanical analysis, were necessary because, for cyanate esters, the glass transition temperatures can far exceed maximum cure temperatures. As a result, a traditional, slow heating rate of 2 °C/min or less would create considerable risk of unwanted *in situ* post-cure prior to reaching the glass transition temperature during the measurement process. A rapid heating rate also minimized the amount of drying that “wet” samples experienced prior to measurement of the glass transition temperature.

To correct for thermal lag, the temperature range was cycled twice well below the glass transition temperature (100-200°C) at the heating rate of interest. For “wet” samples, this cycling was performed once the sample had dried out after measuring the glass transition temperature. During this cycling event, the sample thickness (as indicated by the probe displacement) was affected only by thermal expansion, thus making it a function solely of the average actual temperature. The (thermocouple) temperature difference between two points having the same displacement was then taken as the thermal lag between heating and cooling at the rate of interest. Although this value was nearly constant over most of the heating range; the value corresponding to a thermocouple temperature of 120°C during cooling was chosen as the basis for all measurements, for consistency. The actual sample temperature was then corrected for this thermal lag by subtracting (or adding) half of the previously determined difference from the thermocouple temperature during heating (or cooling, respectively). The typical thermal lag value was 5-7°C for heating rates at 10°C/min, and 6-12°C for heating rates of 20 °C/min. The thermal lag thus computed was with respect to the temperature recorded at the thermocouple, which was placed adjacent to but not touching the outer edge of the sample, rather than the programmed temperature.

Figures 1-3 illustrate the procedure used to determine thermal lag. Figure 1 shows the thermocouple temperature and sample displacement as a function of time during the cycling event. During this event, the displacement of the probe is due only to the cumulative effect of thermal expansion of those parts of the sample that are in good contact with the probe surface. It thus represents the average temperature within the regions of the sample in good contact with the probe. As the air surrounding the probe is heated or cooled (as indicated by the thermocouple temperature), heat is transferred to or from the sample, first to the surface by convection, then to the interior by conduction. As a result, the average temperature in a given region of the sample will lag the surface temperature by a small amount, as can be seen in Figure 1. During periods of heating or cooling at a constant rate, the delay time will remain constant. The temperature difference between the region probed and the thermocouple will therefore be the delay time multiplied by the heating rate.

Figure 2 illustrates how the temperature difference between the region probed and the thermocouple can be determined regardless of the actual boundaries of the region being probed. In Figure 2, the data from Figure 1 are plotted to show the displacement as a function of the thermocouple temperature during cycling. A reproducible loop is obtained, because during heating the region probed is slightly cooler (and therefore at lower displacement), while during cooling it is slightly warmer (and therefore at higher displacement) for a given thermocouple temperature. Since the displacement represents the average temperature of the region probed, points on the loop at the same displacement represent points at which the average temperature of the region being probed are identical. Since this temperature changes linearly with heating rate, the difference in temperature between points with equal displacement will simply be twice the temperature lag of the region probed, as long as the heating and cooling rates used to make the determination are equal.

In Figure 3, the data in Figure 2 are re-plotted after applying a correction for thermal lag to the thermocouple temperature. The correction was determined by taking half of the difference in temperature between the points identified in Figure 2 and scaling the correction to the measured rate of thermocouple heating. As a result, the loop in Figure 2 collapses into a nearly constant and highly linear curve, except near the temperature extremes where the heating rate is not constant. A careful examination of Figure 3 reveals a slight curvature in the displacement near the upper end of the temperature range. This effect could be due to enhanced creep of the sample at higher temperatures, and is almost always present in TMA data of this type. As a result, the correction for thermal lag was computed at an actual temperature corresponding to about the 25th percentile of the range rather than at the mid-point.

