Synergistic Physical Properties of Cocured Networks Formed from Di- and Tricyanate Esters

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S *Supporting Information*
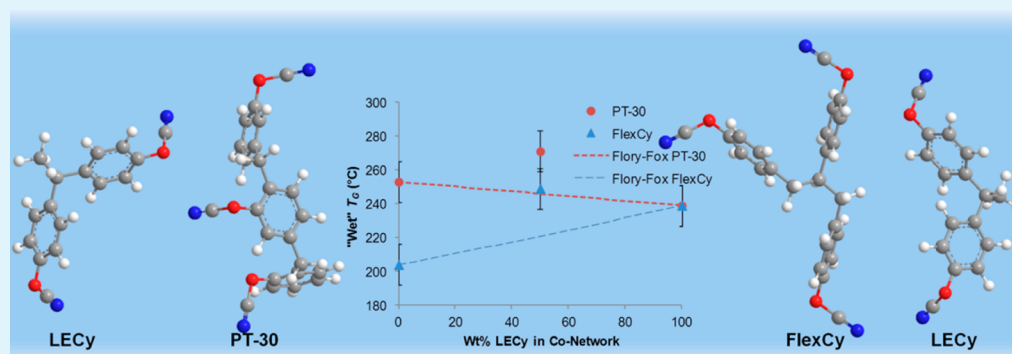
ABSTRACT: The co-cyclotrimerization of two tricyanate ester monomers, Primaset PT-30 and 1,2,3-tris(4-cyanato)propane (FlexCy) in equal parts by weight with Primaset LECy, a liquid dicyanate ester, was investigated for the purpose of exploring synergistic performance benefits. The monomer mixtures formed stable, homogeneous blends that remained in the supercooled liquid state for long periods at room temperature, thereby providing many of the processing advantages of LECy in combination with significantly higher glass transition temperatures (315−360 °C at full cure) due to the presence of the tricyanate-derived segments in the conetwork. Interestingly, the glass transition temperatures of the conetworks after cure at 210 °C, at full cure, and after immersion in 85 °C water for 96 h were all higher than predicted by the Flory−Fox equation, most significantly for the samples immersed in hot water. Conetworks comprising equal parts by weight of PT-30 and LECy retained a "wet" glass transition temperature near 270 °C. The onset of thermochemical degradation for conetworks was dominated by that of the thermally less stable component, while char yields after the initial degradation step were close to values predicted by a linear rule of mixtures. Values for moisture uptake and density in the conetworks also showed behavior that was not clearly different from a linear rule of mixtures. An analysis of the flexural properties of catalyzed versions of these conetworks revealed that, when cured under the same conditions, conetworks containing 50 wt % PT-30 and 50 wt % LECy exhibited higher modulus than networks containing only LECy while conetworks containing 50 wt % FlexCy and 50 wt % LECy exhibited a lower modulus but significantly higher flexural strength and strain to failure. Thus, in the case of "FlexCy", LECy was copolymerized with a tricyanate that provided both improved toughness and a higher glass transition temperature.

KEYWORDS: *thermosetting resin, cyanate ester, polymer blends, polycyanurate networks, flexural properties, cure kinetics*

INTRODUCTION

Among thermosetting networks, polycyanurates have recently received increasing attention due to their combination of outstanding high-temperature properties and ease of processing.[1−3] Among these, dicyanate monomers, such as Primaset LECy (1,1-bis(4-cyanatophenyl)ethane)[4] and 1,4-bis[(4-cyanatophenyl)isopropylidene]benzene,[5] are low-viscosity liquids at room temperature and allow for the most favorable processing characteristics. In contrast, tricyanate esters such as Primaset PT-30[6] offer better high-temperature mechanical and

chemical stability, but often require high temperatures to achieve near complete conversion and the attendant requisite levels of long-term hydrolytic stability. Dicyanates have found a variety of applications ranging from repair of aerospace structures[7] to low-dielectric electronics packaging,[8] while tricyanates have been investigated for more demanding
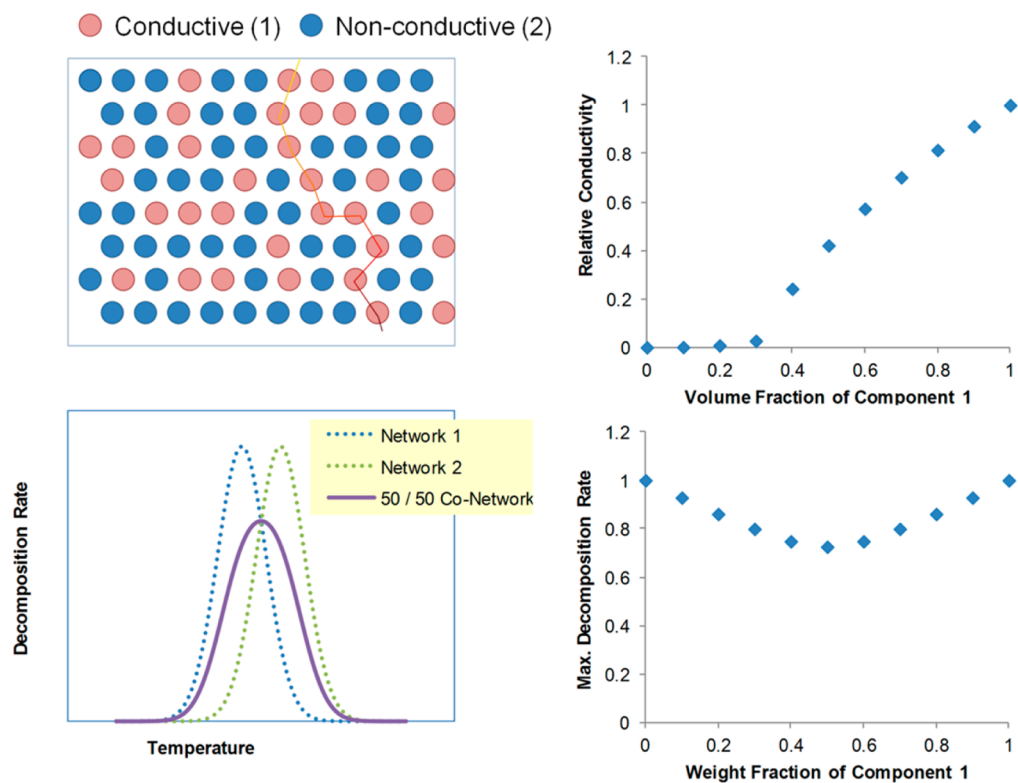
Figure 1. Examples illustrating how the physical properties of systems that are homogeneously mixed can often follow strongly nonlinear rules of mixing. Top: The conductivity (whether electrical, ionic, etc.) as a function of volume fraction (top right) of randomly mixed systems containing efficient conductors and nonconductors often exhibits a form characteristic of the effects of percolation leading to formation of conductive pathways (as illustrated top left). Bottom: The maximum rate of chemical decomposition in a homogeneous conetwork in which the components decompose independently of one another will show a negative deviation from a rule of mixtures if the components decompose at slightly different temperatures.

environments such as nuclear fusion reactors,[9] nanoscale sesnors,[10] and turbine engines.[11,12] Although the past few years have witnessed the development of many new dicyanate[13−32] and tricyanate[33−39] monomers with improved properties, the use of cocured networks formed by blending various monomer types can also provide useful new combinations of properties.[7,20,27,37,40−47] In fact, previous work has shown that, despite the apparent homogeneity of cocured polycyanurate networks, synergistic interactions (herein defined as significant departures from linear rules of mixing for conetwork properties, which can be caused by small differences in the formation of network structures resulting from, for example, mixing of impurities, or to nonlinear physical interactions among mixed network chain segments) among the components frequently occur, leading in many cases to improvements in performance.[47] Figure 1 illustrates two of many known general mechanisms (percolation and staggering) that can lead to nonlinear rules of mixing and, thus, synergistic behavior, in homogeneous multicomponent mixtures.

