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14. ABSTRACT

Polycyanurates (also known as "cyanate ester resins") offer numerous advantages in composite structures for aerospace, energy, and electronics applications, and are often considered as higher-performance replacements for epoxy resins. Though generally low, the moisture uptake and stability in hot water of polycyanurates varies significantly as a function of monomer type and processing conditions. It is therefore important to understand the fundamental mechanisms responsible for water uptake and the resultant implications for the rational design of cyanate ester molecular structure and selection of appropriate processing parameters. Moisture uptake studies of polycyanurates, including ternary co-polymerized blends, monomer chemistries incorporating silicon, and new monomer architectures based on phloroglucinol all revealed a strong correlation with nominal polycyanurate number density. The same trend was apparent in analysis of many commercial cyanate ester products. Dynamic TMA studies revealed a strong negative effect of the presence of catalyst on the retention of Tg in the commercial product Primaset® LECy, similar to effects observed for other cyanate ester resins. The use of less active metal chelate catalysts was shown to reduce the loss in Tg.

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Relationships Among Molecular Structure, Processing, Water Uptake, and Moisture-Induced Degradation in Cyanate Ester Resins

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INTRODUCTION

Polycyanurates (also known as "cyanate ester resins") offer numerous advantages in composite structures for aerospace, energy, and electronics applications, and are often considered as higher-performance replacements for epoxy resins.[1-3] Desirable characteristics of polycyanurates include superior fire resistance,[4] lower moisture uptake,[5] and higher maximum use temperatures than epoxy resins with corresponding temperature-dependent monomer viscosity characteristics.[6] Favorable processing characteristics of cyanate ester monomers include 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[7] or toughening agents.[8] Though generally low, the moisture uptake and stability in hot water of polycyanurates varies significantly as a function of monomer type and processing conditions. It is therefore important to understand the fundamental mechanisms responsible for water uptake and the resultant implications for the rational design of cyanate ester molecular structure and selection of appropriate processing parameters.

Water uptake degrades the performance of polycyanurates in several ways. First, the reaction of ambient moisture with cyanate esters produces carbamates, with a significant acceleration of the reaction rate in the presence of transition metal-containing catalysts.[9] Above 200°C, rearrangement of the carbamates ultimately liberates CO$_2$, resulting in blisters and porosity in cured structures.[10] Secondly, much slower reactions of water with polycyanurates lead ultimately in many cases to the formation of non-cross-linked phenols,[11] lowering the glass transition (and hence, maximum use) temperatures significantly. Finally, physically absorbed ambient moisture in polycyanurate structures will vaporize during rapid heating, potentially leading to catastrophic mechanical failures.[12] While in some cases engineering controls may be utilized to limit exposure to moisture, the development of polycyanurates with reduced moisture uptake represents a more robust and potentially more affordable approach to decreasing or eliminating the loss in performance.

EXPERIMENTAL

Materials. The dicyanate esters of Bisphenol A (Primaset® BADCy), and Bisphenol E (Primaset® LECy) were purchased from Lonza and used as received. Additional cyanate esters included "SiMCy", a silicon-containing analog of Primaset® BADCy synthesized according to published procedures,[5] and PG-Me and PG-EH, two cyanate esters based on phloroglucinol synthesized at NAWCWD China Lake[13] and provided to AFRL for evaluation. The structures of PG-Me and PG-EH are shown in Figure 1. Nonylphenol (technical grade), cobalt (II) acetylacetonate, and nickel (II) acetylacetonate were purchased from Aldrich, and copper (II) acetylacetonate was purchased from ROC/RIC; all 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). For samples containing nickel (II) and cobalt (II) acetylacetonate, the nonylphenol and metal content were independently varied. These batches were retained for up to 30 days. Silicone molds (R2364A, 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. Cyanate esters were mixed and de-gassed for 30 minutes at 95°C and 300 mm Hg, then poured into the prepared mold. The open mold and sample were then placed under flowing nitrogen and cured. The cure schedule for uncatalyzed and Cu-containing systems was 1 hour at 150°C followed by 24 hours at 210°C, while for Ni- and Co-containing systems it was 180°C for 3 hours. Both schedules produced void-free samples 1-3 mm thick. The temperature ramp rate during cure was 5°C/min.

Measurement of Density and Water Uptake. Density was determined by placing selected samples in aqueous solutions of CaCl$_2$ (added as the dihydrate) and varying the CaCl$_2$ 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 CaCl$_2$. Water uptake was determined by placing unused samples in approximately 300 mL of deionized water at 85 °C for 96 hours, with sample dimensions and weight measured before and after exposure.

Dynamic TMA. Dynamic thermomechanical analysis was performed under oscillatory compression to determine the glass transition temperatures of samples before and after exposure to boiling water. The dynamic TMA technique is similar to traditional DMTA, but provides only a relative measure of stiffness as opposed to an absolute modulus. A detailed description of the dynamic TMA experiments is provided elsewhere.[14] For the Co- and Ni- catalyzed samples, the heating rate was 2°C per minute, as opposed to 10°C/min for all other dry samples and 20°C per minute for all other wet samples.

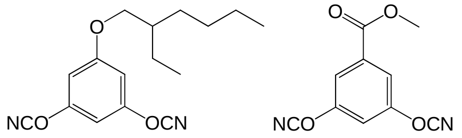

Figure 1. Structures of PG-EH (left) and PG-Me (right).

