

Effect of PEGDE Addition on Rheological and Mechanical Properties of Bisphenol E Cyanate Ester

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ABSTRACT: Cyanate esters are a group of resins with exceptional thermal and mechanical properties and are often blended with lower cost epoxy resins. These blends are often brittle, and a toughening method, such as the addition of soft segments, is necessary. Poly (ethylene glycol) diglycidyl ether, or PEGDE, was added to bisphenol E cyanate ester as a toughening agent. PEGDE was added at loadings of 0–30 wt %, and rheological and mechanical properties were analyzed after curing. As PEGDE loading was increased, the gel point increased accordingly while the activation energy of gelation decreased, indicating PEGDE accelerated the gelation process. Dynamic mechanical analysis results indicated a decrease in glass transition temperature as the PEGDE loading increased. Three-point bending tests yielded similar toughness to the neat BECy at low PEGDE loadings, with a dramatic increase at loadings of 25 and 30 wt % PEGDE. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 463–469, 2013

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INTRODUCTION

Cyanate esters are a class of resins with excellent thermal and mechanical properties. Typical cyanate ester resins exhibit high glass transition temperatures above 200°C and can maintain their outstanding mechanical properties at elevated temperatures. Cyanate esters also have excellent adhesive properties and are often moisture resistant.¹ Because of these exceptional properties, cyanate esters are good alternatives or additions to epoxy-based resins for certain applications, such as aerospace and microelectronics.^{2,3}

Blending of lower cost epoxy resins with cyanate esters will often yield a final cured resin with lower cost and properties intermediate of the two components. Selection of the amount and composition of each component will therefore dictate the final properties.⁴ For example, epoxy systems typically exhibit high water absorption resulting in decreased mechanical performance, especially at high temperatures. The addition of cyanate esters counteracts this effect and helps maintain the desired mechanical properties.⁵ Compared to the epoxy counterpart, the cyanate ester-epoxy blends also exhibit lower dielectric loss, viscosity, and toxicity.⁶

Among the cyanate ester resins, bisphenol E cyanate ester (BECy) is of particular interest, because of its extremely low vis-

cosity of 0.09–0.12 Pa s at room temperature combined with a high glass transition temperature. As shown in Figure 1, this combination of low viscosity and high glass transition temperature makes BECy unique among cyanate ester resins.⁷ BECy resins can also be made into property-specific blends while still retaining their thermal stability.³ In industry, BECy resins are used in a variety of applications, such as repairing bismaleimide/carbon fiber composite panels used in high temperature environments.⁸ The chemical structure of a BECy monomer is shown in Figure 2. Epoxy groups are commonly reacted with cyanate end groups, the reaction is somewhat complex and a simplified reaction is illustrated in Figure 3.⁹ The detailed reaction scheme containing cyanate trimerization, epoxide insertion, and ring cleavage with addition epoxide forming substituted oxazolidinones is explained more thoroughly by Bauer et al.^{10,11} Although such highly crosslinked structures ensure excellent thermal and mechanical properties in BECy resins, it makes them very brittle and toughening is necessary to achieve better fracture toughness.

Toughening mechanisms can be of either physical or chemical nature. When adopting a physical method, the cyanate ester resins are modified with fillers, such as particles, fibers, or woven-mats, yielding toughened cyanate ester composites. Kinloch et al.^{2,12} reported using a selection of fillers, including PES and