Among cocured networks, those formed from blends of dicyanates and tricyanates may be expected to offer a good balance of high-temperature properties and ease of processing. To date, however, there have been relatively few reported studies of cocured networks of this type.[7,20,37,40,43,45] The strong possibility of synergistic interactions, however, implies that cocured networks formed from dicyanates and tricyanates may be identified that effectively combine high-temperature properties similar to tricyanates with ease of processing similar to dicyanates. In order to reliably identify such conetworks,

however, the root causes of synergistic interactions require further investigation.

In this paper, we report on the cure kinetics and physical properties of two different dicyanate/tricyanate ester conetworks. Both conetworks utilize the highly processable monomer Primaset LECy as the dicyanate, but differ in the nature of the tricyanate used. In one case, the tricyanate used is Primaset PT-30, which features rigid network segments and junctions,[6,36] while in the other case the tricyanate used is the monomer 1,2,3-tris(4-cyanatophenyl)propane, also known as "FlexCy" because it features more flexible network junctions and segments.[36] The comparative effects of mixing rigid and flexible network components were thus studied in order to provide insight into the origin of synergistic interactions. In the PT-30/LECy system in particular, it was found that multiple synergistic interactions combine to provide this system with a higher than expected "wet" glass transition temperature (T_G), thereby making it one of the best performing polycyanurate networks for use in wet environments.

■ EXPERIMENTAL SECTION

Materials. Primaset LECy (the dicyanate ester of bisphenol E, or 1,1-bis(4-cyanatophenyl)ethane, and Primaset PT-30 (an oligomeric cyanated phenolic resin) were obtained from Lonza. The tricyanate ester monomer known as "FlexCy" or 1,2,3-tris(4-cyanatophenyl)-propane was synthesized and purified according to a previously reported procedure,[36] but at a scale of approximately 20 g. The chemical structures of these compounds are shown in Figure 2. Nonylphenol (technical grade) was purchased from Aldrich, and copper(II) acetylacetonate was supplied by ROC/RIC; both were used as received.
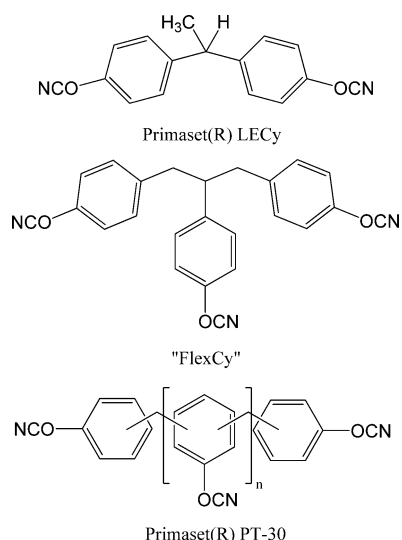
Figure 2. Chemical structures of the cyanate ester monomers used. Note that, for PT-30, *n* is approximately equal to one.

Cured Network Preparation and Characterization. Necessary quantities of FlexCy monomer were prepared by weighing and then melting the powder at 115−130 °C. Necessary quantities of PT-30 and LECy were prepared simply by weighing the required amount of liquid at ambient temperature. The catalyst was prepared by mixing 30 parts of nonylphenol with 1 part copper(II) acetylacetonate at a temperature of 60 °C for 1 h. For conetworks, equal parts of either melted FlexCy or PT-30 were mixed with LECy at a temperature of 95 °C for a minimum of 30 min under a reduced pressure of 300 mmHg, followed by pouring into either a silicone casting mold (13 mm diameter × 3 mm discs) or a fluoropolymer-faced silicone-gasketed vertical 82 mm × 82 mm × 3 mm mold. For preparation of catalyzed samples, the premixed catalyst was always added at 2 parts per hundred to the liquid resin just prior to the 30 min of mixing under reduced pressure. Cure consisted of heating in an oven under nitrogen to 150 °C for 1 h, followed by 210 °C for 24 h, with subsequent cooling to below 150 °C prior to demolding. Heating ramps were 5 °C/min. Additional details such as the mold fabrication procedures have been published elsewhere.[48]

Thermomechanical analysis of cured samples was performed using a TA Instruments Q400 thermomechanical analyzer (TMA) in dynamic (oscillatory compression) TMA mode. The oscillatory compression mode provides qualitative information on the storage and loss components of the sample stiffness, in addition to sample displacement as a function of temperature (for thermal expansion measurements). A heating rate of 10 °C/min was used for "fully cured" dry samples, while a faster heating rate of 20 °C/min (to minimize loss of water during heating) was used for "wet" samples. For "fully cured" dry testing, the samples were tested for thermal lag, heated to 350 °C, then cooled to 100 °C, and finally, reheated to 350 °C, with the data collected during reheating utilized. For "wet" testing, the samples were first heated to 350 °C with data collected and utilized, so as to capture as much information as possible before the samples dried, then, the thermal lag was determined. In all cases, a previously published[57] thermal cycling procedure, using limits of 0 and 200 °C, was used to determine and correct for the thermal lag. The mean compressive load on the samples was 0.1 N, with an oscillatory force applied at an amplitude of 0.1 N and a frequency of 0.05 Hz. Complete details, examples, and the rationale for the cycling procedures have been explained at length elsewhere.[48]

Differential scanning calorimetry was performed on a TA Instruments Q200 under 50 mL/min of flowing nitrogen. Multiple heating programs were utilized for different types of samples. For determination of uncured monomer properties, samples were heated at 5 °C/min to 120 °C and held at 120 °C for 5 min to achieve melting if needed (only for pure FlexCy), then cooled to −90 and

reheated at 10 °C/min to 50 °C to measure monomer T_G. To determine heats of cyclotrimerization, monomers were heated at 10 °C/min to 350 °C, cooled at 10 °C/min to 100 °C, then reheated at 10 °C/min to 350 °C to establish a baseline. For determination of cure kinetics and the parameter λ in the diBenedetto equation, uncured monomer samples were heated at 5 °C/min to 130 °C and held at that temperature for 5 min to melt (if needed) and equilibrate, then heated as quickly as possible (~100 °C/min.) to a predetermined set-point, held at the set-point for 30 min, cooled as quickly as possible (~100 °C/min.) to 0 °C, and then heated to 350 °C at 10 °C/min to effect residual cure. The entire procedure was then repeated with the cured sample in place to establish a baseline. For determination of "as cured" and "fully cured" T_G values, small chunks of oven-cured samples were first heated at 50 °C/min to 350 °C (without modulation). The rapid heating rate is required to minimize in situ cure. When a clear step transition was not visible, the onset of rapid cure (marked by a clearly visible kink in the heat flow rather than a gradual curve) was taken as the sample T_G. Samples were then cooled to 100 °C and reheated to 400 °C using modulated DSC. The base heating rate was 5 °C/min, with a modulation amplitude of 1 °C and period of 40 s. When T_G values exceeded about 325 °C, they tended to appear only in the reversible heat flow curves.