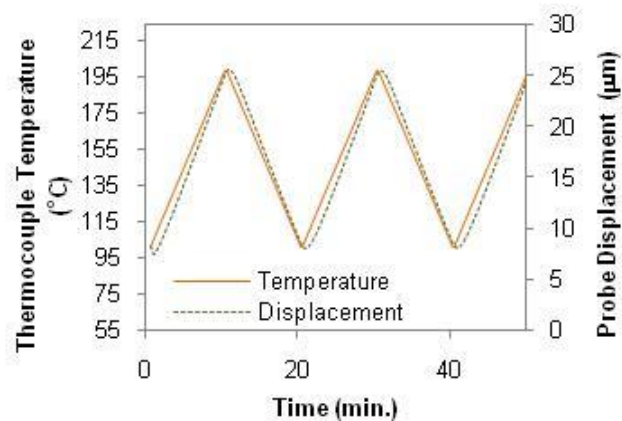


Figure 1. Raw TMA data from sample “Mix2”, showing the effect of thermal lag (due to the time needed for heat to be transferred to the interior of the sample) on probe displacement.

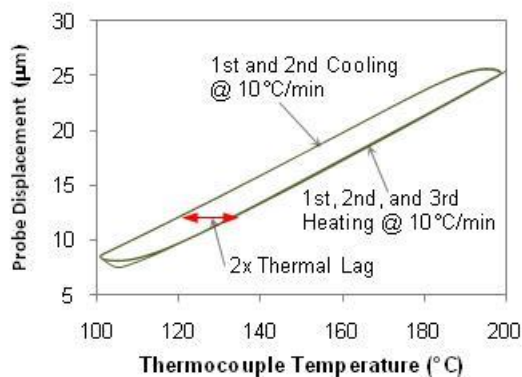


Figure 2. Illustration of how a correction for thermal lag can be computed from the “loop” produced during cyclic heating and cooling of a TMA sample undergoing only thermal expansion and contraction, using the data from Figure 1.

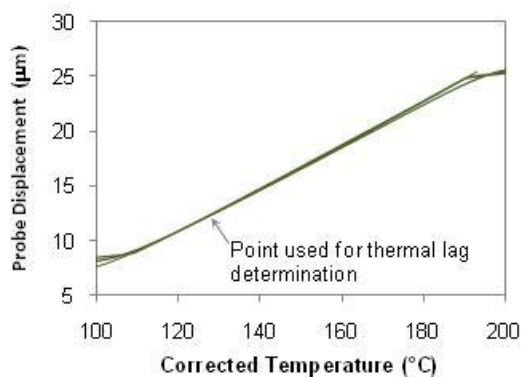


Figure 3. Data from Figure 2, after applying the correction (proportional to heating rate) for thermal lag as illustrated in Figure 2.

3. RESULTS

Our study of cyanate ester resins to date has focused on three different material chemistry aspects that can affect properties. First, we examined the effect of molecular architecture by comparing Primaset® BADCy, Primaset® LECy, SiMCy, and RTCy. For rough comparison purposes, some data for the experimental compound ESR 255 (1,1,1-tris(4-cyanatophenyl)ethane) from literature sources [15] has also been provided though it should be noted that the techniques used to collect this data differ in their details (such as heating rates) from those used with the other three resins. Secondly, we examined the effect of blending the Primaset® BADCy and LECy with each other and with SiMCy. Lastly, we examined the effect of including catalyst on the performance of the Primaset® LECy. Table 1 lists all formulations prepared and tested at AFRL.

Table 1. Sample summary

Sample ID	Component (wt%)				Catalyst Level (phr)
	BADCy	LECy	SiMCy	RTCy	
RT0	0	0	0	100	0
LE0	0	100	0	0	0
LE2	0	100	0	0	2.0
BA2	100	0	0	0	2.0
SM2	0	0	100	0	2.0
Mix1	68	17	15	0	2.0
Mix2	75	0	25	0	2.0
Mix3	0	75	25	0	2.0
Mix4	17	17	67	0	2.0

The chemical structures of LECy, BADCy, SiMCy, and RTCy are shown in Figure 4. As can be seen, adding a methyl group to the central carbon in LECy produces a structure equivalent to BADCy. Similarly, substituting a silicon atom for the central carbon atom in BADCy yields the structure of SiMCy. RTCy can be visualized as a “three armed” version of LECy, having the same chemical functionality but possessing a different cross-linking architecture. In addition, RTCy has three chiral centers, producing four possible stereoisomers. Chemical analysis techniques described elsewhere [14] have shown that a mixture of these stereoisomers is present in RTCy.

