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Prestressed double network thermoset: preparation and characterization

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Abstract An innovative scheme to prepare Prestressed double network (PDN) epoxies is presented using a judicious combination of tetrafunctional curatives that have similar molecular weights but different reaction kinetics. A diglycidyl ether of bisphenol A epoxy monomer was reacted stoichiometrically and sequentially with various molar ratios of an aliphatic polyetheramine curing agent and an aromatic curing agent. Deformation was imposed on the partially cured resins after the formation of the first network, and postcuring was conducted at 50% compressive strain. Physical properties of the resulting PDN epoxies were examined using thermomechanical analysis, dynamic mechanical analysis, uniaxial tensile test, and plane-strain fracture toughness test. The application of prestress resulted in no changes in glass transition temperature, coefficient of linear thermal expansion, and Young's modulus. However, a marked increase in fracture toughness is observed, accompanied by strong birefringence and visible roughness on the fracture surface.

Introduction

The synthesis of an Interpenetrating polymer network (IPN) is considered a promising route of blending immiscible polymers to create high-performance composites [1]. An IPN is defined by Sperling and Mishra [2] as the combination of multiple polymer networks where "at least one of which is polymerized/crosslinked in the immediate presence of the other(s)." Depending on the sequence of network formation, an IPN may be classified as sequential or simultaneous. However, due to different rates of formation of the constituent networks, a true simultaneous IPN is difficult to obtain. Interconnection between the components is also possible, which results in a grafted IPN. Phase separation of network constituents tends to occur because of thermodynamic incompatibility [1].

Double network (DN) hydrogels are sequential IPN's formed via radical chemistry and developed by Gong et al. [3] as a potential candidate for artificial soft tissues. They exhibit excellent strength and toughness even at 90 wt% water content. During their synthesis, a highly crosslinked polyelectrolyte network is swollen with an aqueous solution of monomer and crosslinker for a lightly crosslinked neutral polymer network. Owing to isotropic expansion, the polyelectrolyte chains are merely extended and have no preferred orientation. Gong and coworkers observed that a high-molar ratio of second component to the first is needed to realize improved toughness. They attribute the unusual synergistic effect of two fragile polymers to strongly asymmetric stiffness of two constituents of the IPN. Chain entanglement has been related to load transfer within the matrix [4], and the toughening mechanism is associated with energy-absorbing microfragmentation of the polyelectrolyte network [5].

DN elastomers also show improved physical characteristics over conventional Single network (SN) system. However, they differ from traditional IPN's in that their two-step curing process involves the same polymer, and that the second network is introduced while the first undergoes uniaxial extension. The resulting material obeys the two-network hypothesis of Andrews et al. [6]. When allowed to attain a state of ease, the length of a DN elastomer lies between that of the original unstrained rubber and that of the

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stretched elastomer when the second network is formed. Mechanical behaviors of DN elastomers have been described by a variety of elasticity theories [7–9]. The extent of reinforcement is shown to be dictated by the degree of chain orientation achieved from stretching the first network. Interestingly, a minimum stretch ratio must be surpassed before the Young's modulus, toughness, and strength measured parallel to the direction of elongation start to rise progressively with larger strain level [10–13]. A similar threshold for drastic changes of modulus and coefficient of thermal expansion (CLTE) is found in DN thermoplastic elastomers [12, 13]. Since the constituent networks are interlocked and incompletely relaxed, Singh and Lesser [12, 13] explained the phenomena in terms of entropic competition and ensuing heat exchange between the two components. The transition is thought to occur when the two networks move from a competitive to collaborative regime.

In an earlier paper by Detwiler and Lesser [14], the synthesis and initial characterization is presented for a tetrafunctional-amine cured DN epoxy, a novel type of IPN with asymmetric stiffness imparted by the combination of aliphatic and aromatic networks. Several advantages offered by the careful choice of curing agents are summarized here: (1) relatively constant molecular weight between crosslinks across the whole composition range, (2) systematic variation of chain stiffness by adjusting the ratio of the aliphatic curative to the aromatic curative, and (3) the possibility of subjecting partially cured resin to rigorous mechanical testing and further processing. Herein we report the synthesis and initial characterization of Prestressed double network (PDN) epoxies. Unlike DN thermoplastic elastomers in our earlier work [12, 13], the PDN epoxies are below their glass transition temperatures (T_g's) at room temperature.

In this article, we present a strategy to fabricate a PDN glass, by imposing a deformation step on a partially cured network followed up by a second step cure. Herein, we illustrate how to fabricate such a system using an arbitrary amount of strain (50%) to produce a new class of DN epoxies with strain energy stored within the system. Additional studies are conducted to investigate how basic physical and mechanical properties are altered by the application of prestress.

Experimental

Materials

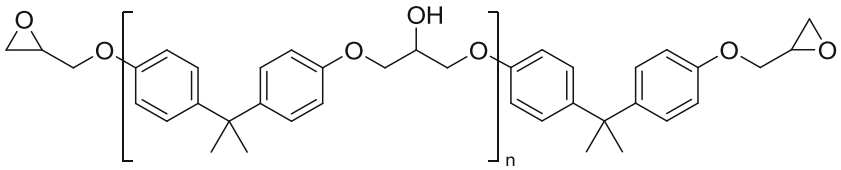
Diglycidyl ether of bisphenol A (DGEBA or D.E.R. 332 from Dow Chemical, Epoxide equivalent weight: 171–175 g/eq) was chosen for its narrow molecular weight distribution. As mentioned previously, the curing agents were selected based on molecular weights, stiffness, and reaction kinetics. Polyetheramine (Jeffamine D230, MW ~240 g/mol) was supplied by Huntsman, and 4,4′-diaminodiphenyl sulfone (DDS, MW: 248.3 g/mol) was obtained from Acros Organic. The structures of the chemicals are given in Table 1.