Thermogravimetric analysis (TGA) was carried out using a TA Instrument Q5000 apparatus under 60 mL/min of either nitrogen or air. For TGA analysis, ~2 mg chunks of cured discs were heated at 10 °C/min to 600 °C. The density of cured samples was determined via neutral buoyancy of 13 mm × 3 mm discs in CaCl$_2$/deionized water mixtures, as described elsewhere.[49] Some cured discs were placed in 250 mL of deionized water at 85 °C for 96 h as a means of testing the effects of exposure to hot water. Flexural tests were performed according to ASTM D6272-02 with a support span of 76.2 mm and a load span of 1/3 of the support span on rectangular specimens measuring 82 mm × 12 mm × 3 mm. Crystal data for LECy was collected at $T = 100$ (K) using a Kusing Bruker 3-circle, SMARTAPEX CCD with c-axis fixed at 54.748, running the SMART V 5.625 program. Graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation was employed for data collection and corrected for Lorentz and polarization effects using SAINT V 6.22 program and reflection scaling. This data (CCDC 943070) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

■ RESULTS AND DISCUSSION

Properties of Co-Cured Networks and Key Synergies. *Processability of Monomers.* The crystal structure of the LECy monomer plays a key role in its especially favorable processing characteristics. This structure, which is based on single crystal X-ray Diffraction measurements, and has not been reported previously to our knowledge, is shown in Figure 3. The crystal shows disorder, which is primarily the result of two cocrystal-
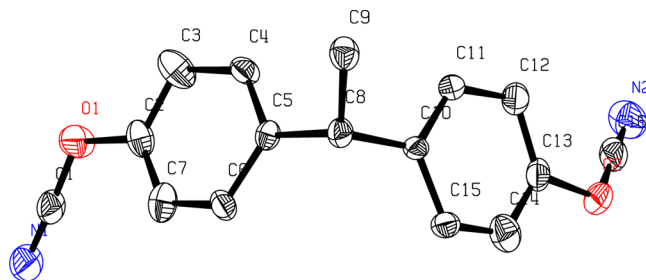

Figure 3. X-ray crystal structure of LECy (carbon, black; oxygen, red; nitrogen, blue). Significant disorder was found on the bridging carbon. Hydrogen atoms and disorder not shown for clarity (see the Supporting Information for more images). Thermal ellipsoids are shown at 50%.

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lized forms being present (additional images are shown in the Supporting Information). The disorder, which is associated primarily with the bridge between the aryl cyanate ester groups, is a critical feature. It allows the cocrystallized form to act as a eutectic, lowering the melting point of LECy from an expected value of 50−100 °C to its reported value of 29 °C and stabilizing the supercooled liquid.

Importantly, the suppression of crystallinity in LECy also extends to blends with other monomers. In previous work, we showed that 50 wt % mixtures of LECy with the dicyanate ester of Bisphenol A and with 4,4′-bis(cyanatophenyl)dimethylsilane existed as liquids that we were unable to crystallize to any extent.[47] Likewise, the 50 wt % mixtures of both PT-30 (a semisolid oligomeric resin) and FlexCy (mp 107 °C) were stable liquids at room temperature that did not crystallize and flowed readily. As a result, the LECy/tricyanate blends qualitatively retained the favorable processing characteristics of LECy.

By DSC, the uncured mixtures exhibited a single T_G that, at −34 °C, was near the expected intermediate value between that of LECy and its comonomer. Figure 4 illustrates the
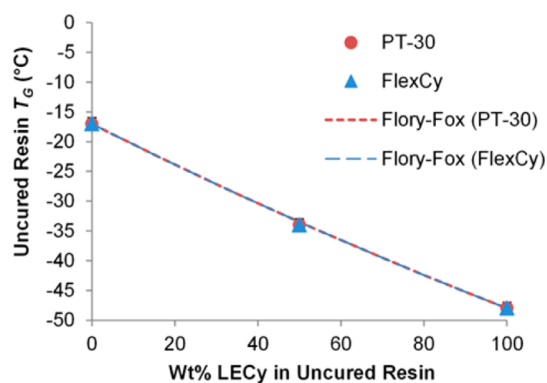
Figure 4. Glass transition temperature of uncured blends of FlexCy and PT-30 with LECy, as a function of composition.

composition dependence of the T_G of the FlexCy and PT-30 monomer blends in graphical form. Additionally, the breadth of the glass transition remained unchanged for the FlexCy/LECy blend, at about 3 °C for LECy, FlexCy, and the 50/50 wt % blend of the two. For PT-30, which due to its oligomeric character, has a broader glass transition spanning 5 °C, the 50 wt % blend with LECy retained a glass transition spanning 5 °C. Thus, both the location and the breadth of T_G for these systems indicate complete miscibility above a length scale of ~10 nm. In corroboration, we observed no evidence for phase separation of the mixed monomers, which retained excellent clarity and stability as homogeneous liquids in storage at room temperature over the entire period of observation (up to several days). We also found no evidence of phase separation in cured samples, which retained complete clarity.

T_G at Full Conversion and Thermal Expansion. In contrast to the T_G values in the uncured state, the T_G values for fully cured conetworks appear to show some deviation from the Flory−Fox theory (as depicted in Figure 5). Thermal degradation of polycyanurate networks can make a significant contribution to the DSC signal at temperatures at or above 350 °C; thus, an estimate of the fully cured T_G is difficult to obtain for many of these networks. In some cases, modulated DSC is able to show a step change in reversible heat capacity while a
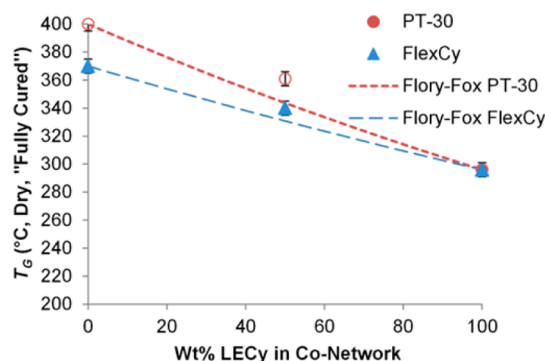
Figure 5. Glass transition temperature (by modulated DSC) for fully cured conetworks containing PT-30 or FlexCy and LECy, as a function of LECy content. Open symbols indicate estimates from indirect methods (see the Supporting Information for details).

small amount of degradation is occurring, so for LECy, FlexCy, and the LECy/FlexCy conetwork, the values in Figure 5 came directly from modulated DSC measurements. For PT-30 and its conetwork with LECy, modulated DSC was unable to definitively determine a T_G. For PT-30 itself, extensive DMA testing has shown the T_G to be very close to 400 °C at full cure,[6] but for the PT-30/LECy conetwork previous measurements were unavailable. We thus resorted to an indirect method. The addition of 2 parts per hundred by weight nonylphenol in catalyzed cyanurate networks lowers the glass transition temperature by approximately 20 °C. In the conetworks with added nonylphenol, the lowered T_G was detectable by modulated DSC, and thus a reasonably precise estimate of the T_G of the uncatalyzed network was inferred. Complete details, with corroborating evidence and raw data, are provided in the Supporting Information.

Although the exact magnitude of the deviation from the Flory−Fox theory is less certain for the PT-30/LECy conetwork, for the FlexCy/LECy conetwork it is a small but significant (given a measured precision of 2−3 °C) positive deviation of about 7 °C. For the PT-30/LECy conetwork, even after plasticizing the network through addition of 2 wt % nonylphenol, the T_G is still above the prediction of the Flory−Fox theory. Therefore, it is likely that a significant positive deviation exists, even if the computed deviation of 14 °C carries some additional quantitative uncertainty (±10 °C is a reasonable intuitive estimate of the uncertainty level in this particular case). By themselves, such positive deviations are too small to be of much technological importance; however, when combined with other sources of positive T_G deviation in partly cured networks, as will be discussed below, the total effect can become technologically significant.