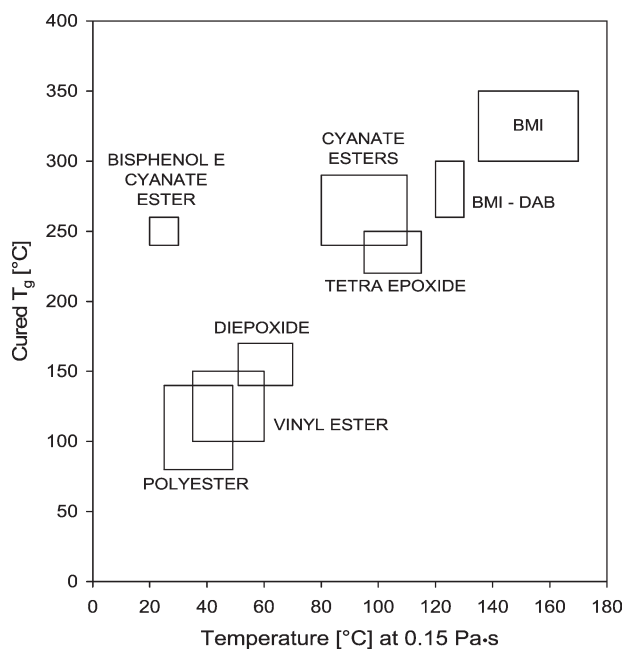


Figure 1. Glass transition temperature versus temperature of the prepolymer to achieve a viscosity of 0.15 Pa·s.³

a polyester copolymer, with filler loads ranging from 10 to 30%. Among inorganic fillers, mica provides the most promising results: 100% increase in fracture energy with 10% mica loading. The addition of 25% thermoplastic poly(ether sulfone) may increase the fracture energy of cyanate esters by more than 800%. In another experiment, Sheng et al.¹³ added alumina nanoparticles to BECy to form a nanocomposite. The alumina particles had a catalytic effect on the BECy cure, and rheology investigations of the BECy suspensions showed an increase in viscosity. Ganguli et al.¹⁴ and Wooster et al.¹⁵ reported creating nanocomposites from cyanate esters, using layered silicates and achieving a 30% increase in modulus and toughness. More recently, carbon nanotubes were used to drastically increase the impact strength of cyanate esters owing to their high tensile strength and stiffness.¹⁶ One of the primary drawbacks to physical toughening methods is that they almost always lead to significant increases in the viscosity of the prepolymer resin.

When adopting a chemical route to toughening, mono-functional cyanate esters may be incorporated to reduce crosslink density, or cyanate ester monomers with enhanced flexibility may be synthesized resulting in polymers with increased toughness. Thermoplastics, such as polysulfone, are often incorporated using solution blending, by dissolving the thermoplastic in a solvent and adding the cyanate ester monomers.¹⁷ Designing and synthesizing novel cyanate ester monomers may be an alternative way to achieve tougher cyanate esters. For example,

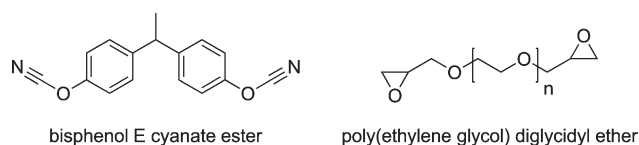


Figure 2. Chemical structures of BECy and PEGDE.

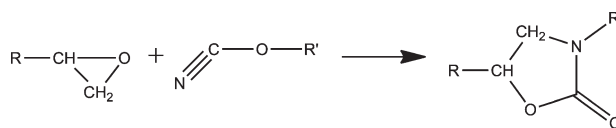


Figure 3. Simplified reaction between epoxy and cyanate end groups.

introducing “soft” segments, such as ether linkages, into the monomers creates spacer groups between the reactive cyanate ester end groups, resulting in tougher polymers. An oligomeric cyanate ester resin containing multiple ether linkages was successfully developed to enhance the processability of cyanate esters.¹⁸ Hamerton et al.¹⁹ synthesized a class of cyanate ester monomers with variable ethylene glycol groups in the backbone resulting in cured polymers with increased toughness.

A chemical approach to toughening BECy was employed in this study. Poly(ethylene glycol) diglycidyl ether (PEGDE, Figure 2), which contains “soft” ethylene glycol segments, was mixed with BECy at various loadings from 0 to 30 wt %. PEGDE has a low viscosity and is highly miscible with BECy. The epoxy end groups of PEGDE react with BECy, and the resulting BECy/PEGDE resin was expected to have an increased toughness while maintaining a low viscosity at room temperature. The effect of PEGDE on the gel behavior of BECy was investigated through rheology testing. The mechanical properties of the cured polymers were evaluated by dynamic mechanical analysis (DMA) and three-point bending flexural tests.