Network formation

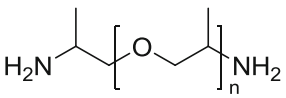
The procedures for preparing Single network (SN) epoxy cured with one curative, either polyetheramine or DDS, and those for Double network (DN) epoxies cured with both polyetheramine and DDS have been described in the first paper of the series [14]. The cure schedule was chosen to insure that further advancement in conversion would be

Table 1 Chemical structures of the epoxide monomer and curing agents

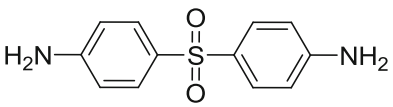
Diglycidyl ether of bisphenol A (DGEBA)



Polyetheramine (Jeffamine D230)



4,4′-diaminodiphenyl sulfone (DDS)



minimal. The initial network formation step of a PDN epoxy was identical to that of a DN epoxy. Polyetheramine and DDS with molar ratios ranging from 9:1 to 1:9 were mixed with stoichiometric amounts of DGEBA at elevated temperatures. Plaques were first cast between two release-coated glass plates separated by a 6- or 3-mm thick Teflon spacer. The polyetheramine fraction was reacted at 100 °C for 6 h in a nitrogen-purged oven (Step I in Fig. 1). The partially cured resin was briefly heated to 150 °C to soften and immediately deformed on a PHI compression molding machine to 50% of its original height (Step II in Fig. 1). DDS was then reacted at 200 °C for 6 h to yield the second network while the first network was under strain (Step III in Fig. 1). Note that samples with 80, 90 and 100% DDS contents are postcured for 4 h at 200 °C and for 2 h at 220 °C.

The resulting epoxy was not allowed to reach its equilibrium state. It was "prestressed" and "unrelaxed" (Fig. 1) because the load was released only after cooling it to room temperature or into the glassy state. Some elastic recovery took place upon unloading for samples with low DDS fraction. However, strain energy was stored in the unrelaxed resins. Strain energy was released by heating an unrelaxed epoxy above its glass transition temperature (T_g). After such treatment, the sample was referred to as "relaxed" (Fig. 1). Its thickness was between that of the partially cured resin and that of the unrelaxed resin.

As the result of different network compositions and processing histories, a sample naming system was adopted for the ease of comparison. The sample name consists of two or three letters, a number between 0 and 1, inclusive, and sometimes the letter "U" or "R." The acronyms, SN, DN, and PDN, refer to Single network, Double network, and PDN as defined above. The numbers refer to the molar fraction of DDS used to synthesize the resins. The letters "U" or "R" denotes an unrelaxed or a relaxed PDN epoxy.

Thermomechanical analysis

Thermomechanical analysis was performed with TMA 2940 (TA Instruments) in expansion mode at a constant load of 0.05 N and a heating rate of 3 °C/min. Each specimen was tested twice over the same temperature range, and held isothermal for 5 min at the end of the first heating to erase previous thermal history. Note that unrelaxed PDN epoxy with 10% DDS content (PDN 0.1U) developed surface cracks as the resin passed through its T_g, which suggested that the particular IPN could not sustain the release of strain energy without failure.

For PDN resins, specimens were tested both parallel and perpendicular to the direction of prestressing for possible anisotropy. With the instrument cell constant equal to unity, the coefficients of linear thermal expansion (CLTE) in the glassy and rubbery states were determined by dividing dimension change of the specimen by its original dimension and the corresponding temperature change.

The T_g values were taken as inflection points for unrelaxed PDN resins due to their sudden stepwise dimension changes, and as extrapolated intersection points for other resins with gradual variations in dimensions.

Dynamic mechanical analysis

Dynamic mechanical properties of single cantilever beam specimens were measured on DMA 2980 (TA Instruments) at a single frequency of 1 Hz and a heating rate of 3 °C/min. Analysis of the rubbery regime was difficult due to the lack of sufficient stiffness once the epoxies were above their glass transition temperatures. Relaxed PDN samples were therefore prepared by heating the unrelaxed resins at T_g +20 °C for about 10 min in a nitrogen-purged oven. The T_g values were taken as the maxima of the loss

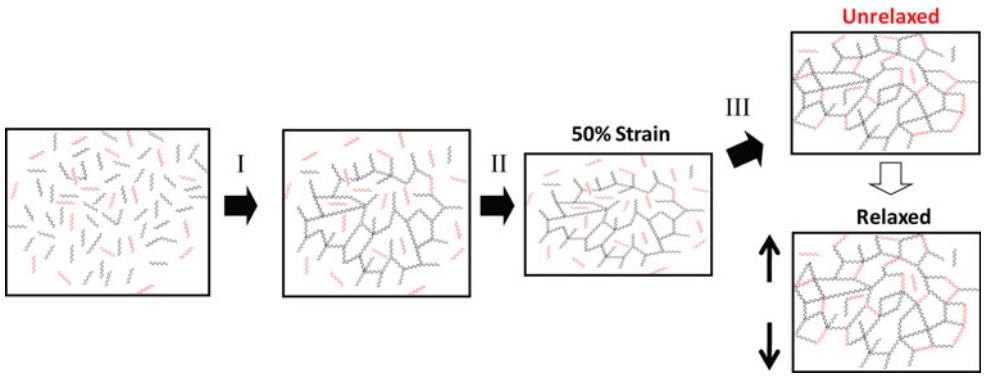


Fig. 1 Sample preparation scheme of PDN epoxies. The *black* and *red wavy lines* stand for polyetheramine and DDS, respectively. After the first cure (*Step I*), essentially all polyetheramine had reacted to form the first network while most DDS remained unreacted. The partially cured resin was then compressed by 50% (*Step II*). While in the deformed state, DDS was reacted to introduce the second network (*Step III*). The resulting epoxy is unrelaxed because of the strain energy stored in it. It became relaxed and had some thickness recovery after heating above its glass transition temperature

moduli (E''). The full width at half maximum (FWHM) was calculated as described in elsewhere [14].

Tensile test

3 mm thick ASTM D638 tensile specimens (Type I) were machined to size using a Tensilkut router and standard metal die. The testing was conducted on Instron 5800 with a high-precision 2″ strain gauge at a crosshead speed of 1 mm/min and 20 °C. Each reported value of Young's modulus, yield stress and strain at break was an average of 4–6 measurements.