One possible explanation for the deviation in T_G at full cure involves a known synergistic effect of network copolymerization of components with differing rigidity characteristics. As shown in previous work on dicyanate blends,[47] the coefficient of linear thermal expansion (CLTE) in a conetwork does not follow a strictly linear rule of mixtures if the bulk moduli of the network segments differ from one another. Instead, the CLTE in an equimolar mixture is expected to deviate toward the CLTE of the more rigid component. In the case of polycyanurates, as in most thermosetting networks, more rigid segments give rise to a lower CLTE; thus, the equimolar copolymerization of monomers with differing rigidity characteristics is expected to lead to a negative deviation from a linear rule of mixtures for

the CLTE. As illustrated in Figure 6, this negative deviation is exactly what is observed, to a lesser extent for the FlexCy/LECy
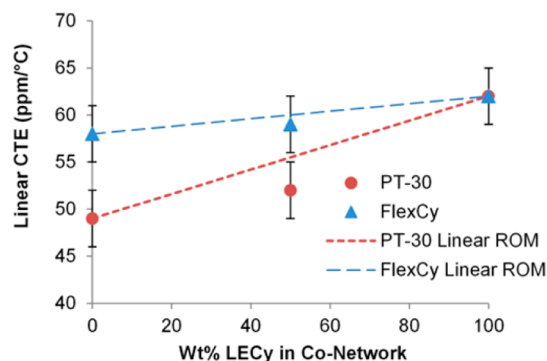
Figure 6. Coefficient of linear thermal expansion for PT-30 and FlexCy conetworks with LECy, compared to predictions based on a linear rule of mixtures.

conetwork and a greater extent for the PT-30/LECy conetwork. Note that although the conetworks are 50/50 wt % mixtures, all components have a very similar equivalent weight, and thus the conetworks are nearly equimolar as well. As illustrated in previous work, PT-30 networks are more rigid than FlexCy networks, as corroborated by the lower CLTE. Thus, in combination with LECy, the deviation in CLTE is expected to be more significant for PT-30, as observed. In the same previous work on dicyanate blends,[47] we also noted that there is an inverse correlation between the CLTE and the T_G at full cure for conetworks, just as there is for linear polymers. A lower than expected CLTE would therefore indicate a higher than expected T_G at full cure, just as found experimentally.

"As Cured" and "Wet" T_G. From the technological standpoint, the very high T_G values at full cure for these polycyanurate conetworks means that full cure will likely not be achieved in practice. Instead, the actual T_G of a "cured" system will be limited primarily by the cure temperature. In order to understand whether the synergies described above are likely to be present under more realistic cure temperatures, T_G values were measured on networks cured for 24 h at 210 °C. Figure 7 reveals that under these conditions, a positive deviation from the expected rule of mixtures remains for both FlexCy/LECy and PT-30/LECy conetworks. Note that these values are obtained based on the onset of the cure exotherm for rapidly heated DSC samples, which is the only technique available for
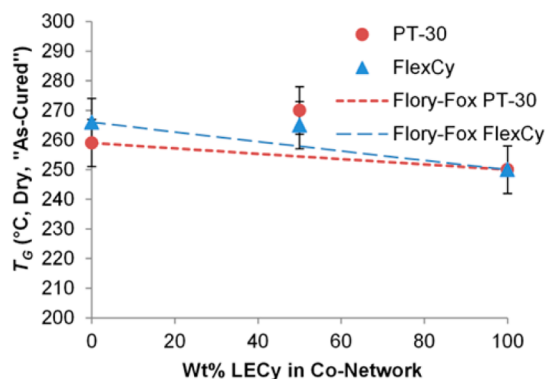
Figure 7. "As cured" T_G of PT-30 and FlexCy conetworks with LECy after 24 h at 210 °C.

reliably estimating the "as cured" T_G under these circumstances (a detailed explanation, with raw data, is provided in the Supporting Information). In accordance with previous studies of cyanurate networks cured under these conditions, the "as cured" T_G values all fall into a narrow range between about 245 and 275 °C.[39] Also in accordance with numerous previous studies of cyanurate networks,[21,39,50,51] the less rigid FlexCy-containing conetworks exhibit T_G values at least as high, or slightly higher, than corresponding networks containing the more rigid PT-30.

For many applications, the actual maximum use temperature for cyanurate networks is based on the "wet" T_G, that is, the glass transition temperature after exposure to a predetermined set of hot/wet conditions (in this case, immersion in 85 °C water for 96 h). Thus, the large positive deviation from the rule of mixtures in the "wet" T_G for the conetworks shown in Figure 8 is perhaps the most important synergistic property observed
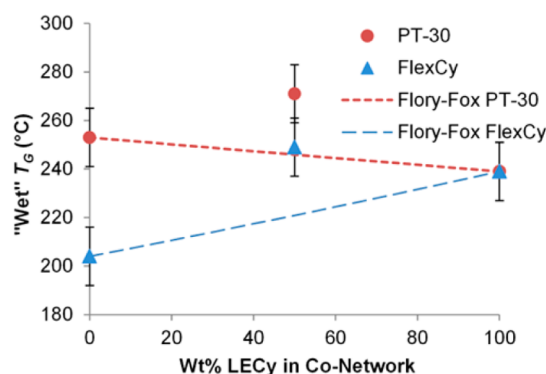

Figure 8. T_G after immersion in 85 °C water for 96 h of PT-30 and FlexCy conetworks with LECy.

in this study. Not only is the deviation from the rule of mixtures large, but the absolute value of "wet" T_G for the PT-30/LECy system is the highest we have ever measured for a polycyanurate network. Interestingly, for the networks containing only PT-30 or LECy, the "wet" T_G is the same or slightly lower than the "as cured" T_G (considering the uncertainty of about 10 °C), whereas for networks containing FlexCy the "wet" T_G is 17 °C lower than the "as cured" T_G for the FlexCy/LECy conetwork and 62 °C lower for the FlexCy network. Thus, there is also a synergy in the amount by which the T_G is lowered by exposure to hot/wet conditions. For this characteristic, the deviation from a simple linear rule of mixtures is just 10 °C for the 50/50 wt % PT-30/LECy conetwork, similar to the measurement error and the measured deviations for both "as cured" and "fully cured" networks. For the corresponding FlexCy/LECy conetwork, however, the decrease in T_G is 19 °C less than expected based on a rule of mixtures; that is, the "wet" T_G for the conetwork is 19 °C higher than a prediction based on the observed "as cured" T_G for the conetwork itself and a predicted decrease after exposure to hot/wet conditions based on a linear rule of mixtures. What this result means is that, for the FlexCy/LECy system, the synergy in "wet" T_G is due not only to the synergy in "as cured" T_G but also to a difference in the degradation of the network.

Synergistic effects in the degradation of polycyanurate networks under hot/wet conditions would likely result from the inherent nonlinearity of the degradation process. Over many years of monitoring polycyanurate network degradation in hot water, we have observed that discoloration and

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embrittlement tends to develop along a sharp spatial front, starting first at sample corners and edges, and then propagating inward, rather than developing uniformly throughout the sample. The underlying phenomenon responsible for this behavior is believed to be similar to that which produces "Type II" diffusion in polymers,[52,53] namely, degradation of the network lowers the resistance to mass transfer, allowing higher concentrations of water to interact with the network and thereby accelerating the degradation process. Since the degradation process accelerates significantly over time, a 50% reduction in the initial rate of degradation (achieved by, for instance, copolymerization with a monomer that is resistant to degradation) may result in much more than a 50% reduction in the extent of degradation over an extended period of time. Such an effect is likely the reason that polycyanurate networks containing near 50% copolymerized epoxy exhibit many times the galvanic corrosion resistance of pure polycyanurate networks.[54]

Thermochemical Stability. In addition to hydrolytic degradation, deviations from simple linear rules of mixtures may also be found in the thermochemical degradation of polycyanurate networks. Figures 9 and 10 present TGA data in
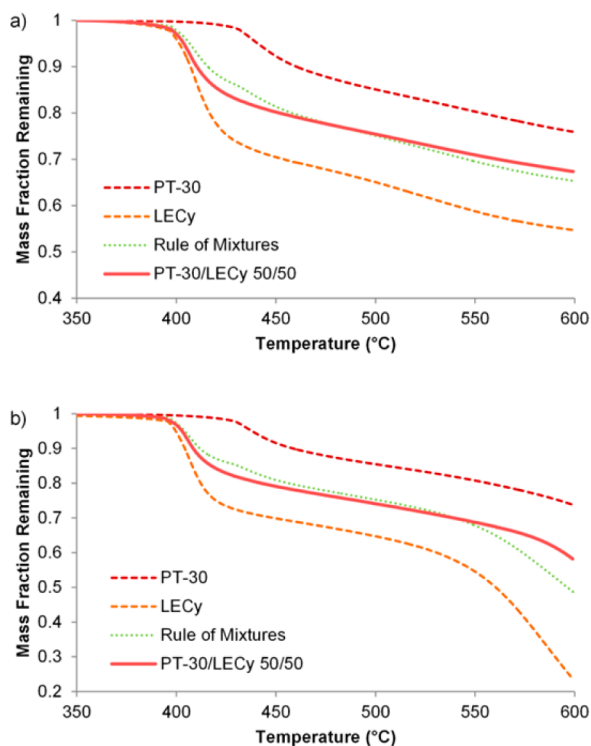
Figure 9. TGA data for PT-30, LECy, and PT-30/LECy 50/50 conetwork, compared to predicted curve based on linear rule of mixtures (a) in nitrogen (b) in air.