EXPERIMENTAL

Materials

BECy is a commercially available resin and was purchased from Bryte Technologies (Morgan Hill, CA) as EX-1510. The liquid phase organometallic-based catalyst (EX-1510B) was supplied with the resin. PEGDE was purchased from Sigma-Aldrich Inc. (St. Louis, MO) with an average M_n of 526.

Specimen Preparation

PEGDE was added to the BECy monomer until the desired loading by weight was reached. The total weight of the mixture was approximately 10 g. A liquid catalyst was added to the remaining mixture at a loading level of 3 phr with respect to BECy. Catalyzed samples were used for all tests in this study. After mixing with a magnetic stirring bar for 5 min, the mixture was poured into a high temperature silicone rubber mold ($27 \times 48 \times 8 \text{ mm}^3$) and degassed at room temperature for 1 h under vacuum. Then, the sample was cured in a programmable convection oven: heated to 180°C at a heating rate of 1°C/min; isothermally cured at 180°C for 2 h; heated to 250°C at 1°C/min, and isothermally cured for another 2 h; cooled down to room temperature at a cooling rate of 2°C/min. The cured samples of neat BECy were prepared following the same procedure.

Rheological Testing

Catalyzed BECy/PEGDE specimens were tested for rheological properties using a TA Instruments (New Castle, Delaware) AR2000ex stress-controlled rheometer with a forced gas environmental test chamber, utilizing parallel plate geometry (25-mm diameter disposable aluminum). All tests were conducted

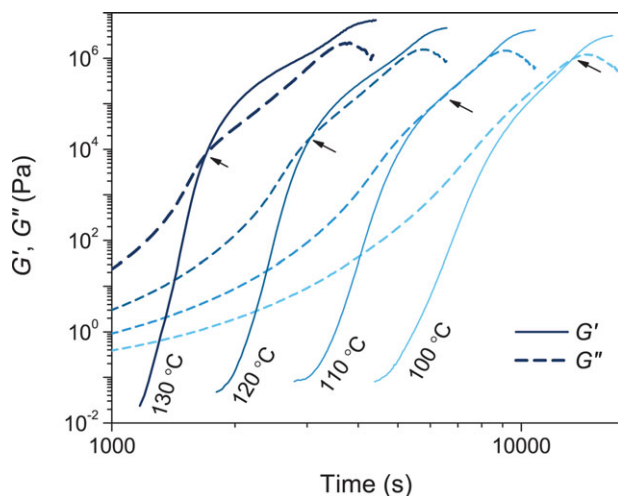


Figure 4. Typical rheological curves: storage shear modulus (G') and loss shear modulus (G'') of neat BECy, curing at isothermal temperatures of 100, 110, 120, and 130°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

under isothermal conditions in stress control-oscillatory mode at an amplitude of 1000 Pa and 1 Hz. A gap of 0.5 mm was used, and a specimen volume of 0.25 mL was transferred to the parallel plates using a 1-mL syringe. A 2-min equilibrium period was allowed for each specimen to reach the isothermal temperature before collecting data. For each composition, there were four isothermal curing tests: 100, 110, 120, and 130°C, respectively.

DMA

A dynamic mechanical analyzer Q800 (TA Instruments, New Castle, DE) with a liquid nitrogen gas cooling accessory was used to evaluate mechanical properties of cured specimens. A diamond saw was used to cut samples with dimensions of $27 \times 5 \times 0.5 \text{ mm}^3$. A constant amplitude of 0.025% strain at 1 Hz was applied throughout all tests, with a static load tracking at 125% of the dynamic force. A tension film fixture with a length of 20 mm was utilized for each test. All specimens were tested at in a temperature ramping mode: temperature was ramped from 30 to 330°C at a heating rate of 3°C/min.