Plane-strain fracture toughness

3 mm thick miniature compact tension (mini-CT) specimens with 20 mm width were prepared following ASTM standard D5045-99 [15]. The thickness satisfied the requirement for achieving plane-strain condition across the crack front. Load–displacement curves were recorded by an Instron universal testing machine (Model 4411) at a crosshead speed of 0.5 mm/min and 20 °C. Fracture toughness (K_q) was computed using the following equation:

$$K_q = \frac{P_c f(x)}{BW^{1/2}} \tag{1}$$

where P_c is the critical load in kilonewton (kN), B is the specimen thickness in centimeter (cm), W is specimen width in cm, and K_q is in MPa $m^{1/2}$. The use of K_q instead of K_{IC} denotes the use of a mini-CT specimen. The geometric factor $f(x)$ is a dimensionless power function in terms of x, which is equal to a/W, or the ratio of the precrack length to specimen width.

$$f(x) = \frac{(2+x)(0.886+4.64x-13.32x^2+14.72x^3-5.6x^4)}{(1-x)^{3/2}} \tag{2}$$

Each reported fracture toughness value was an average of 4–8 measurements.

Images of the fractured specimens were taken with a Nikon D40 digital camera with cross polarizers. Microscopic details of the fracture surfaces were imaged using a non-contact optical profilometer Zygo NewView 7300 in stitch mode.

Results and discussion

Molecular weight between crosslinks

Discussion on the molecular weight between crosslinks has been presented in the first paper of the series [14], and is briefly summarized here for completeness. The curing agents, polyetheramine and DDS, possess inherently dissimilar chain stiffness and curing kinetics. However, they have the same number of amine functionalities and comparable molar masses. Thus, nearly constant molecular weight between the crosslinks (M_c) exists in the two constituents of Double network (DN) and PDN epoxies. More importantly, this careful selection of curing agents enables systematic investigation of these IPN thermosets with asymmetric stiffness imparted by the combination of aliphatic and aromatic networks. From stoichiometry of the reagents, M_c for amine-cured epoxy is given by [16]

$$M_c = \frac{2(M_e + \sum_{x=2}^{\infty} \frac{M_x}{x} \Phi_x)}{\sum_{x=3}^{\infty} \Phi_x} \tag{3}$$

where M_e is the epoxy equivalent weight of the epoxide monomer, x is the functionality of the amine, M_x is the molecular weight of the amine having x functionality, and Φ_x is the molar fraction of amine hydrogens from x-functional amine. As listed in Table 2, M_c is about 470 g/mol across the whole composition range. This provides a model system for studying the effects of stiffness and prestress on the material properties.

Thermomechanical properties

The use of uniaxial compression can create transversely isotropic materials that behave differently in directions parallel and perpendicular to prestressing. Plotted in Fig. 2 are the first heating traces of representative Double network (DN) and PDN epoxies on TMA. With increasing aromatic amine content, a similar increase in T_g is detected in DN and unrelaxed PDN resins. The apparent increase is caused by the substitution of flexible polyetheramine with rigid DDS crosslinks, which places additional constraint on the molecular motion of polymer chains within the networks [17]. Interestingly, the unrelaxed PDN epoxy with 20% DDS content (PDN 0.2U) exhibits much greater dimension change near its T_g and wider transition temperature span than the corresponding DN epoxy (DN 0.2). The expansion in the direction parallel to prestressing is

Table 2 Estimated molecular weights between the crosslinks of PDN epoxies

% DDS	0	10	20	30	40	50	60	70	80	90	100
M_c (g/mol)	470.0	470.4	470.8	471.2	471.7	472.1	472.5	472.9	473.3	473.7	474.2

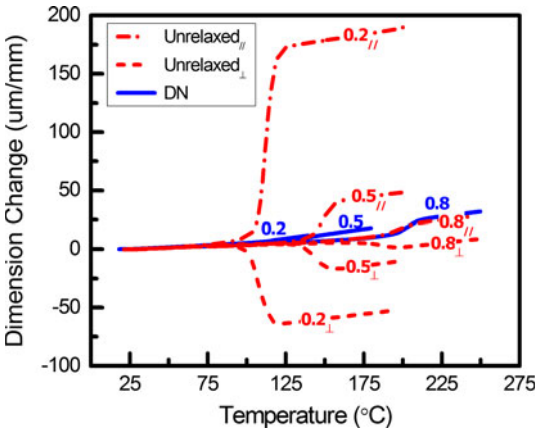


Fig. 2 Dimension changes of epoxies during first heating on TMA. The *numbers* 0.2, 0.5, and 0.8 denotes the molar fraction of DDS used to synthesize the resins. *Unrelaxed*$_{//}$ unrelaxed PDN tested parallel to the prestressing direction, *Unrelaxed*$_{\perp}$ unrelaxed PDN tested perpendicular to the prestressing direction, *DN* double network

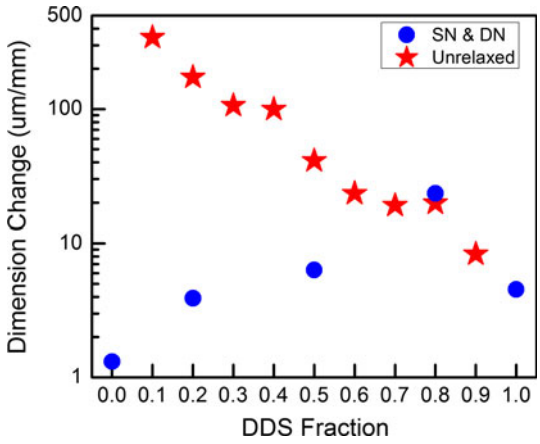


Fig. 3 Dimension changes of epoxies going from glassy to rubbery state normalized by thickness prior to testing. *SN and DN* Single network and double network, *Unrelaxed* unrelaxed PDN

more pronounced than the contraction in the direction perpendicular to prestressing, nearly a factor of three in the case of PDN 0.2U. These results indicate that that glass transitions of PDN epoxies can be severely complicated by their thermomechanical history, namely, the prestressed network formation process. The unrelaxed resin is at a metastable state [18], due to the strain energy stored in it. The input of thermal energy during the first heating accelerates the segmental motion of the macromolecules and facilitates structural recovery of the polyetheramine network to its initial or undeformed state. However, the deformation is not completely reversible due to straining of the interlocking DDS network, which is formed while the first network is in a deformed state. Note that the glass transition temperatures (T_g's) appear to be independent of prestress and testing directions.