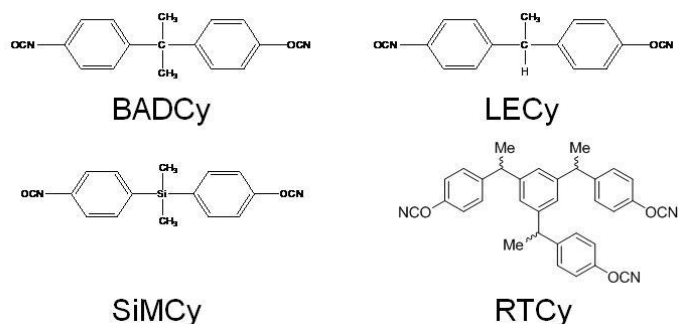


Figure 4. Chemical structures of the cyanate ester monomers studied.

Note that Mix1 and Mix2 are rich in BADCy, Mix3 is rich in LECy, and Mix4 is rich in SiMCy. Due to its high reactivity, a catalyzed version of RTCy could not be formed into a high quality specimen using the cure methods investigated. Thus, to facilitate comparisons we prepared an additional specimen of LECy with no catalyst added (sample LE0) having similar dimensions. According to DSC analysis of residual enthalpy of cure [14], the conversion of LE0 on curing at 210°C for 24 hours was about 90% despite the absence of catalyst.

3.1 Physical Properties Prior to Exposure

Table 2 summarizes the DSC data obtained on the various monomers and their mixtures. The reported melting points (T_m) correspond to peak endotherm temperatures from the first heating on the as-mixed and de-gassed sample. Thus, the extent of crystallinity in the samples is unknown, meaning that the enthalpy of melting values are not those of the pure compounds. In Table 3, the density, CTE, and dry dynamic TMA data are listed for each sample. Based on earlier work with cyanate esters, the best estimates of the standard deviations for these data are 1-2 °C for DSC and TMA temperatures, 10-15% of the reported value for heats of melting and cure, and 1 ppm/°C for CTE values. For the density measurements, tests with replicate samples indicated a standard deviation of 0.001 g/cm³.

Table 2. DSC analysis of uncured and *in-situ* cured cyanate esters

Sample ID	T_m (°C)	ΔH_m (J/g)	ΔH_{cure} (J/g) ^a	ΔH_{cure} (kJ/eq.) ^{a,b}	$T_{cure-max}$ (°C)	$T_{g,in-situ-cure}$ (°C) ^c
RT0	n/a	n/a	660	110	323	281
LE0	n/a	n/a	730	93	314	288
LE2	n/a	n/a	630	83	204	291
BA2	79	55	680	95	199	298
SM2	55	13	590	87	201	274
Mix1	66	8	680	94	199	296
Mix2	67	4	560	79	209	297
Mix3	n/a	n/a	600	82	207	284
Mix4	n/a	n/a	630	92	201	266

^aResidual cure after de-gassing at 95°C for 30 min.

^bAssumes pure monomer

^cTotal cure consists of 95°C for 30 min, ramp to 350°C at 10°C/min, and cool to 100°C at 10°C/min.