Three Point Bending Tests

Three point bending flexural tests were performed to further analyze the mechanical properties of the samples. Compared to tensile testing, this method was more easily performed and allowed for improved strength comparison between samples. A diamond saw was used to cut samples with dimensions of $27 \times 3 \times 3 \text{ mm}^3$. The three point bending tests were performed on an Instron Universal Testing Machine with a customized sample support. Standard ASTM D790 was followed for all testing. The testing speed was set to 1 mm/min, and the span length was 20 mm. Each value reported is the average of at least five specimens for each composition.

Polarized optical microscopy was used to determine the cause for the darkening of the samples after cure. An Olympus Model

BX51-TRF microscope was used, along with a LTS-350 hotstage and a TMS-94 temperature controller, all from Linkam.

RESULTS AND DISCUSSION

Rheological Testing

PEGDE is a low molecular weight epoxy, which can be utilized for cyanate ester cyclotrimerization.⁷ In addition, the PEGDE used in this study has a lower viscosity than the BECy monomer. All these factors could affect the curing behavior of BECy. Before curing, the PEGDE and BECy monomer are miscible and homogeneous once mixed. To investigate such effects, catalyzed BECy/PEGDE specimens were prepared and evaluated by dynamic oscillatory rheology. For each composition, the specimens were tested at four different isothermal temperatures to determine the activation energies.

Figure 4 shows dynamic mechanical properties of the neat BECy, curing at isothermal temperatures of 100, 110, 120, and 130°C, respectively. The storage and loss shear moduli (G' and G'' , respectively) increase with reaction time at elevated temperatures. Consequently, G' , which represents the elastic component of the response to applied dynamic shear force, increases faster than G'' , which represents the viscous component. The crossover point of G' and G'' is loosely defined as the gel point, indicating that a chemical network has formed, and the material's response is dominated by elastic behavior.^{20,21} Isothermal temperature is a crucial factor for gel time: the time to reach the gel point is dramatically reduced when higher temperatures are applied. For neat BECy, an increase of 10°C in isothermal temperature results in a 50% reduction in gel time.

The gel time (t_{gel}) is an indicator of the apparent activation energy (E) for gelation. As the network structure is a unique function of conversion, it can be considered constant and independent of isothermal temperatures.²² Therefore, gel time and isothermal temperature follow an Arrhenius relationship, assumedly:

$$\ln t_{\text{gel}} = \ln A' + \frac{E}{RT} \quad (1)$$

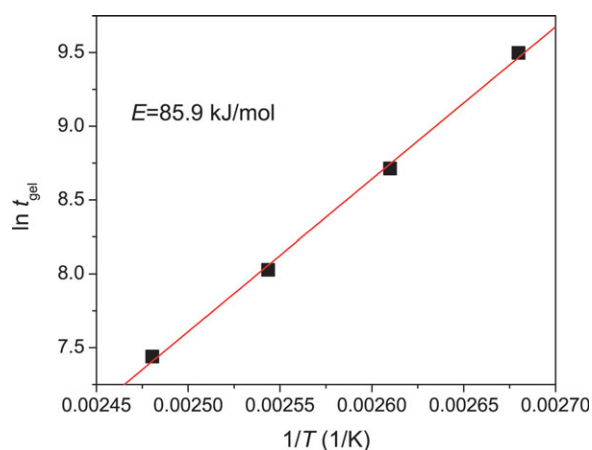


Figure 5. Arrhenius plot of $\ln t_{\text{gel}}$ versus $1/T$ for neat BECy ($R^2 > 0.99$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