nitrogen and in air for PT-30 and FlexCy conetworks with LECy. Each figure shows that TGA trace of the two single-component networks, a predicted TGA curve based on a linear rule of mixtures for the degradation rates at temperatures above 350 °C, and, finally, the observed TGA curve for the conetwork. Under nitrogen, the FlexCy/LECy conetwork shows modest deviations from the rule of mixtures, with an onset of degradation closer to that of LECy and with an extent of degradation close to the prediction from the rule of mixtures. In air, the onset of initial degradation of the conetwork also
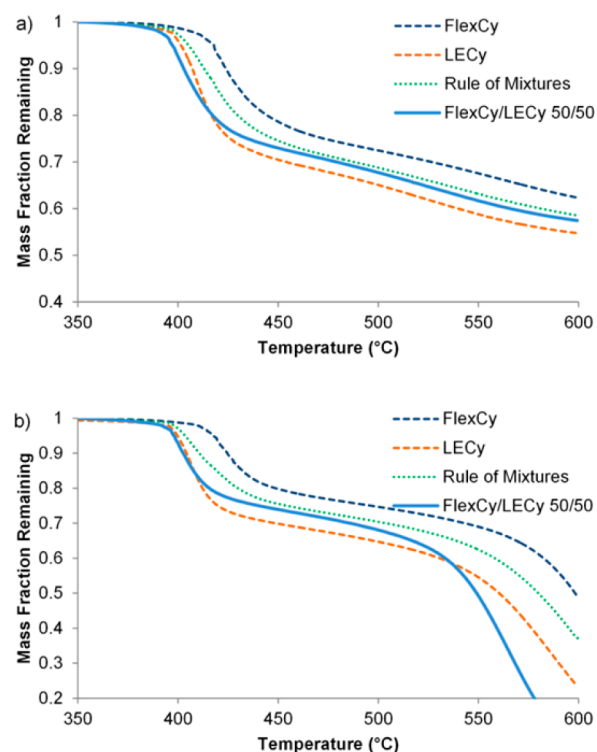
Figure 10. TGA data for FlexCy, LECy, and FlexCy/LECy 50/50 conetwork, compared to predicted curve based on linear rule of mixtures (a) in nitrogen (b) in air.

closely tracks LECy, and the char yield after the initial degradation is close to the prediction from the rule of mixtures, but the onset of the secondary degradation is earlier and more extensive in the conetwork than in either component. For PT-30/LECy conetworks, the patterns are almost identical: the onset of degradation in nitrogen and in air matches the less stable LECy, and the char yields are well approximated by a linear rule of mixtures. The onset and extent of secondary degradation in air, however, are later and less extensive, respectively, for the PT-30 conetwork compared to predictions based on a rule of mixtures, bearing a close resemblance to the behavior of PT-30 if corrected for the higher mass loss in the earlier degradation step.

The framework of "kinetics vs thermodynamics" represents one useful way of interpreting the TGA results. In this framework, char yields, which represent the end state of a decomposition event, reflect a kind of thermodynamically controlled variable (though in reality the decomposition kinetics and mechanisms are important) and therefore should depend on composition in a simple way. In previously reported work,[39] we have shown that the char yields of cyanurate networks after the first decomposition event are generally predictable based on the presence of simple chemical groups (methylene versus isopropylidene, for instance) in the network segments. In a heating experiment, onset temperatures, however, depend much more on the kinetics of decomposition, which are unlikely to follow simple, linear rules. The foregoing statement is especially true when secondary decomposition, which involve a strong dependence on the dynamics and products of the initial decomposition, are considered.

Interestingly, for the initial thermal decomposition, the combination of the more stable tricyanates with the less stable LECy results in a less stable material than expected based on a

Table 1. diBenedetto Parameters and Estimated Conversions for Polycyanurate Networks

network	T_{G0} (°C)	$T_{G\infty}$ (°C)	λ	α (as cured)	α (T_G = 210 °C)
LECy	−48 ± 1	296 ± 2	0.39 ± 0.06	0.94 ± 0.01	0.89 ± 0.02
PT-30	−17 ± 5	400 ± 10[a]	0.42 ± 0.05	0.82 ± 0.02	0.74 ± 0.02
FlexCy	−17 ± 5	370 ± 5	0.36 ± 0.04	0.88 ± 0.02	0.80 ± 0.02
PT-30/LECy 50/50	−34 ± 1	361 ± 10[b]	0.40 ± 0.07	0.89 ± 0.03	0.80 ± 0.04
FlexCy/LECy 50/50	−34 ± 1	340 ± 3	0.34 ± 0.03	0.92 ± 0.01	0.85 ± 0.01

[a]Estimated from ref 6 (see Supporting Information section S2). [b]Estimated from the value for the catalyzed system (see Supporting Information section S2).

rule of mixtures. Such an effect would be the result of a self-amplifying process, in which the breakdown of the network facilitates further decomposition, just as in hydrolytic degradation. However, whereas in hydrolytic degradation the combination of "weak" and "strong" elements results in a protective effect because network breakdown is slowed, in the initial thermal degradation the "weak" constituents dominate the behavior. Such a result may be because, in thermal degradation, the byproducts of degradation of the "weak" component can actively destroy both the "weak" and the "strong" components.

To summarize, a survey of a few key performance properties of the tricyanate/dicyanate conetworks revealed several key synergistic effects: (1) an expected negative deviation from a linear rule of mixtures for the coefficient of linear thermal expansion, which appears to lead to (2) a somewhat expected small positive deviation from the Flory−Fox equation for the T_G at full conversion (3) a small positive deviation from the Flory−Fox equation for the T_G after cure at lower temperatures, an effect that is somewhat surprising given that the cure temperature, and not the rigidity of the conetwork, is the primarily determinant of T_G under these conditions, (4) a large positive deviation from the expected "wet" T_G, which appears to be due to a combination of factors, (5) a negative deviation from a linear rule of mixtures for the onset temperature of degradation, and (6) variable behavior for the onset of secondary decomposition, which is not a surprise given the likely complexity of the contributing factors. Among these, the synergies involving "as cured" and "wet" T_G are both the most difficult to explain without further investigation, as well as being very important technologically. These two synergies, and their root causes, are thus the focus of the following section.

Contributing Factors for Synergistic Interactions. As mentioned previously, the "wet" T_G for a polycyanurate network can be thought of in terms of two components. The "as cured" dry T_G that characterizes a sample at the start of the hot/wet exposure, and the drop in T_G that occurs during exposure due to network degradation. Therefore, an analysis of the synergies affecting the "wet" T_G requires an analysis of the synergy involved in the "as cured" T_G.

Factors Affecting Synergy in "As Cured" T_G. The diBenedetto equation[55] has been shown to provide a highly reliable, single-valued relation between the T_G and conversion in cyanurate networks.[5,56,57] In order to understand changes in "as cured" T_G, the first factor to be examined is conversion, followed closely by the kinetics of cure that are responsible for the observed conversion. Parameters for the diBenedetto equation were obtained for all conetworks based on the parameters for the component networks, and are presented in Table 1 along with estimates of the conversion after the completion of cure and the conversion corresponding to the point of vitrification during cure (that is, the point at which T_G

and the cure temperature are equal). Details of these calculations and a discussion of uncertainties are provided in the Supporting Information. In all cases, the conversions achieved are significantly above the vitrification point, with 30−50% of cyanate esters remaining at the point of vitrification converted to cyanurates.