3.1.1 Effect of Monomer Structure

As shown in Table 2, the enthalpy of cure for the pure compounds ranged from 83-110 kJ per mole of cyanate ester groups, which is in agreement with numerous other studies [2] and also consistent with a standard deviation of 10-15% of the reported value. The catalyzed monomer structures also all cured at around the same temperature, thus the reactivity of cyanate groups in these monomers appears quite similar. Of the four compounds studied, melting points were seen for only BADCy and SiMCy. The widely reported melting point of BADCy is 79°C [2], while the melting point reported previously for SiMCy is 60°C [8], in reasonable agreement with the results shown in Table 2. Although LECy has a reported melting point of 29°C [2], it did not crystallize after melt blending. The RTCy also exhibited no signs of crystallinity via DSC. The presumably low melting point of this compound may be due to a combination of factors, including its similarity in chemical functionality to LECy, as well as the presence of multiple stereoisomers.

Table 3. Density and TMA analysis of cured cyanate esters

Sample ID	Density (g/cm ³)	Volume (cm ³ /mol)	CTE (m/m°C) ^a	T _{g, E''} (°C)	T _{g, tan δ} (°C)	tan δ at T _{g, tan δ}	E' Ratio ^b
RT0	1.177	436.4	59 x 10 ⁻⁶	301	305	0.40	0.48
LE0	1.234	214.2	65 x 10 ⁻⁶	281	282	0.52	0.39
LE2	1.220	216.6	66 x 10 ⁻⁶	283	288	0.57	0.22
BA2	1.201	231.7	61 x 10 ⁻⁶	267	272	0.62	0.32
SM2	1.173	251.0	76 x 10 ⁻⁶	276	280	0.48	n/a ^c
Mix1	1.195	232.7	63 x 10 ⁻⁶	31	316	0.62	0.11
Mix2	1.187	237.7	65 x 10 ⁻⁶	304	306	0.60	0.26
Mix3	1.211	224.0	71 x 10 ⁻⁶	247	251	0.61	0.32
Mix4	1.190	238.1	71 x 10 ⁻⁶	268	271	0.59	0.25

^adetermined at 150°C, average of values determined on 2nd and 3rd heating

^bThe value of E' at T_{g, tan delta} + 30°C divided by the value of E' at T_{g, tan delta} - 30°C

^cValue not determined due to early run termination

As expected, the data in Table 3 show that the molar volume increases in the order LECy, BADCy, SiMCy, RTCy. RTCy is considerably more differentiated in terms of architecture than the others, so detailed comparisons including it are more difficult. Among the remaining three resins, adding a methyl group to LECy (to give BADCy) increased the volume by 15.0 cm³/mol, while substituting a silicon atom for the quaternary carbon atom in BADCy (to produce SiMCy) added 19.3 cm³/mol. According to correlations developed by Bicerano, [16], the extra methyl group would have added about 17.0 cm³/mol while substitution of silicon for carbon would have added 23.5 cm³/mol. These correlations are for linear polymers rather than tightly cross-linked thermosetting resins, so it is not surprising that the actual added volumes were somewhat less than predicted. Analogous correlations for the van der Waals volume predicted increases of about 9.5 cm³/mol for both the methyl addition and silicon substitution. Since the van der Waals volume is based on the sizes of atoms and the lengths of chemical bonds, the rated accuracy of its predicted value (1.8% standard error) should be valid for thermosetting resins.

The packing coefficient of a solid refers to the ratio of the van der Waals volume to the total volume. The total volume of most amorphous polymers equals 1.5 times the van der Waals volume to within 10% [17], that is, their packing coefficients are around 0.67. For crystalline cyanate esters such as BADCy, the packing coefficients are typically 0.68-0.7 [2]. Based on the preceding data, the local packing coefficients for methyl addition and silicon substitution were about 0.65 and about 0.5, respectively. Thus, the addition of a methyl group to form BADCy from LECy should have little effect on packing, while the substitution of silicon to form SiMCy should decrease the overall packing coefficient, and therefore increase the free volume, of the system. Since an increase in free volume is correlated with a lower glass transition temperature (T_g), the density data and correlations for van der Waals volume lead to the expectation that BADCy and LECy will exhibit a similar T_g, while SiMCy will show a lower T_g. In fact, the DSC T_g data for *in-situ* cured LECy, BADCy, and SiMCy exhibited these relationships.

