Glass Transition Temperatures of Epoxy Modified with Pendent Nano-Organic Rigid-Rod Compounds

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Glass Transition Temperatures of Epoxy Modified with Pendent Nano-Organic Rigid-Rod Compounds

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Pendent nanoscale organic rigid-rod compounds are molecular fiber-like materials that can be used to reinforce the polymer matrix. In this study, 4,4'-diphenylmethane diisocyanate (MDI) was used to covalently connect a number of organic rigid-rod compounds [4'-hydroxyphenyl-4-hydroxy-benzoate (HPHB), phenyl 4-hydroxybenzoate (HPB), 4,4'-isopropylidenediphenol (BSPA), and 2-naphthol (NPT)] to the secondary hydroxyl groups of the epoxy resin. These reactions were monitored using Fourier transform infrared (FT-IR) spectroscopy; the products were characterized using nuclear magnetic resonance (NMR) spectroscopy. The glass transition temperatures of the organic rigid-rod compounds modified epoxy resins were investigated through differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Thermogravimetric analysis (TGA) was used to detect the values of Td and the thermal stabilities of the polymers.

Keywords epoxy, nano-scale, rigid-rod compound, self-reinforced, thermal properties

Introduction

Fiber-reinforced polymer composites are used widely in materials applications. Several kinds of fibers have been applied as reinforcing materials, including carbon fibers,[1,2] glass fibers,[3–6] aramid fibers, and ultrahigh-molecular-weight polyethylene (UHMWPE) fibers.[7,8]

Epoxy resins possess many properties that favor their use in various industrial applications, including high processability, thermal resistance, chemical resistance, low

shrinkage, and good mechanical and dielectric properties. Hsieh et al.[9,10] attempted to prepare blends between epoxy resins and polyurethane materials. Epoxy resins have also been modified with other materials to enhance the mechanical properties,[11] thermal properties,[12] and nano-miscibility.[13,14] Several modified blend and composite structures are possible, including simultaneous interpenetrating polymer networks (IPN), semi-IPNs, sequential IPNs, and molecular composites. The morphology of the IPN structure is dependent upon the compatibility, cross-linking density, composition, and the rate of polymerization of the two components.

Molecular composites possess several advantages over normal macro-composites; i.e., 1) excellent compatibility (homogeneous dispersion), 2) complete interfacial adhesion (i.e., they can be regarded as homogeneous from a macroscopic point of view), and 3) no thermally induced stress (they do not exhibit the shear yielding or cavitation behavior observed for macro-composites). The mechanical properties and morphological compatibility of the molecular composites can be improved through the attachment of pendent groups. The modifications due to the pendent groups also exert some effects on the IPNs' morphologies, including their compatibility, cross-linking density, composition, and the polymerization rate of the two components.

Our aim in this study was to synthesize nanoscale, organic rigid-rod-appended self-reinforced epoxy materials through attachment of organic rigid-rod compounds to the secondary hydroxyl groups of epoxy resin. We investigated the effects that the various structures of the organic rigid-rod compounds and their weight percentages had on the resulting thermal properties of the self-reinforced epoxy materials.

Experimental

The sources of the materials used in these experiments are listed in Table 1. Epoxy resin (diglycidylether of bisphenol A, DGEBA; EEW = 186) was heated at 60°C and degassed under vacuum overnight prior to use.