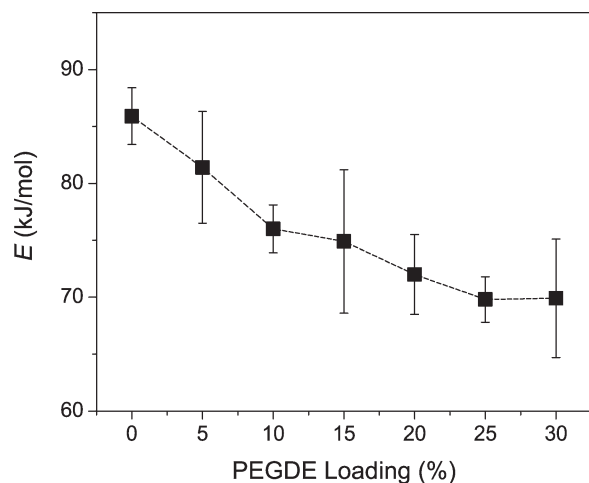


Figure 6. The effect of PEGDE on activation energies.

where A' is a constant related to the reaction model, R is the universal gas constant, and E is the apparent activation energy for gelation. A plot of $\ln t_{\text{gel}}$ versus $1/T$ gives a slope proportional to E (Figure 5). As the PEGDE loading is increased, the activation energy for gelation decreases (Figure 6), indicating that PEGDE accelerates gelation. This positive impact may be attributed to the lower viscosity of the PEGDE/BECy mixture, allowing unreacted BECy monomer and other reaction sites (e.g., epoxy end groups of PEGDE) to diffuse more easily, increasing the overall reaction rate. When PEGDE is added to BECy, the viscosity is reduced further resulting in very low viscosities that are difficult to measure with rheological instruments.

DMA

Thermal mechanical properties of specimens with various PEGDE loadings were evaluated by DMA. Similar to oscillatory rheology measurements, a sinusoidal force is applied to a specimen and the response is recorded. The storage (E') and loss modulus (E'') represent the material's ability to elastically store energy and dissipate loss, respectively. For a viscoelastic mate-

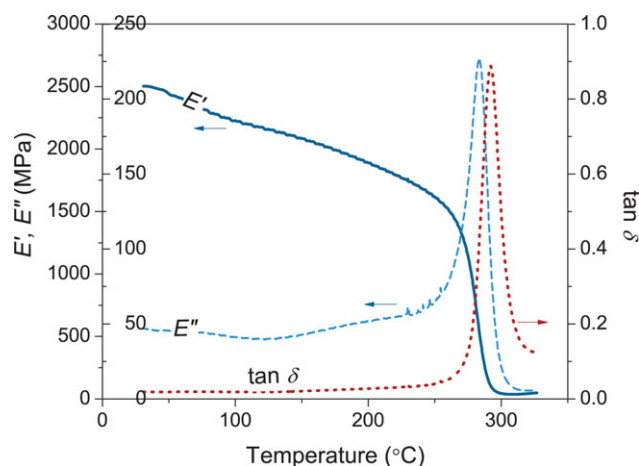


Figure 7. Typical DMA curves: storage modulus (E'), loss modulus (E'') and $\tan \delta$ for neat BECy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rial, the deformation usually falls behind applied force by a phase angle δ , which is used to define the damping as:

$$\tan \delta = \frac{E''}{E'} \quad (2)$$

Figure 7 shows a typical plot of DMA results for neat BECy. The storage modulus E' is approximately 2500 MPa at a temperature of 35°C and decreases with increasing temperatures.