The T_g data obtained from dry TMA measurements on discs cured at 210°C, however, did not show the same trend. Although both LECy and SiMCy showed T_g values that were similar to those obtained via DSC, the T_g obtained for BADCy via TMA was around 30°C lower. Though not cured at temperatures higher than 210°C prior to measurement, during the TMA measurements, the samples were heated to 350°C at a rate of 10°C/min, thereby replicating the *in-situ* DSC cure profile. Thus, an easy method of assessing the effects of the differing cure profiles of TMA and DSC samples on the resultant T_g values is simply to re-run the TMA

sample after the initial scan. When a previously tested sample of BADCy was scanned a second time in the TMA, the Tg of the sample increased to around 305°C, matching the value expected on the basis of the DSC results. When a previously tested LECy sample was scanned a second time, however, the Tg actually decreased by 5-10°C, to around 280°C.

The differences in cure under discussion, although discernible, are likely quite small in terms of the overall conversion of monomer. The Tg of cyanate esters is quite sensitive to small differences in the extent of cure at high conversions [2]. Interestingly, for RTCy, the Tg measured after cure in the DSC was lower than that found by dry TMA after curing at 210°C. This result, along with the slight decrease in the Tg of LECy seen after heating to 350°C, may be due to thermal degradation of these materials (which are quite similar in chemical functionality though differing in cross-link architecture) when exposed to temperatures above 300 °C.

The coefficient of thermal expansion (CTE) values obtained via TMA were within 2 ppm/°C of those reported for BADCy and LECy [2]. The CTE value obtained for SiMCy was somewhat lower than previously reported [8], but still well above that of either BADCy or SiMCy. The CTE value for RTCy was slightly lower than that of BADCy. Generally, there is an inverse relationship between CTE values and the glass transition temperature for polymers. Thus, the relative CTE values for the resins studied may simply reflect their relative glass transition temperatures in the fully cured, non-degraded state.

Although RTCy had the highest molar volume of all the resins examined, it possesses an “extra” effective cross-link in the form of the trisubstituted benzene ring, which further constrains molecular motion once the cyanurate rings form. As a result, it has an effective cross-link density about 50% higher than the other resins when cured. This difference in architecture may explain the distinctive features of the dry TMA data, including a lower peak value of $\tan \delta$ and a smaller relative drop in E' above Tg, associated with the RTCy sample.

3.1.2 Effect of Blending and Catalyst Level

Blending of the cyanate ester monomers brought about several benefits in physical properties. For blends rich in BADCy (Mix1 and Mix2), crystallization was mostly suppressed, and for blends rich in LECy and SiMCy (Mix3 and Mix4, respectively), it was completely eliminated, allowing for (possibly supercooled) liquid processing at room temperature. The Tg values obtained via DSC tended to follow the Gordon-Taylor equation, with the exception of Mix3, which was anomalously low. The Tg of Mix3 by TMA was also anomalously low, and a second scan of this sample increased the Tg by almost 40°C, showing both a lack of full cure at 210°C and possibly a lower degree of cure even after heating to 350°C. On the other hand, the mixtures rich in BADCy exhibited higher than expected Tg values, to a small extent when measured via DSC after cure to 350°C, and to a larger extent when measured via TMA after cure at 210°C. The CTE values for the blends were within 2 ppm/°C of the results predicted by a simple linear (in volume fraction) rule of mixtures. The DSC cure parameters also were not significantly affected by blending. The density values were generally in line with a linear rule of mixtures, with the exception of Mix4, which showed an anomalously high density.