The magnitude of dimension change during the glass transition also diminishes with increasing aromatic content (Fig. 2). Little difference exists between the traces of unrelaxed PDN epoxy with 80% DDS content (PDN 0.8U) tested parallel to the prestressing direction and the corresponding DN epoxy (DN 0.8). The observation suggests that the prestress decreases monotonically with DDS fraction. In other words, partially reacted resins did not necessarily experience an equal level of stress when subjected to the same amount of strain. This is an expected result considering that the gel point estimated from Flory-Stockmayer theory is 0.577 for networks based on difunctional epoxide monomer and tetrafunctional amines [19]. Although a small amount of DDS may react during the first cure, the overall extent of the first crosslinking reaction is expected to decrease with increasing amount of the aromatic curing agent. Therefore, partially cured resins with higher aromatic content are probably sol-glasses, which have lower network connectivity and can flow more easily under load when heated above T_g. The presence of unreacted small DDS molecules and lightly crosslinked polymer chains can help relieve the stress caused by the subsequent uniaxial compression step. Note that the slopes in the glassy and rubbery regimes appear to be the same for resins with the same composition.

A qualitative measure of the prestress in an unrelaxed PDN epoxy is given in Fig. 3, which is obtained by normalizing the thickness recovery of a resin going from the glassy to the rubbery state with its thickness prior to testing. The stepwise dimension change of unrelaxed PDN epoxies decreases significantly with increasing DDS fraction, for example, a drop of near one order of magnitude from 10 to 50% DDS content. It appears to level off between 60 and 80% DDS contents before decreasing again. As noted in the previous paragraph, little difference is observed between PDN 0.8U and DN 0.8. The observation indicates that PDN epoxies with 80% aromatic content or greater have no prestress in them. However, a more rigorous analysis considering cure shrinkage and elastic recovery is needed to confirm the result.

Figure 4 shows the second heating traces of the same epoxies illustrated in Fig. 2. With the removal of the strain energy or previous thermal history, relaxed PDN epoxies show less drastic dimension changes near the glass transition. For example, the magnitude is one order less for the relaxed PDN epoxy with 20% DDS content (PDN 0.2R) when compared to the unrelaxed resin (PDN 0.2U) tested parallel to the prestressing direction. PDN 0.2R has lower T_g in the direction parallel to prestressing than that in the direction perpendicular to prestressing, which is in turn lower than that of the corresponding DN epoxy (DN 0.2). However, the same trend isn't observed for epoxies with 50 and 80% DDS contents. The difference is probably due to random scattering of the data. Note again that the slopes in

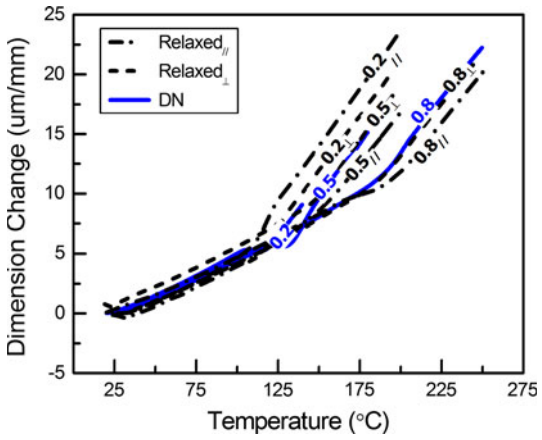


Fig. 4 Dimension changes of epoxies during second heating on TMA. The *numbers* 0.2, 0.5, and 0.8 denotes the molar fraction of DDS used to synthesize the resins. *Relaxed*$_{//}$ relaxed PDN tested parallel to the prestressing direction, *Relaxed*$_{\perp}$ relaxed PDN tested perpendicular to the prestressing direction, *DN* double network

the glassy and rubbery regimes appear to be the same for resins with the same composition.

The glass transition temperatures of unrelaxed and relaxed PDN resins tested on the TMA in the direction parallel to prestressing (Fig. 5a), and in the direction perpendicular to prestressing (Fig. 5b) are plotted against DDS fraction along with the control samples. The solid line represents the prediction from the rule of mixtures. The dashed curve is the theoretical behavior suggested by the Fox equation for homogeneous polymer blends [20]

$$\frac{1}{T_g} = \frac{w_a}{T_{g,a}} + \frac{w_b}{T_{g,b}} \tag{4}$$

where w_a is taken to be the weight fraction of D230, w_b is the weight fraction of DDS, $T_{g,a}$ and $T_{g,b}$ are the glass transition temperatures of Single networks cured with purely D230 (SN 0) and purely DDS (SN 1), respectively. Note that DGEBA was ignored in the calculation of weight fractions, and that only amine curing agents were considered. No change is found among T_g's of PDN epoxies measured parallel and perpendicular to the prestressing direction. Therefore, the effect of anisotropy on T_g is negligible.

As shown in Fig. 5a, b, the T_g's of the unrelaxed PDN epoxies match rather well with the trend predicted by the Fox model. In contrast, the T_g's of the relaxed samples exhibit somewhat random deviations from the theoretical behavior. These could be due to random scattering of the data. The strain energy stored in the PDN epoxies is hypothesized to result in decreased T_g values by lowering the amount of additional thermal energy required to surmount the barrier of glass transitions [21]. The extent of T_g reduction is expected to follow the level of prestress in the resins (Fig. 3) and decreases with increasing DDS content.