RESULTS AND DISCUSSION

The water uptake data for all samples investigated is shown in Table 1, along with the density data where available. The compositions of the blend samples (made by co-polymerizing BADCy, LECy, and SiMCy) were as follows: Blend TCE-1: 68 wt% BADCy, 17 wt% LECy, 15 wt% SiMCy; Blend TCE-2: 75 wt% BADCy, 25 wt% SiMCy; Blend TCE-3: 75 wt% LECy, 25 wt% SiMCy; Blend TCE-4: 17 wt% BADCy, 17 wt% LECy, 67 wt% SiMCy; Blend TCE-5: 75 wt% BADCy, 25 wt% LECy. The catalyst composition abbreviated in the table provides the level of nonylphenol (NP) in phr by weight as well as the type and level of metal present (in ppm by weight).

Table 1. Water Uptake and Density Data for Polycyanurates

Monomer	Catalyst (phr/ppm)	Water Uptake (%)	Density (g/cc)
BADCy	2 NP / 160 Cu	2.1	1.201
LECy	None	2.3	1.234
LECy	2 NP / 160 Cu	2.3	1.220
SiMCy	2 NP / 160 Cu	1.7	1.173
Blend TCE-1	2 NP / 160 Cu	2.3	1.195
Blend TCE-2	2 NP / 160 Cu	2.2	1.187
Blend TCE-3	2 NP / 160 Cu	2.2	1.211
Blend TCE-4	2 NP / 160 Cu	2.0	1.190
Blend TCE-5	2 NP / 160 Cu	2.2	1.208
PG-EH	None	0.9	1.15
PG-Me	None	8.5	1.40

Table 1 clearly shows a very wide range of water uptake values. The water uptake data in Appendix A.2 of Reference 2 also shows a wide range of values, with the product RTX-366 being lowest at 0.6% and the product REX-371 highest at 3.8% (note that the method of measurement differed slightly for these sample, but that the values reported therein for LECy and BADCy are similar to those reported herein.)

In Figure 2, the water uptake is plotted versus cyanurate ring number density of the polyaromatic dicyanate samples. The cyanurate ring number density was calculated based on the observed density, monomer molecular weight and functionality, and extent of cure determined with the aid of the deBenedetto equation (with Tg = -50°C assumed for no cure and the Tg for "full cure" based on dynamic TMA measurements of dry samples after heating to 350°C at 10°C per minute)

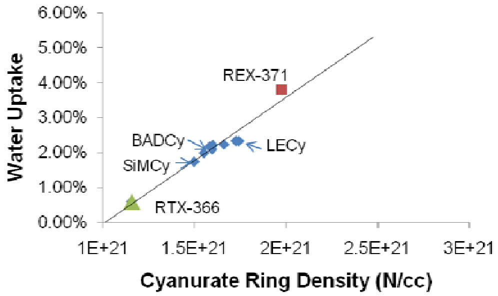

Figure 2. Water uptake versus cyanurate ring number density.

Figure 2 shows a clear correlation between cyanurate ring density and water uptake for the dicyanate (blue diamond) samples reported in Table 1, and the two labeled products found in Reference 2. The quality of this correlation improved significantly when the degree of cure of the blend samples was taken into account, thus the cyanurate ring density, rather than cyanate ester monomer density, provided the best correlation. The trend was consistent with the data for the PG samples, although neither sample fell on the dicyanate trend line. For the PG samples, then, the effect of cyanurate ring density appears to be significantly more pronounced.

In Table 2, the effect of catalyst on the dry and wet Tg of LECy samples is shown. The reported Tg values are based on the peak in the loss component of oscillatory deformation, and are corrected for sample thermal lag.[14] The activity of the catalysts increases in the order Ni < Co < Cu, as evidenced by the dry Tg values (a higher Tg is indicative of more complete cure under the chosen conditions). Note that when no catalyst was present, the TMA method resulted in some in-situ cure of the remaining cyanate ester groups, thus the true Tg of the Cu-containing sample was likely a few degrees lower than the temperature found by dynamic TMA. Despite the aforementioned limitation, Table 2 demonstrates a clear correlation between catalytic activity and the drop in Tg after exposure to boiling water. The most active system (Cu) showed a drop in Tg that was about 25°C less than that of the least active catalyzed system. These effects were also consistent with reports[11] of the effect of catalyst on the loss in Tg when samples of PT-30, a novolac type polycyanurate similar to REX-371, was exposed to boiling water.

Table 2. Tg Values from Dynamic TMA for LECy with Various Catalyst Types

Monomer	Catalyst Type	Dry Tg (°C)	Wet Tg (°C)	Difference (°C)
LECy	None	<281	230	<51
LECy	Cu (II)	283	180	103
LECy	Co (II)	264	169	95
LECy	Ni (II)	258	184	74

CONCLUSIONS

Moisture uptake studies of polycyanurates, including ternary co-polymerized blends, monomer chemistries incorporating silicon, and new monomer architectures based on phloroglucinol all revealed a strong correlation with nominal polycyanurate number density. The same trend was apparent in analysis of many commercial cyanate ester products. Dynamic TMA studies revealed a strong negative effect of the presence of catalyst on the retention of Tg in the commercial product Primaset® LECy, similar to effects observed for other cyanate ester resins. The use of less active metal chelate catalysts was shown to reduce the loss in Tg. .

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