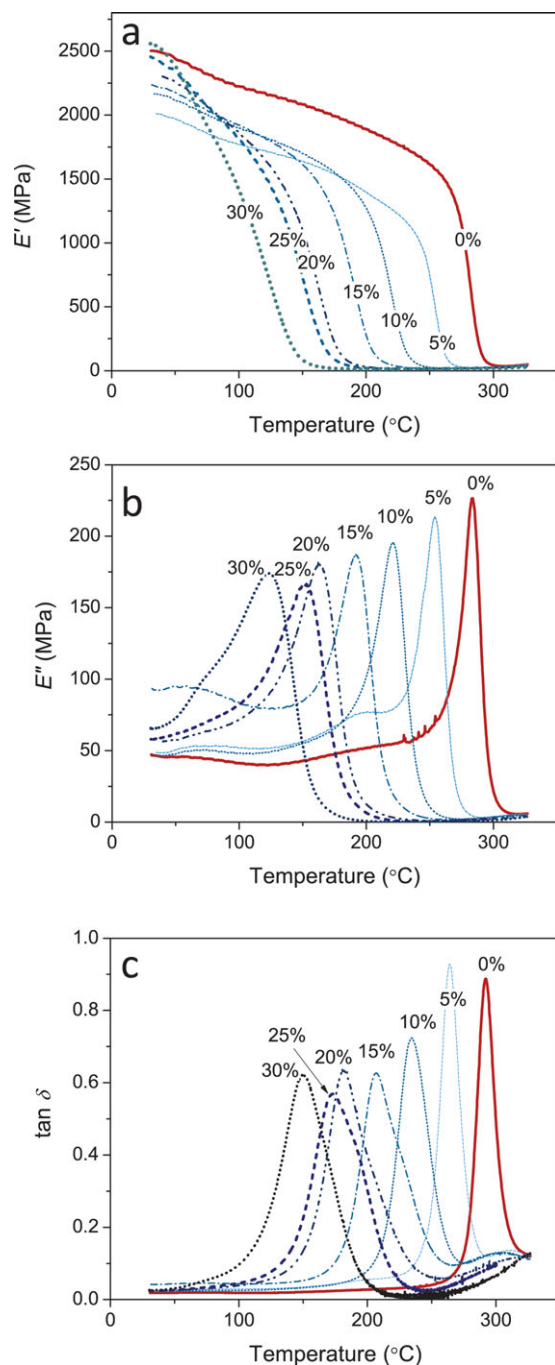


Figure 8. DMA plots for all samples: (a) storage modulus; (b) loss modulus; (c) $\tan \delta$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Summary of Properties of BECy with Various Loadings of PEGDE.

PEGDE content (wt %)	E' at 35°C (MPa)	T_g^* (°C)	E_{gel} (kJ/mol)	Flexural modulus (GPa)	Maximum strain	Maximum stress (MPa)	Toughness (MPa)
0	2500	283.0	85.9	1.96 ± 0.14	0.16 ± 0.02	211.5 ± 10.0	21.6 ± 4.9
5	2010	253.9	81.4	2.03 ± 0.08	0.14 ± 0.01	207.0 ± 5.8	17.3 ± 2.5
10	2166	220.9	76.0	2.19 ± 0.11	0.14 ± 0.01	214.1 ± 3.0	18.9 ± 2.2
15	2224	191.8	74.9	2.29 ± 0.06	0.14 ± 0.01	212.5 ± 1.2	20.0 ± 1.3
20	2302	164.4	72.0	2.33 ± 0.11	0.14 ± 0.01	206.1 ± 2.1	19.0 ± 1.5
25	2438	151.3	69.8	2.21 ± 0.01	0.26 ± 0.01	187.3 ± 1.0	36.8 ± 2.6
30	2542	123.6	69.9	2.22 ± 0.04	0.26 ± 0.02	174.3 ± 1.1	38.6 ± 2.5

*Peak temperature of loss modulus.

The sudden drop of E' indicates the glass transition, and the following plateau can generally be seen for crosslinked materials. The loss modulus E'' is more sensitive to molecular motions in the polymer chain than E' . The peak of E'' is taken as a clear indicator of glass transition temperature (T_g) in this study. The presence of only one peak in all samples indicates that the PEGDE was successfully incorporated into BECy to create a single phase.