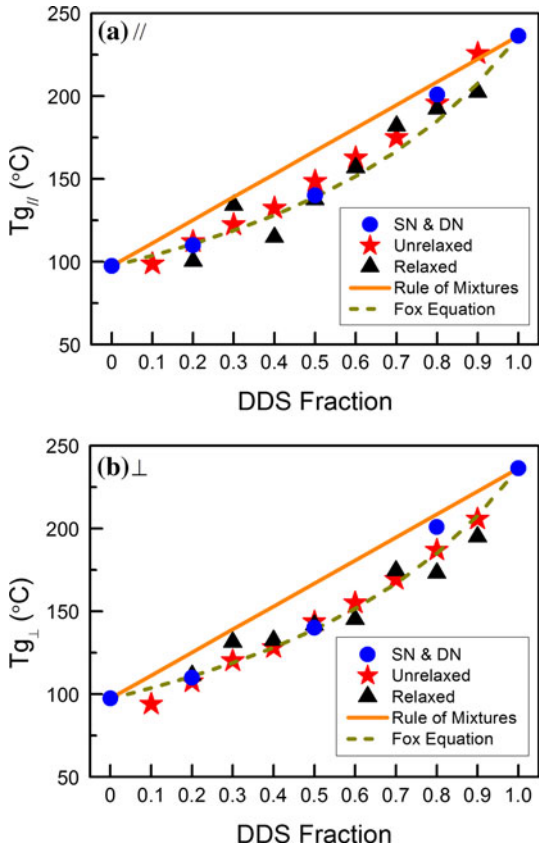


Fig. 5 Glass transition temperatures of epoxies measured on TMA. **a** Parallel to the prestressing direction, **b** Perpendicular to the prestressing direction. *SN and DN* single network and double network, *Unrelaxed* unrelaxed PDN, *Relaxed* relaxed PDN

However, no appreciable difference in T_g is observed after the removal of strain energy.

As illustrated in Fig. 6a, b, both the rubbery and glassy coefficients of linear thermal expansion (CLTE) of the PDN epoxies and the control samples are generally insensitive to change in network composition. These results are consistent with the findings of Ogata et al. [22], who reported that the rubbery CLTE of epoxies decreases with increasing crosslinking density, and that the glassy CLTE increases with increasing crosslinking density. Since the molar crosslinking density is uniform among all PDN blends, no change in CLTE due to composition is expected. The effect of testing directions is also negligible. The presence of strain energy is expected to lead to decreased CLTE as in the case of DN thermoplastic elastomers [12, 13]. However, no advantage of prestress is seen on the CLTE's of PDN resins. The discrepancy is probably due to the limited degree of chain orientation achievable by deforming the IPN thermoset to 50% strain in compression. The maximum strain level that typical epoxies can sustain without fracture is considerably lower than elastomers, due to the much higher crosslinking density of epoxies. Note that deforming the resins by uniaxial compression is

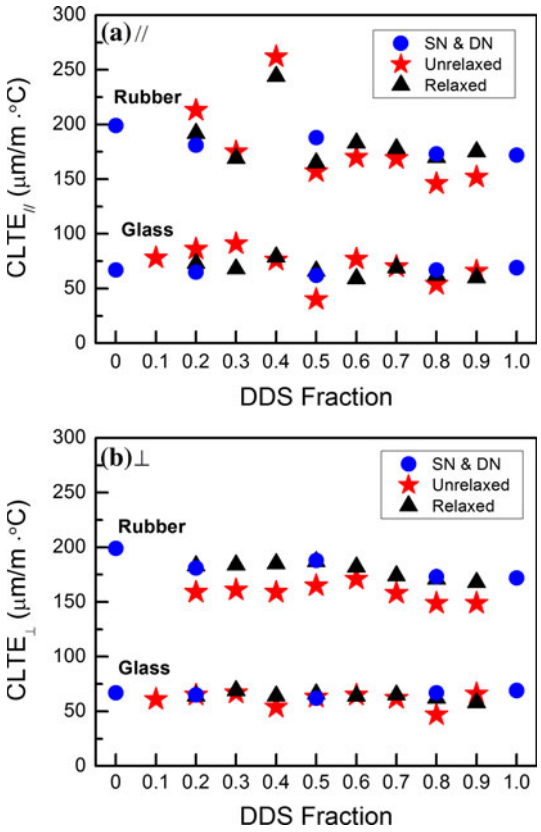


Fig. 6 Coefficients of linear thermal expansion of epoxies. **a** Measured parallel to the prestressing direction, **b** Measured perpendicular to the prestressing direction. *SN and DN* single network and double network, *Unrelaxed* unrelaxed PDN, *Relaxed* relaxed PDN

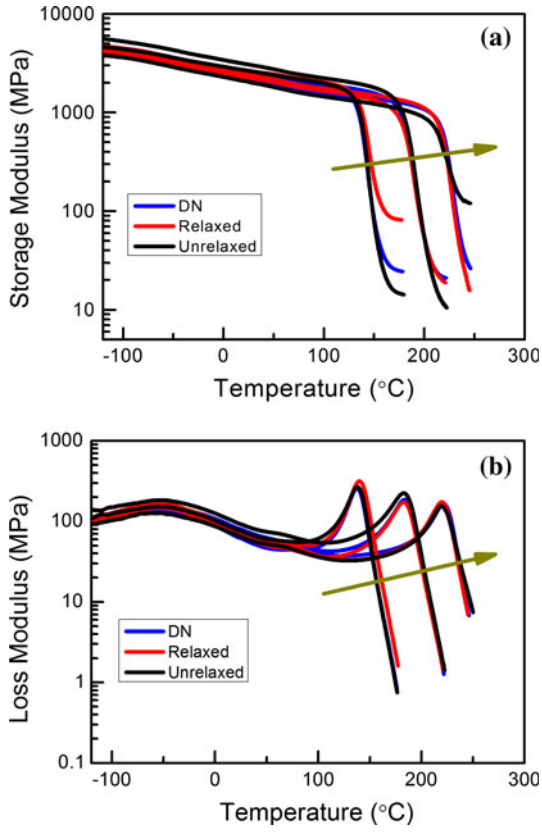


Fig. 7 Dynamic mechanical measurements of some representative epoxies. **a** Storage moduli, **b** Loss moduli. The *arrows* point in the direction of increasing DDS content. *DN* double network, *Relaxed* relaxed PDN, *Unelaxed* unrelaxed PDN

equivalent to that by biaxial tension. For a brittle polymer, property improvement from biaxial orientation can be less significant than that from uniaxial orientation due to finite extensibility of the polymer chains [23].