The long cure time at 210°C allowed the LECy without catalyst to achieve nearly the same Tg as the catalyzed version, suggesting that a high degree of cure was obtained in both samples, despite a nearly 100°C difference in DSC peak exotherm temperatures. DSC and FT-IR analyses reported elsewhere [14] showed a conversion of around 90% for the uncatalyzed LECy, compared to near 100% for the uncatalyzed RTCy and the catalyzed LECy. In addition, the uncatalyzed LECy system exhibited a slightly higher density, which may be due to its lower degree of cure, since LECy is known to expand during the final stages of cure [18]. Otherwise, the dry properties of the resins were not greatly affected by catalyst level for LECy. The catalyst type and level have been shown to be important, however, for properties such as long-term thermo-oxidative and hydrolytic stability [2,11].

3.2 Effect of Moisture

The two key experiments used to assess the effect of moisture on the samples were weight gain and “wet” TMA, with a summary of the results provided in Table 4. Initially, we attempted to use the same protocol for both dry and wet TMA experiments (these runs are noted in the table), however, we noticed that the use of this protocol enabled a significant amount of water to be lost during the determination of thermal lag. Since, ideally, the only changes in the sample should be due to thermal expansion when determining the thermal lag, an unnecessary complication was introduced. Moreover, since the window for determining thermal lag encompassed T_g in some samples but not others, and since drying rates tend to increase rapidly above T_g , another source of undesired variability was introduced.

To address these issues, the protocol was altered in two ways. First, the determination of thermal lag was moved to the end of the measurement, at which point the samples were dry and mechanically stable. Although there could be a slight difference in the thermal lag between a wet and a dry sample, we could detect no systematic change. Moreover, such a difference would have only a minor impact on the results, changing the reported T_g values by at most 5°C. Second, the heating rate was doubled to 20°C/min, in order to minimize drying of the sample during the ramp to T_g . The thermal lag at this heating rate was still a manageable 6-12°C in a typical run.

Table 4. Weight gain and TMA of cyanate esters after 96 hour water boil

Sample ID	Weight Gain (%)	Thickness (mm)	$T_{g, E''}$ (°C)	$T_{g, \tan \delta}$ (°C)	$\tan \delta$ at $T_{g, \tan \delta}$	$T_{\text{first-failure}}^a$
RT0	2.3	1.20	249	254	0.37	No failure
LE0	2.1	1.45	230	239	0.45	249
LE2 ^b	2.3	3.51	180 ^c	181 ^c	0.27 ^c	187
BA2	2.1	2.16	187	192	0.59	226
SM2	1.7	2.42	183	193	0.52	243
Mix1 ^b	2.3	2.33	210	218 ^c	0.41 ^c	224
Mix2 ^b	2.2	2.72	194	197 ^c	0.36 ^c	204
Mix3	2.2	2.16	201	211	0.62	237
Mix4	2.0	2.60	190	196	0.48	227

^aas determined by the peak temperature for the first recorded “spike” in $\tan \delta$

^bmeasured using the same protocol for dry TMA samples

^c T_g occurred near the onset of mechanical failure, thus the true peak could be up to 10°C higher, with an uncertain peak value, depending on the extent of masking by mechanical instability effects

In Table 4, the disc thickness values have also been listed. At present, the effect of disc thickness on the measured parameters is unknown, however, a thinner disc may dry out faster and be less prone to mechanical failure due to bubble formation. For samples greater than 2 mm thick, the data seemed to show no effect of thickness on T_g when measured via the peak in E'' . When considering data collected using the updated protocol, the effect of thickness on mechanical failure temperature also seemed to be small, however, a smaller range of values were examined. Although additional experiments are needed resolve these issues completely, the data thus far suggest that as long as the sample thickness is controlled between 2 and 3 mm, meaningful comparisons among samples can be produced.

3.2.1 Effect of Monomer Structure

While the moisture uptake of BADCy and LECy was similar, the moisture uptake of SiMCy was noticeably lower, despite its chemical similarity to BADCy. These results were in accord, both in terms of the values measured, and the trend, with previously reported data on these compounds [2,8]. The moisture uptake of RTCy was nearly identical to that of LECy. Since these two monomers differ in cross-link architecture rather than chemical functionality, the result was not surprising. It should be noted, though, that the values reported for RTCy were slightly lower than the 2.8% weight gain values reported for ESR255 [15], and PT-30 resin [2].