E' versus temperature curves are compared in Figure 8(a). For the whole temperature range, E' of neat BECy is higher than that for other specimens with PEGDE. Incorporation of PEGDE not only reduces the crosslink density of the entire network but also introduces “soft” segments in the network. This factor also contributes to the reduction of T_g . PEGDE also increases the storage modulus of BECy/PEGDE at lower temperatures. The BECy/PEGDE with the lowest loading of PEGDE (5%) had the lowest E' with 2000 MPa at 35°C. However, higher PEGDE loads help E' “recover.” The BECy/PEGDE specimen containing 30% PEGDE had an E' of about 2500, similar to that of neat BECy (Table I). This may be caused by the increase in secondary bonding as PEGDE loading is increased, due to dipole–dipole interactions.

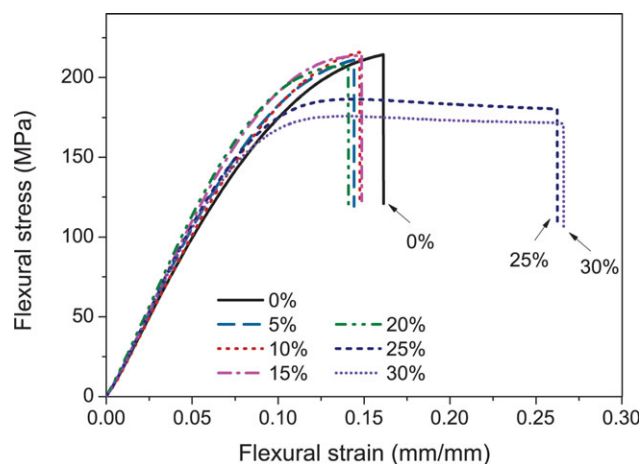


Figure 9. Selected three-point bending flexural test results for BECy/PEGDE samples with various loading levels of PEGDE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8(b) shows the comparison of loss modulus versus temperature curves for all specimens. It is obvious that the peak of E'' is shifted to lower temperatures as PEGDE loading increases. The shifting and broadening of peaks seem to be linearly related to the reduction of T_g . The lower and broader peaks suggest that there are constraints present in the amorphous phase, such as longer polymer chains, causing more entanglements. Higher PEGDE loads resulted in less crosslinked sites and longer chain segments between these sites. This is also indicated by the more pronounced shoulder just before the major peak. These shoulders represent the β -transition, or short-range movements, of polymer chains before the major glass transition (α -transition) takes place. $\tan \delta$ curves [Figure 8(c)] provide more information about the behavior at temperatures beyond the glass transition. As PEGDE increases, the crosslinking density decreases and linear portions between crosslinking sites increase, resulting in a more pronounced shoulder right after the glass transition peak.

Three Point Bending Tests

Figure 9 shows selected flexural strain–stress curves for specimens with various loadings of PEGDE. Neat BECy and BECy/PEGDE with PEGDE loadings up to 20% show “typical” brittle thermoset behavior: when the material is loaded to its ultimate strength, the specimen fractures suddenly. PEGDE loadings of 25 and 30% exhibited higher flexural strains and lower flexural stresses at fracture. The flexural modulus can be calculated from the tangent of the initial linear portion of strain–stress curves. Addition of PEGDE slightly increased the flexural modulus, and specimens containing 20% PEGDE exhibited the highest flexural modulus value with 2.3 GPa [Figure 10(a)].

In terms of maximum strain or strain at break [Figure 10(b)], the specimens with 25 and 30% PEGDE showed the best results, with an 80% enhancement in maximum strain. For the maximum stress, specimens with 0, 5, 10, 15, and 20% PEGDE loading all had a maximum stress at break that decreased with addition of PEGDE. However, the specimens with 25 and 30% PEGDE loading showed yielding behavior corresponding to a significant increase in the strain mentioned above, and the maximum stress occurred at yield point. The flexural toughness is defined as the total area under the stress–strain curve.²³ Loadings of PEGDE at 20% and lower did not significantly affect toughness. Because of the noteworthy enhancement of