To understand how the conversion changes during cure, the rate of reaction as a function of time for temperatures from 210 to 290 °C is plotted in Figures 11 and 12 for the PT-30/LECy
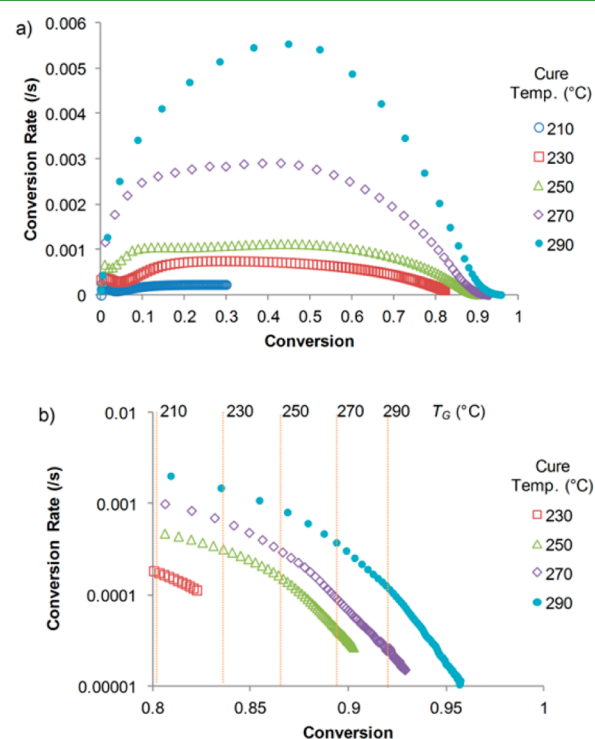
Figure 11. Conversion rate as a function of conversion for 50/50 PT-30/LECy conetwork at various temperatures: (a) linear scale and (b) logarithmic scale near the region (indicated) where the cure temperature equals T_G (T_G values estimated from conversions via the diBenedetto equation are indicated with vertical lines; note the uncertainty in the T_G values is about 15 °C).

and FlexCy/LECy conetworks, respectively. An additional plot in each figure shows the kinetics in the vicinity of the vitrification point. In general accordance with the findings of Deng and Martin,[58] the reaction rate should exhibit an exponential dependence on conversion in the diffusion-controlled regime. The straight lines seen in the logarithmic plots (Figures 11b and 12b) confirm this general model, although near the T_G more complex behavior, such as predicted by the recently proposed model by Corezzi et al.,[59] may also describe the data. Note that corresponding kinetic data for

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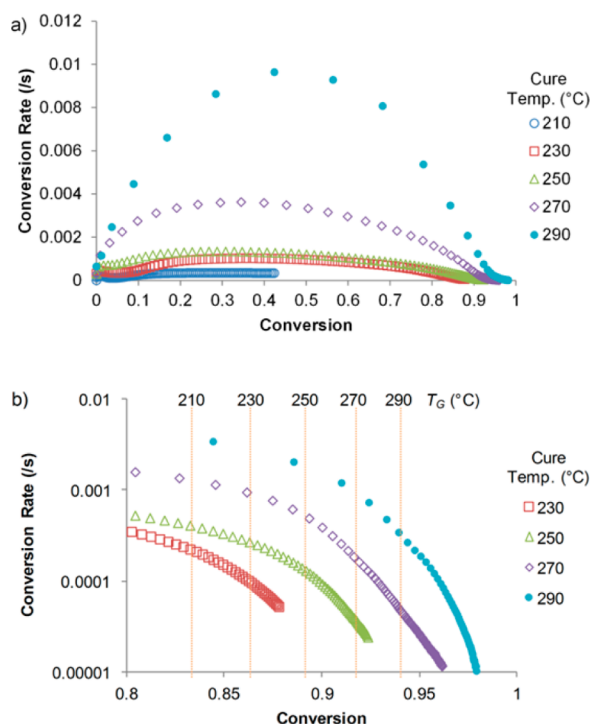
Figure 12. Conversion rate as a function of conversion for 50/50 FlexCy/LECy conetwork at various temperatures: (a) linear scale and (b) logarithmic scale near the region (indicated) where the cure temperature equals T_G.

LECy,[60] FlexCy,[36] and PT-30[36,61] has already been published. Even though the FlexCy/LECy conetwork develops at a significantly faster rate during the chemically controlled regime, the similarity in Figures 11b and 12b indicates that vitrification suppresses these differences, resulting in very similar overall rates of reaction for the two conetworks. Due to the faster chemically controlled kinetics, vitrification will take place sooner at 210 °C for the FlexCy/LECy conetwork, but the difference in time (roughly 10 min based on the observed rates of cure and the general shape of the conversion rate curve) is very small compared to the total cure time of 24 h, about 23 h of which is after vitrification. Therefore, the chemically controlled kinetics are of little consequence for the final conversion.

In cases where the rate of conversion after vitrification is similar, the most important factor in determining the T_G is the sensitivity of the T_G to conversion, which correlates most closely to the value of T_G at full cure (the other parameters in the diBenedetto equation that relates T_G to conversion tend to be similar for most cyanurate networks). As a result, the T_G in networks with flexible segments, such as LECy, tends to increase more gradually as conversion proceeds, and the "as cured" T_G tends to be lower in these networks after long periods of cure at temperatures well below the "fully cured" T_G (all else being equal). On the other hand, the ability of cyanurate networks to cure completely is clearly affected by steric hindrance around the available cyanate ester groups, as illustrated by recent studies of cyanate esters derived from creosol.[23] Networks with highly rigid segments are also likely to suffer from these steric effects, which is, in general why they are unable to attain T_G values much higher than their more flexible counterparts even when the T_G at full cure is very high, as recently discussed by us in more detail.[39] The interaction

among these two competing factors (higher sensitivity of T_G to small changes in conversion balanced by steric effects that decrease the ability to cure completely) is therefore the likely source of the observed nonlinear behavior that drives deviations from expected values based on the rule of mixtures. Any nonlinearities in the T_G at full cure as a function of composition, such as those present in the PT-30/LECy conetworks, will accentuate the deviations.

Network Degradation under Hot/Wet Conditions. As mentioned previously, the nonlinear dependence of the decline in T_G during hot/wet exposure on composition is likely due primarily to the nonlinear kinetics of the degradation process. In addition, it is important to determine whether or not other synergistic effects play a role. Two such effects would be unexpected levels of water uptake, which have been shown to occur in dicyanate blends,[47] or deviations from a linear rule of mixtures with respect to density, since changes in free volume could help or hinder the degradation reaction. Figure 13 shows
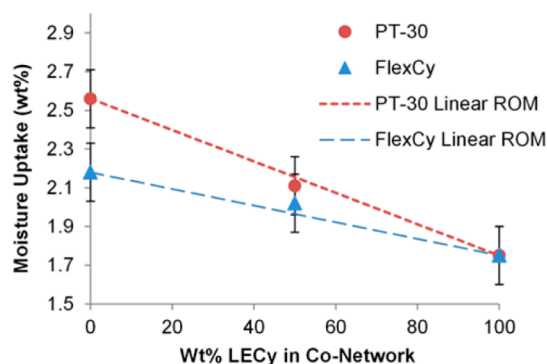
Figure 13. Water uptake (after immersion at 85 °C for 96 h) for PT-30, FlexCy, and LECy conetworks as a function of composition.

that the water uptake appears to follow a linear rule of mixtures quite closely, while Figure 14 indicates only a small deviation
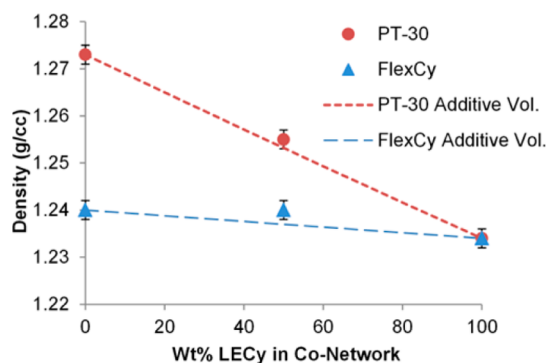
Figure 14. Density (after cure at 210 °C for 24 h) for PT-30, FlexCy, and LECy conetworks as a function of composition.

from the assumption of additive volumes for density, on par with the measurement uncertainty. We therefore cannot definitively attribute any of the observed synergy in "wet" T_G to these two factors. Another possibility to consider is the presence of impurities that act as catalysts for hydrolysis of the networks.