The Tg values after exposure to boiling water for BADCy, LECy, and SiMCy were all similar, again in accordance with previously reported data [2,8], thus the rate of hydrolysis and its effect appear to have been very similar in all three monomers. The “wet” Tg value for RTCy is quite a bit higher, although when compared to a LECy sample of similar thickness and with the same catalyst loading, the difference is much more modest. It should be noted that the “wet” heat deflection temperature (HDT) values of the tri-functional ESR255 and LECy were reported as 254°C and 183°C, respectively (both used the same catalyst loading level), thus there is evidence to suggest that switching to the “three armed” version of LECy would have raised the “wet” Tg.

With the exception of the RTCy sample, bubbling and, in some cases, cracks, appeared in all of the specimens during TMA testing after exposure to boiling water. This phenomenon is of particular interest because of similar mechanical failures seen during the rapid heating of composite specimens containing high-temperature resins. These failures were reportedly due to the rapid release of water and other volatiles [13]. In addition, the effects of moisture and elevated temperature on blistering in printed circuit boards containing cyanate ester resins are well documented [12]. Bubble formation during the TMA test creates a characteristic signal set (a sudden, drastic expansion of the sample and an anomalous drop in E' with concurrent spikes in E'' and tan δ) and thus can be tracked during the experiment. Tracking showed that these failure events occurred over a narrow temperature range. In repeated runs using different samples of the same material, this temperature range was reproducible to within 10°C.

Consequently, the nearly 20°C higher failure temperature for SiMCy as compared to BADCy indicates that the lower moisture uptake of SiMCy may lead to a lower chance of catastrophic failure during rapid heating of composite specimens. In addition to the higher failure temperature, the extent of damage to the sample also appeared to be significantly less for SiMCy. In Figures 5 and 6, the dynamic TMA traces for both BADCy and SiMCy during bubble formation are compared. The effects in BADCy were much more dramatic, a result corroborated by visual inspection of the samples after the conclusion of the test.

The RTCy sample showed no failures at all during heating, despite the fact that a LECy sample of similar thickness and the same catalyst loading did fail. It may thus also be the case that a higher effective cross-link density reduces the propensity of bubble formation in the sample. The formation of bubbles in the sample is likely to be the result both of rapid vaporization of water as well as the reaction of water with uncured cyanate ester groups to form CO₂ through the carbamate route [12].

3.2.2 Effect of Blending and Catalyst Loading

Interestingly, the moisture uptake and failure temperatures of mixtures of BADCy, LECy, and SiMCy did not exhibit much change from the levels for pure BADCy and LECy. Even Mix4, with 67wt% SiMCy, shows virtually no reduction in moisture uptake or improvement in failure temperature. The “wet” Tg's of some mixtures were slightly higher than those of the pure components, although it should be pointed that for Mix1 and Mix2, the dry Tg values were higher as well. A future study of additional blend composition will clarify the nature of these anomalies.