Dynamic mechanical properties

TMA measures T_g based on changes in CLTE. In contrast, Dynamic mechanical analysis (DMA) measures T_g based on changes in mechanical stiffness within the linear viscoelastic region. The DMA technique can provide more sensitive T_g measurement than TMA since a drop of several decades in the storage modulus is accompanied by a peak in the loss modulus at the glass transition. Plotted in Fig. 7a, b are the storage and the loss moduli of representative PDN epoxies and the control samples. No consistent trend can be established regarding the change in either moduli. The T_g values shown in Fig. 8 tend to be about 10 °C higher than those tested on TMA because of the difference in the experimental time scale [17]. The data points for the control samples are taken from the first paper of the series [14]. The glass transition temperatures are again unaffected by the application of prestress. Unlike the TMA results shown in Fig. 5a, b, however, the dependence of T_g's on the DDS fraction appears to switch from a fox-like behavior to one predicted by the rule of mixtures.

Shown in Fig. 9a are the alpha relaxation peaks of the same epoxies as illustrated in Fig. 7b. The loss moduli are normalized with respect to the peak maxima and shifted by T_g. The asymmetric peak shape is probably due to the presence of a beta relaxation that spans a wide temperature range (Fig. 7b). Some overlap between the two transitions is also possible. The full width at half maximum (FWHM) of the alpha relaxation peaks are shown in Fig. 9b. The data points for the control samples are taken from an earlier paper by Detwiler and Lesser [14]. A general trend is observed among PDN resins and the control samples. With increasing DDS fraction, the width of the alpha transition first increases, plateaus between 40 and 80% DDS contents, and then decreases. The departure of relaxed PDN epoxies with 60, 70, and 90% DDS contents from the general trend could be caused by more stretched or asymmetric relaxation peaks.

The beta relaxation peaks normalized with respect to the peak maxima of loss moduli are shown in Fig. 10. The transitions occur at around −60 °C for all PDN resins and

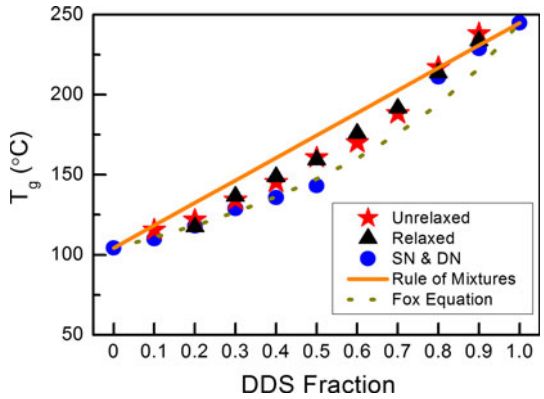


Fig. 8 Glass transition temperatures of epoxies measured on DMA. *Unrelaxed* unrelaxed PDN, *Relaxed* relaxed PDN, *SN and DN* single network and double network

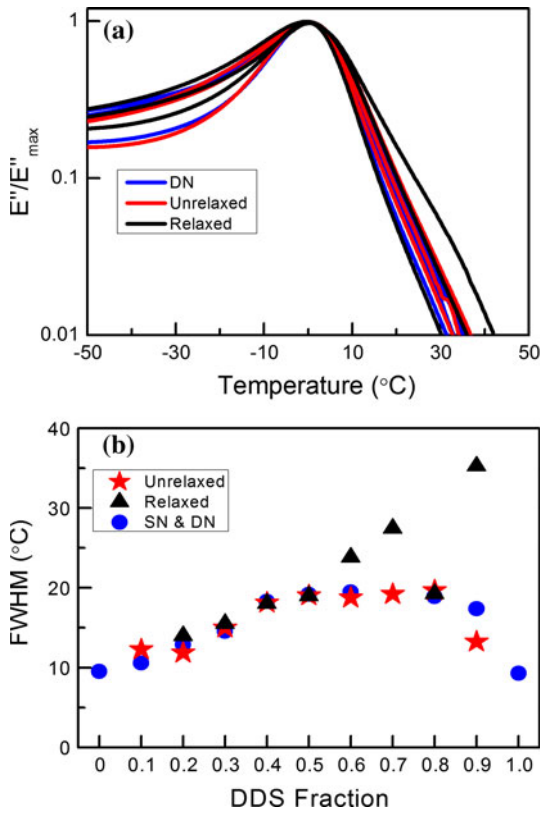


Fig. 9 **a** Normalized alpha relaxation peaks of the same epoxies as in Fig. 7, **b** Full width at half maximum (FWHM) of the alpha relaxation peaks. *Unrelaxed* unrelaxed PDN, *Relaxed* relaxed PDN, *SN and DN* single network and double network

control samples. The result is in agreement with the recent work of Monnerie and co-workers [24], who attributed the appearance of beta transition to the localized and cooperative motions of the network repeat units, including the hydroxypropylether segment and the phenyl ring. Since the same structural units are present in PDN resins and the control samples, no change in the beta relaxation temperatures is expected. The shape of the relaxation peaks shows