One interesting final note on the hydrolysis of these networks comes from a comparison of the presently reported data (for systems cured at 210 °C for 24 h) with previously

reported data for systems cured at 210 °C for 24 h, then postcured for 30 min at 290 °C.[36] For the FlexCy network, the water uptake for the postcured network was about 60% higher than that without postcure, and the "wet" T_G was about 25 °C higher. For PT-30, the water uptake in the postcured network was about 100% higher and the wet T_G was actually about 10 °C lower after postcure. These comparisons help to confirm that, despite their similar chemical structure, networks based on FlexCy and PT-30 respond to moisture differently. Although the "rule of thumb" for cyanurate networks is that at least 85% conversion is required to provide adequate hydrolytic stability, and all networks in this study approached or met that condition, the optimum in "wet" T_G under the test conditions employed appears to lie at very different points in the 85−100% conversion range, being lower for PT-30 and higher for FlexCy.

Catalyzed Networks. Although the simpler, uncatalyzed networks are most useful for understanding the nature and causes of synergistic interactions in cyanurate conetworks, the catalyzed conetworks must also be considered. First, it is important to verify that the synergistic effects are present in catalyzed networks, since in industrial applications, catalyzed networks are used almost exclusively. Second, the production of large samples (such as those needed for measurement of mechanical properties) requires catalysis (cyanate ester monomers possess sufficient volatility to vaporize to a significant extent during the time−temperature protocols required for cure of highly pure uncatalyzed monomers, thus it is difficult to make large, void-free samples without catalysis).

The use of the catalyst (in this case 2 parts per hundred by weight of a 30:1 by weight solution of nonylphenol to copper(II) acetylacetonate, which results in 160 ppm Cu in the monomer) has a dramatic effect on cure, as seen in the comparative DSC traces for the 50/50 FlexCy/LECy network shown in Figure 15. The features of the traces are typical of cyanate esters with this type and loading level of catalyst. In Table 2, a comparison of the key properties of the catalyzed and uncatalyzed conetworks reveals mainly modest and expected differences, such as increases in water uptake, decreases in density, and decreases in T_G at full cure.[7] Interestingly, the T_G values after cure at 210 °C for 24 h are lower for the catalyzed conetworks. Intuitively, one might expect that catalysis, by facilitating more rapid cure, would result in a greater degree of conversion, as observed for LECy. In the highly pure LECy, however, vitrification was observed to take up to 16 h without catalyst, compared to less than 90 min for the catalyzed system, so in a 24 h cure the catalyzed system does have appreciably longer to cure in the glassy state, resulting in a higher final conversion. In contrast, in the conetworks, even the uncatalyzed systems vitrify in about an hour, so both catalyzed and uncatalyzed systems have nearly the same amount of time to cure in the glassy state. Under these conditions, the conversion achieved is nearly the same for catalyzed and uncatalyzed networks (compare data in Tables 1 and 3). Because catalysis depresses the T_G at full cure slightly due to incorporation of nonylphenol into the cyanurate network, the same extent of conversion causes a smaller rise in T_G. These data show yet another example of how multiple factors may interact to contribute to the "as cured" T_G value.

Flexural testing of the catalyzed conetworks also suggests an important aspect of the nature of the molecular chain segments in FlexCy and PT-30 compared to LECy. Figures 16−18 show the raw force/displacement curves for the catalyzed 50/50 PT-30/LECy, 50/50 FlexCyLECy, and LECy networks, respec-
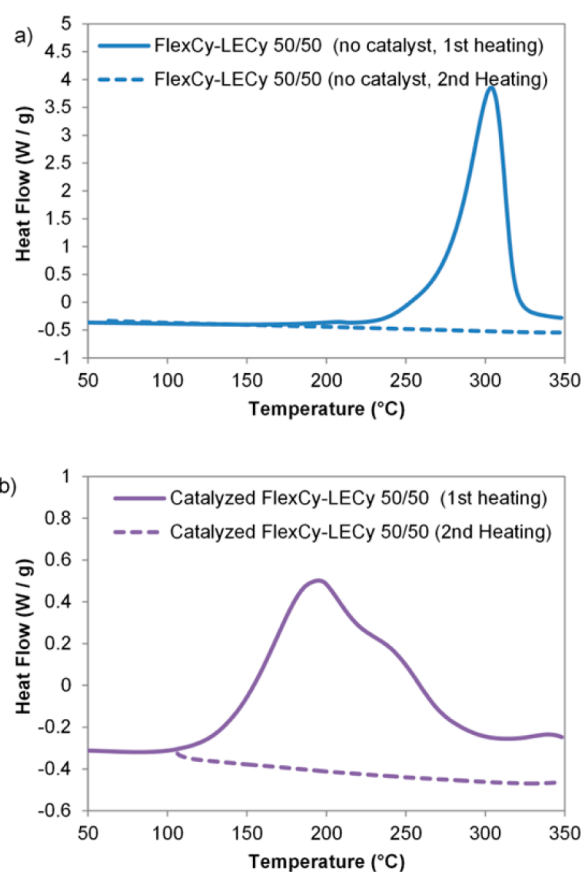
Figure 15. Nonisothermal DSC traces for (a) uncatalyzed and (b) catalyzed 50/50 wt % FlexCy/LECy monomer blends, showing typical features for all systems studied.
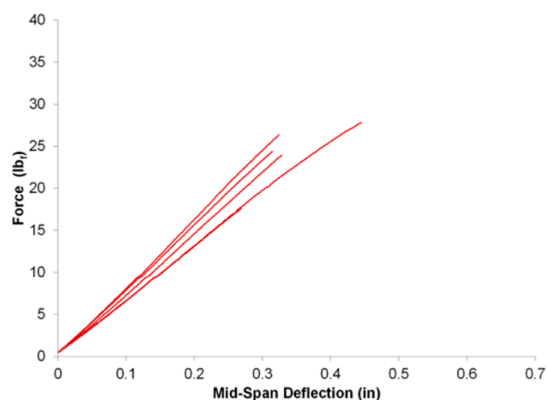
tively, with the resultant mechanical properties provided in Table 3. The PT-30/LECy networks showed a higher modulus and similar strain to failure compared to LECy networks cured under the same conditions (210 °C for 24 h as the final step), thus indicating reinforcement. PT-30 is slightly higher in density than LECy, and although it possesses a similar equivalent weight, the branch points in the PT-30 monomer may become network junctions on cure, meaning that a 50/50 PT-30 LECy network can attain significantly more network junctions per unit volume than LECy at full conversion. (The actual junction densities for ideal networks, which take into account conversion and dilution by nonylphenol, but not the potentially very important factor of internal cyclization,[62] are provided in Table 3).