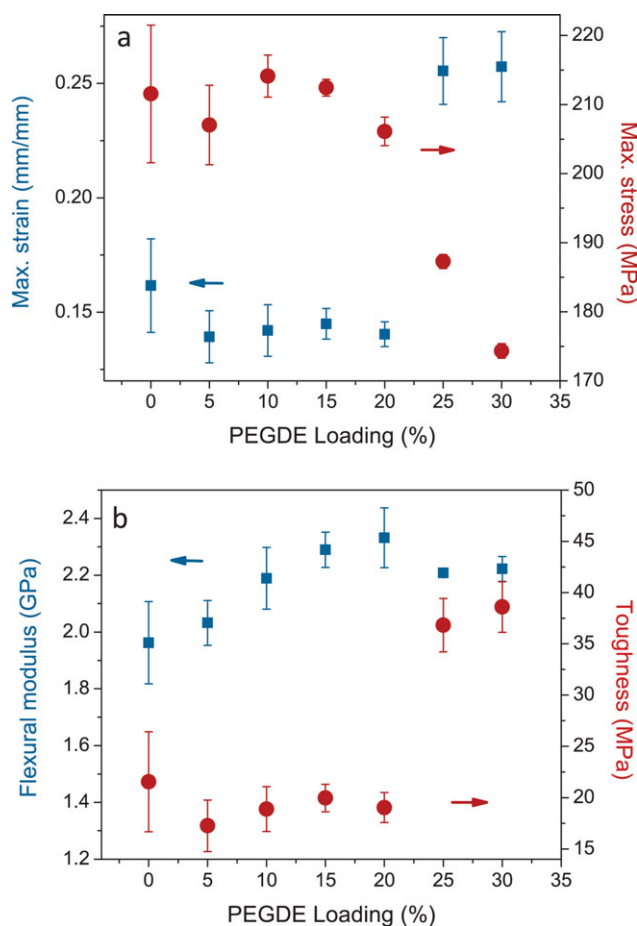


Figure 10. Summary of flexural test results: (a) Flexural modulus and toughness; (b) Maximum strain and stress. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maximum strain, the specimens with 25 and 30% of PEGDE loads showed an increase in toughness by about 80% compared to neat BECy [Figure 10(a)]. It is worth noting that at loadings of 25 and 30% PEGDE little change is seen in flexural modulus while the toughness shows a dramatic increase. The addition of PEGDE does not affect the flexural modulus, but significantly affects the flexural strain and therefore the toughness. Zero to 20% PEGDE is not a sufficient amount to carry the stress after yielding. At 25 and 30% PEGDE a critical loading has been reached and the PEGDE may carry the stress allowing for much more elongation before fracture. The properties of the BECy at the various PEGDE loadings are summarized in Table I.

Polarized optical microscopy was used to detect thermal degradation. Sample colors turned opaque brown after curing, indicating either thermal deterioration of the PEGDE or a cloud point typical for phase separation. It could not be determined at what point during the cure process this change took place. A specimen with 25% PEGDE loading was examined under a microscope with a heating stage. The sample was first heated to 180°C for 10 min, without revealing any change in color. After heating the sample to 250°C for several minutes, a slightly

yellowing occurred around the edges indicating a degradation or phase separation.

CONCLUSIONS

PEGDE was incorporated into BECy resulting in a polymer with increased toughness while maintaining a low viscosity. The miscibility of the PEGDE in the BECy monomer as well as the low viscosity of the mixture resulted in easy processing. The real time monitoring of rheological behavior of BECy/PEGDE under isothermal curing suggested that PEGDE may accelerate the gelation of BECy. Incorporation of PEGDE reduced the crosslinking density of the final BECy/PEGDE network and introduced “soft” segments into the network. As a result, glass transition temperatures decreased. Higher PEGDE loadings caused a slight increase in flexural modulus. At low loading levels, toughness of BECy/PEGDE was similar to that of neat BECy. However, at PEGDE loading levels of 25 and 30%, toughness was dramatically increased by approximately 80% from 21.6 MPa (neat BECy) to 36.8 and 38.6 MPa (25 and 30% PEGDE, respectively). This is due to the significant increase in flexural strain once PEGDE reaches these higher loadings.

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