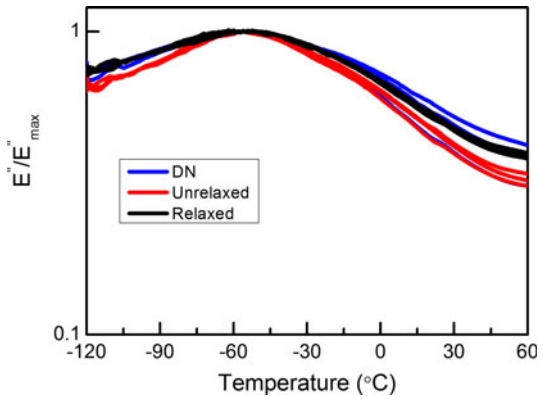


Fig. 10 Normalized beta relaxation peaks of the same epoxies as in Fig. 7

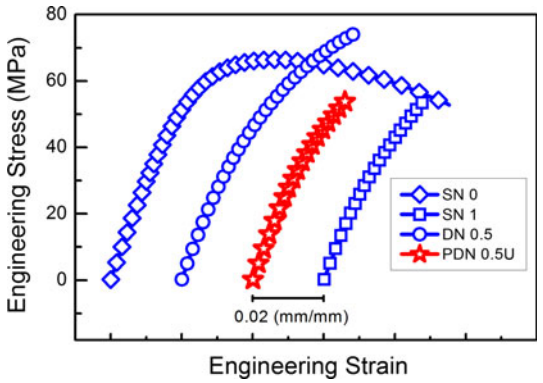


Fig. 11 Representative tensile stress–strain curves of epoxies. *SN 0* single network cured purely with polyetheramine, *SN 1* single network cured purely with DDS, *DN 0.5* double network with 50% DDS content, *PDN 0.5U* unrelaxed PDN with 50% DDS content

little variation with change in DDS fraction or removal of strain energy. Since the width of the beta transition is known to be sensitive to changes in crosslinking density [24], the result also corroborates that the molar crosslinking density is constant over the entire composition range.

Tensile response

Shown in Fig. 11 are tensile stress–strain curves of Single network epoxies cured with purely D230 (SN 0) and purely DDS (SN 1), DN epoxy with 50% DDS content (DN 0.5), and unrelaxed PDN epoxy with 50% DDS content (PDN 0.5U). The most ductile resin, SN 0, deforms through yield and exhibits the largest elongation at break. The most rigid resin, SN 1, is expected to show the smallest elongation at break. However, as shown in Table 3, PDN 0.5U fails at similar strain level as SN 1. In contrast, DN 0.5 fails at considerably higher strain. The result underscores the finite extensibility of network chains in the prestressed resin. As a result of the uniaxial compression step, some polymer chains in the polyetheramine network are already stretched

Table 3 Tensile testing results

Resin	E (GPa)	σ_y (MPa)	ϵ_{break} (mm/mm)
SN 0	2.95 ± 0.05	66.8 ± 0.5	0.086 ± 0.020
SN 1	2.48 ± 0.08	n/a	0.028 ± 0.009
DN 0.5	2.68 ± 0.03	n/a	0.049 ± 0.010
PDN 0.5U	2.70 ± 0.02	n/a	0.026 ± 0.007

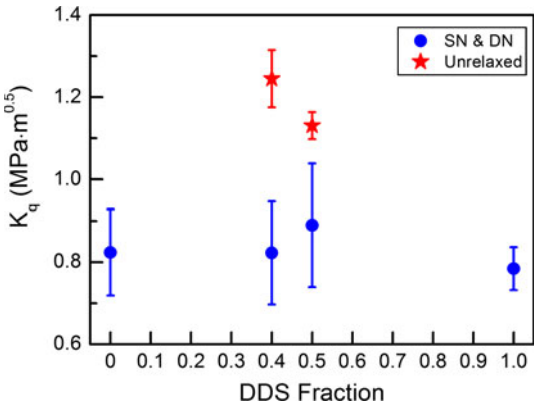


Fig. 12 Fracture toughness of epoxies. *SN and DN* single network and double network, *Unrelaxed* unrelaxed PDN

and aligned in the tensile testing direction prior to testing. Based on the compression testing results in the first paper of the series [14], at 50% compressive strain, the first network of the PDN epoxy is probably in the strain hardening region. Thus, only a small amount of additional strain can be tolerated before reaching the extensibility limit of the network. The Young's moduli are also given in Table 3. SN 0 and SN 1 show the highest and lowest moduli, respectively. The tensile modulus of DN 0.5 also appears to obey the rule of mixtures. However, unlike DN elastomers, no reinforcement is seen when comparing DN 0.5 and PDN 0.5U. Again, the diminished response is probably due to the brittle nature of the resins, which restricts the degree of chain orientation achievable by uniaxial compression before catastrophic failure occurs.

Plane-strain fracture toughness

Compared to tensile testing, fracture toughness testing is more sensitive to intrinsic material properties and changes in network structures, since the precrack acts as the largest flaw in the material [25]. Depending on the combination of testing rate and temperature, a crack can propagate in a continuous or "stick–slip" manner [26, 27]. All miniature compact tension (mini-CT) specimens in this study failed in a brittle fashion, thus the maxima in load–deflection curves were taken as the critical loads in calculating fracture toughness. As shown in Fig. 12, Single network epoxies cured with purely D230 (SN 0) and purely DDS

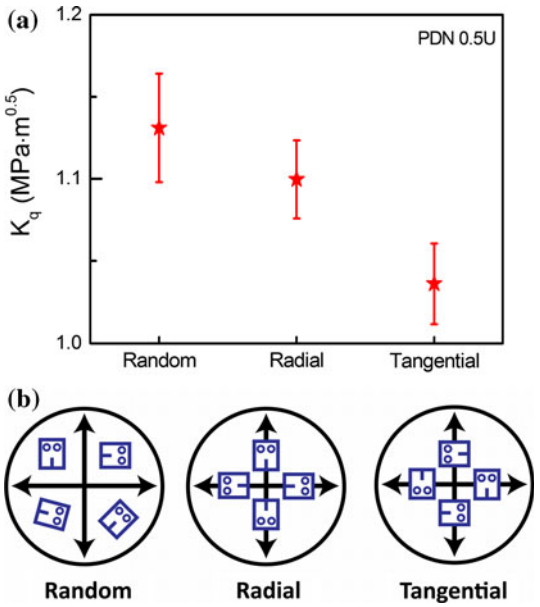


Fig. 13 **a** Fracture toughness of unrelaxed PDN with 50% DDS content along different precrack directions, **b** Precrack directions with respect to biaxial orientation in the samples