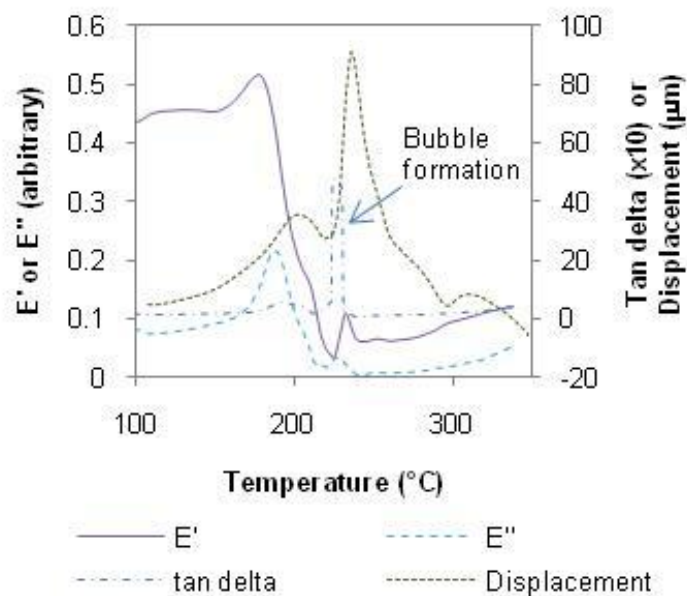


Figure 5. “Wet” TMA data for sample BA2 (BADCy), with the bubble formation event marked. The peaks at around 200°C are the typical signals associated with the glass transition.

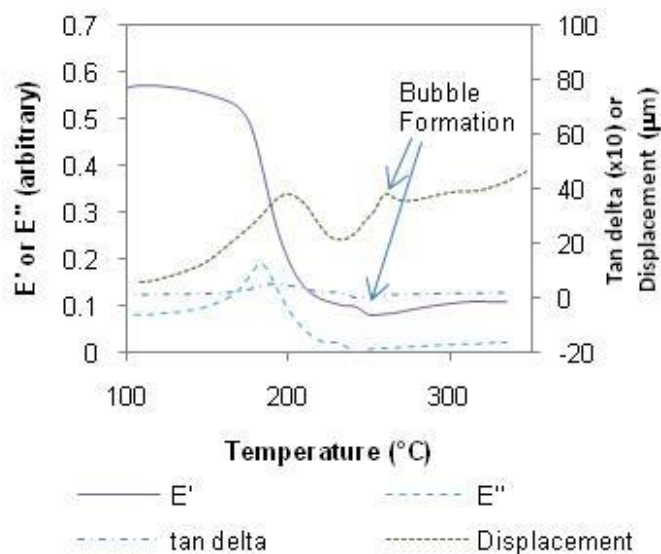


Figure 6. “Wet” TMA data for sample SM2 (SiMCy), with the bubble formation event marked. Note (by comparison to BADCy in Figure 5) the much reduced impact of the event on the TMA signals compared to the changes associated with the glass transition

The incorporation of catalyst did appear to have a significantly negative effect on “wet” T_g, although some of the difference may be due to thickness and protocol effects. Although the particular catalyst used (copper (II) acetylacetonate) has been shown to be superior to other common metal ligand systems in terms of retention of properties under wet conditions [11], it is also known to accelerate hydrolysis significantly when incorporated into cyanate esters. Moreover, it should be noted that the cure time used in this study was especially long (24 hours) in order to ensure that all samples could be adequately cured without resorting to high temperatures. With shorter cure times, an uncatalyzed cyanate ester resin would likely fail to achieve adequate cure, and as a result, its retention of properties on exposure to boiling water would likely be worse, not better, than the catalyzed version.

4. CONCLUSIONS

Key insights into the mechanisms of moisture uptake in cyanate ester resins have been gained through comparative study of different molecular architectures, blend compositions, and the effect of catalyst. Although quite similar in composition to Primaset® BADCy and LECy, SiMCy was observed to absorb significantly less moisture despite having a higher free volume and somewhat lower glass transition temperature. This result, for a system catalyzed with 1.9 phr nonylphenol and 160 ppm Cu(II), as the acetylacetonate, matched previously published results for uncatalyzed versions of the same resins. While the presence of the catalyst had only a minor impact on the overall amount of moisture absorbed, in Primaset® LECy it was observed to decrease the “wet” glass transition temperature considerably. Increased resistance to moisture degradation despite a similar level of water uptake was seen in the tricyanate RTCy, an effect similar to that observed for other tricyanate monomers such as the experimental compound ESR255. The properties of cyanate ester blends were generally in line with simple rules of mixtures, although a few interesting anomalies were identified. These will be the subject of a future investigation.

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