One might imagine that a higher ideal network junction density leads in general to shorter chain segments with fewer motional degrees of freedom between junction points, and therefore to mechanical reinforcement. However, the FlexCy/LECy network also has a much higher ideal network junction density than the LECy network (see Table 3) because, like PT-30, the FlexCy monomer contains branch points that may become network junctions on cure (Figure 1 of ref 36, reproduced in the Supporting Information, illustrates these concepts graphically). Despite a high probability of having more junctions per unit volume, and shorter (on average) chain segments with fewer degrees of freedom between junctions, the FlexCy/LECy networks showed a lower modulus and a higher strain to failure than the LECy networks, resulting in significantly higher flexural strength. Half of the junctions
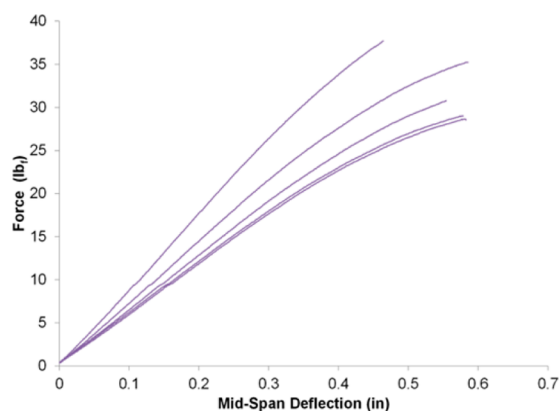
Table 2. Comparison of Key Physical Properties: Catalyzed and Uncatalyzed Cyanurate Networks

property	typical uncertainty[a]	FlexCy/LECy		PT-30/LECy		LECy	
catalyst?		no	yes	no	yes	no	yes
T_G @full cure (°C)	±3	340	316	361 ± 10[b]	341	296	282
T_G @210 °C/24 h cure (°C)	±12	265	234	270	256	250	264
"Wet" T_G (°C)	±12	249	236	271	243	239	193
water uptake (wt %)	±0.15	2.02	2.56	2.11	2.26	1.75	2.34
density (g/cm³)	±0.003	1.240	1.230	1.255	1.253	1.234	1.220

[a]Uncertainties for "Wet" T_G, water uptake, and density are based on previous statistical analyses of data collected using these techniques for polycyanurate blends; uncertainties for the other variables are based on replicated data. [b]This T_G value was estimated from the value for the catalyzed network (see Supporting Information section S2)
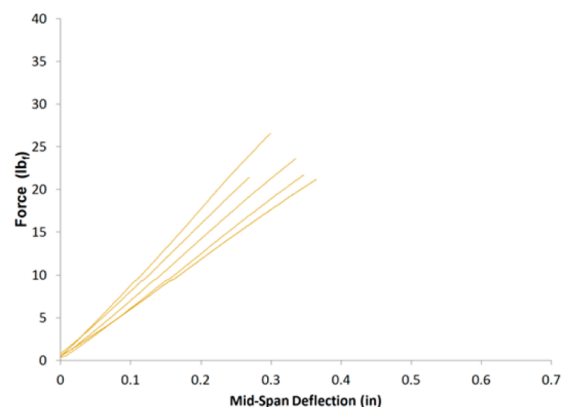

Figure 16. Flexural test data for five rectangular specimens (25.4 mm span × 12.7 mm × 3 mm) of catalyzed 50/50 wt % PT-30/LECy cured at 210 °C for 24 h.

Figure 18. Flexural test data for five rectangular specimens (25.4 mm span × 11.5 mm × 3 mm) of catalyzed LECy cured at 210 °C for 24 h.

Figure 17. Flexural test data for five rectangular specimens (25.4 mm span × 12.7 mm × 3 mm) of catalyzed 50/50 wt % FlexCy/LECy cured at 210 °C for 24 h.

particularly at high conversions when the final stages of sample cure are accomplished below T_G,[63] as is the case for all the networks studied. Thus, while the data presented here provides interesting suggestions about the effect of various types of network junctions, more definitive answers with respect to comparisons with LECy will require a complete accounting of the effects of conversion on mechanical properties. The actual network structures, which likely contain at least some monomer or oligomer cyclization, will also play an important role. A full accounting of these effects, which may differ for each of the systems studied, is beyond the scope of the present work.

■ **CONCLUSIONS**

The cocyclotrimerization of two tricyanate ester monomers in equal parts by weight with Primaset LECy, a liquid dicyanate ester, has been shown to provide synergistic performance benefits. Most importantly, the formation of stable, homogeneous monomer blends that remain in the supercooled liquid state for long periods at room temperature provides many of the processing advantages of Primaset LECy in combination with significantly higher glass transition temperatures (315 to 360 °C at full cure). Interestingly, the glass transition temperatures of the conetworks after cure at 210 °C, at full cure, and after immersion in 85 °C water for 96 h were all higher than predicted by the Flory−Fox equation, most significantly for the samples immersed in hot water. In fact, uncatalyzed conetworks comprising equal parts by weight of PT-30 and LECy retained a "wet" glass transition temperature near 270 °C. These synergistic effects are likely to have arisen due to multiple factors, including previously discovered nonlinearities in the coefficient of thermal expansion for conetworks with components of differing bulk modulus (which is expected to lead to slightly higher glass transition

potentially provided by FlexCy involve an aliphatic carbon rather than an aromatic ring (again, see the illustration in the Supporting Information). These junctions would be expected to have more freedom of motion in the network.

On the whole, the mechanical property data indicate that the presence of FlexCy (in at least some cases, when comparing samples prepared identically) provides a toughening rather than a reinforcing effect. This effect is particularly useful because it indicates that "flexible" network junctions could constrain motion sufficiently to provide a significant improvement in T_G while improving toughness, a rare combination. An important caveat, however, concerns the effects of different sample conversions. In polycyanurate networks, the mechanical behavior can depend on conversion in unexpected ways,

Table 3. Mechanical Properties of LECy and Conetworks with PT-30 and FlexCy

sample	conversion	ideal network junction density (mmol/cc)	dangling end density (mol/cc)	flexural modulus (MPa, RT)	flexural strength (MPa, RT)	strain at break (RT)
LECy	0.98 ± 0.01^a	2.96 ± 0.03^b	0.17 ± 0.03^c	3340 ± 90	69 ± 7	0.021 ± 0.002
PT-30/LECy 50/50	0.90 ± 0.02^a	3.93 ± 0.06^b	0.42 ± 0.06^c	3780 ± 70	77 ± 13	0.020 ± 0.004
FlexCy/LECy 50/50	0.91 ± 0.02^a	3.91 ± 0.06^b	0.39 ± 0.06^c	2960 ± 120	98 ± 3	0.034 ± 0.002

^{a}Based on diBenedetto equation with the T_G at full cure taken from catalyzed system data and all other parameters from equivalent uncatalyzed system. ^{b}Assumes no more than one dangling −OCN per monomer; includes former monomer branch points (when no dangling −OCN is present) and chemical cross-links; assumes no side reactions or formation of unentangled cyclic structures and equal conversion of conetwork components. ^{c}Includes both residual −OCN and nonylphenol aliphatic ends incorporated into cyanurate network; assumes 100% incorporation of phenol, no side reactions, and equal conversion of conetwork components.

temperatures than expected at high conversions) and highly nonlinear improvements in the hydrolysis resistance performance when network components of differing hydrolytic susceptibility are copolymerized, similar to previously observed behavior in polycyanurate conetworks. In contrast to hydrolysis resistance, the thermochemical stability of the conetworks showed performance that was, in some way, worse than predicted by a linear rule of mixtures, with the onset of degradation for conetworks dominated by that of the thermally less stable component, while char yields after the initial degradation step were close to values predicted by a linear rule of mixtures. Values for moisture uptake and density also showed behavior that was not clearly different from a linear rule of mixtures. Investigations of the catalyzed conetworks showed the expected effects of catalysis, namely much faster cure kinetics, a modest decline in glass transition temperatures at high conversions, and modest increases in moisture uptake. An analysis of the flexural properties of the catalyzed systems also revealed that while conetworks containing PT-30 (when cured under identical conditions) provided higher modulus compared to networks containing only LECy, conetworks containing FlexCy provided toughening with a modest decline in elastic modulus. Thus, in the case of FlexCy, many of the benefits of copolymerizing higher T_G cyanate esters with LECy were realized while also improving toughness.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Section S1: Additional X-ray graphics. Section S2: "Fully cured" T_G values by modulated DSC and supporting thermal analysis data. Section S3: "As cured" T_G values by rapid DSC scan. Section S4: estimation of diBenedetto equation parameters. Section S5: FlexCy and PT-30 network structures (from ref 23). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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