(SN 1), DN epoxies with 40 and 50% DDS contents (DN 0.4 and DN 0.5) have about the same fracture toughness (K_q). In marked contrast, the unrelaxed PDN resins with 40 and 50% DDS contents (PDN 0.4U and PDN 0.5U) exhibit more than 30% increase in K_q over the control samples. The result is rather interesting because no additive is incorporated, and the prestressed epoxies are single-phase materials as suggested by T_g measurements on TMA and DMA. Furthermore, PDN resins appear transversely isotropic since not more than 4% variation in K_q is found among mini-CT specimens of PDN 0.5U precracked in random, radial, and tangential directions (Fig. 13). Note the difference in vertical scale between Figs. 13a and 14. Improvement in mechanical properties via the utilization of prestress or deformation-induced molecular orientation has been reported for other glassy polymers. Archer and Lesser [28] studied the mechanical response of polymethylmethacrylate (PMMA) with compressive prestress. Although the deformation was small, significant improvement in impact performance is observed. Weon et al. [29] oriented PMMA using large strain simple shear, and found significant increases in both fracture toughness and impact resistance.

The detailed toughening mechanisms are still under investigation. However, two interesting features are observed. Shown in Fig. 14a, b are polarized digital images of mini-CT specimen of DN 0.5 and PDN 0.5U, respectively. Note that the propagating cracks are arrested before these two specimens fail completely. The whitening regions or stress concentrations on DN 0.5 are due to the mini-CT specimen fabrication process and fracture toughness testing. In marked contrast, a marble-like texture is

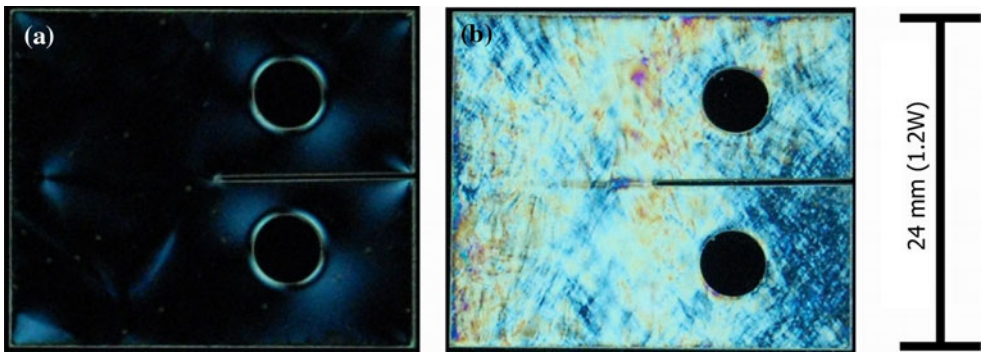


Fig. 14 Polarized digital images of representative miniature compact tension specimens after fracture: **a** double network with 50% DDS content, **b** unrelaxed PDN with 50% DDS content

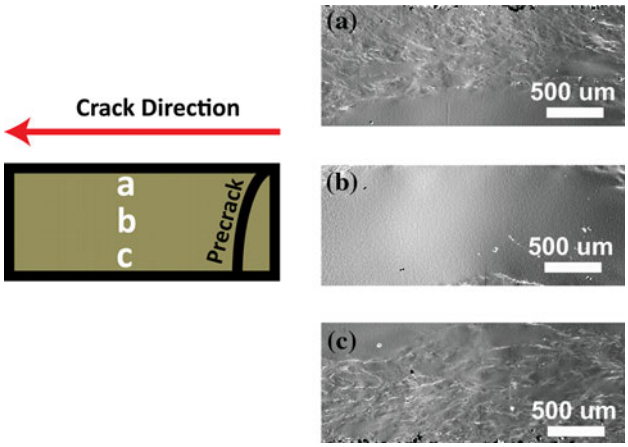


Fig. 15 Fracture surfaces of an unrelaxed PDN with 50% DDS content. The sketch at the left shows the relative positions where the images are taken on the miniature compact tension specimen

seen extending across the surface of PDN 0.5U. Such feature is the direct results of the uniaxial compression step, which induced biaxial orientation. Strong birefringence is preserved even after polishing the sample to expose regions away from the fracture surfaces. Fracture surfaces of a representative PDN 0.5U mini-CT specimen are shown in Fig. 15. SN and DN epoxies have featureless fracture surfaces, which are characteristic of brittle failure in unmodified epoxies. The center of the fracture surface of PDN resins is also featureless (Fig. 15b). However, the edge regions exhibit significant surface irregularities or roughness (Fig. 15a, c). The result suggests that pronounced local plastic deformation takes place during the fracture events.

Conclusions

The article presents a novel preparation method for PDN epoxies, which is a new type of Interpenetrating polymer network (IPN) thermoset. The synthesis steps involve the use of an aliphatic and aromatic tetrafunctional amine curing agents with comparable molecular weights but different chain stiffness and cure kinetics. Constant molecular weight between the crosslinks exists across the entire composition range of the resins. Prestress is generated by forming the rigid second network while the ductile first network is under large uniaxial deformation.

The prestress in the epoxies decreases with increasing amount of aromatic curing agent. When heated above its glass transition temperature to remove the strain energy, an unrelaxed resin expands in the direction parallel to prestressing and contracts in the direction perpendicular to prestressing. The T_g's of the PDN epoxies measured on TMA and DMA show little dependence on prestress, and no effect of orientation is observed with different testing directions on TMA. The width of the alpha transition varied with composition, but not with prestress. The prestress does not alter the coefficients of linear thermal expansion, or Young's modulus. However, a significant increase in fracture toughness is observed. The molecular mechanisms responsible for the toughness enhancement are the subject of further investigation.

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