Preparation of 4′-Hydroxyphenyl, 4-Hydroxybenzoate (HPHB)
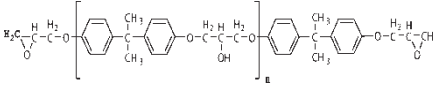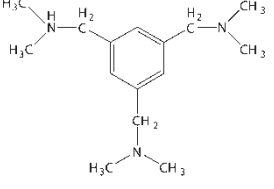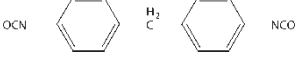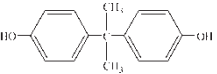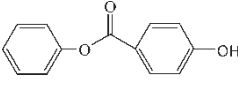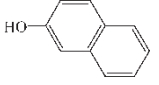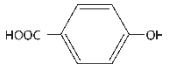
Hydroquinone (1.0 mol) and *p*-hydroxybenzoic acid (0.1 mol) were added into a reaction vessel and stirred at 60°C under nitrogen atmosphere for 2 h. A large amount of distilled water was poured into the reaction mixture to precipitate the white product, which was isolated through filtration and purified through several recrystallizations from ethanol/water (1/1, v/v) to provide HPHB as a white solid. The synthesis of HPHB is presented in the following scheme:
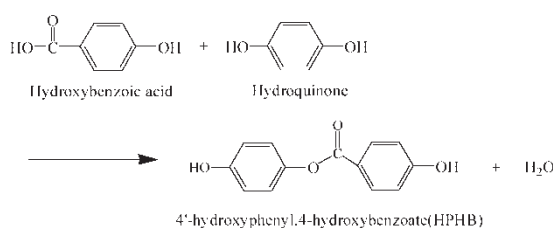
Preparation of DGEBA Modified with Pendent Nano-Organic Rigid-rod Compounds

DGEBA (1 equivalent) was placed into a reaction kettle. Dry nitrogen gas was passed through the reaction kettle to remove oxygen and moisture. 4,4′-Diphenylmethane

Table 1
Experimental materials

Designation	Description	Chemical structure
DGEBA	Diglycidylether of bisphenol A; Dow Chem. (USA)	
DMP-30	2,4,6-Tris(dimethylamino-methyl) phenol; Jin-Men Chem. Co. (Taiwan)	
MDI	4,4′-Diphenylmethane diisocyanate; TCI Chem. Co. (Japan)	
BSPA	4,4′-Isopropylidenediphenol; Acros Organics (New Jersey)	
HPB	Phenyl 4-hydroxybenzoate; Acros Organics (New Jersey)	
NPT	2-Naphthol; Acros Organics (New Jersey)	
—	p-Hydroxybenzoic acid; Acros Organics (New Jersey)	
—	Hydroquinone; Acros Organics (New Jersey)	

diisocyanate (MDI; 2 equivalents) was then poured into the kettle and mixed with DGEBA. The reaction temperature was maintained at 80°C while the mixture was agitated vigorously. An FT-IR spectrometer was used to monitor the changes in the intensity of the signal of the isocyanate group (NCO, $2270 \, cm^{-1}$) at regular intervals. When this peak intensity reached half of its original value (with reference to the signal for the 1,4-disubstituted benzene rings at $840 \, cm^{-1}$), the pendent secondary hydroxyl groups (OH) on the side chains of DGEBA had reacted completely with the NCO groups of MDI. At this stage, a certain amount (1.5, 3.09, 5.70, or 7.49 wt.%) of an organic compound [4′-hydroxyphenyl-4-hydroxybenzoate (HPHB), phenyl 4-hydroxybenzoate (HPB), 4,4′-isopropylidenediphenol (BSPA), or 2-naphthol (NPT)] was added into the reaction mixture and the temperature was raised to 120°C. Again, the signal for the NCO groups was monitored at $2270 \, cm^{-1}$. When its peak intensity disappeared, all of the OH groups of the organic compound (HPHB, HPB, BSPA, or NPT) were deemed to have reacted completely with the NCO groups of the MDI moieties.

Curing of DGEBA Modified with Pendent Nano-Organic Rigid-rod Compounds

2,4,6-Tris (dimethyl aminomethyl) phenol (the curing agent for epoxy resin and 3 phr based on the epoxy resin) and the nanoscale organic rigid-rod-appended self-reinforced DGEBA polymer were mixed for 30 s using a high-torque stirrer and then placed in aluminum molds with chromium plating. The compression mold procedure was applied at 120°C for 1 h and at 150°C for 2 h under high pressure (150 kg cm^{-2}) to develop cross-links.

Test Methods

Infrared spectra were obtained using a BIO-RAD FTS-40 FT-IR spectrophotometer operated at a resolution of 4 cm^{-1}. The sample was applied directly onto a KBr pellet prior to detection of the NCO group content. Dynamic mechanical analysis (DMA) was performed using a Du Pont 983 instrument. The operating temperature ranged from -110 to $+180$°C and the heating rate was 4°C min^{-1}; the frequency was set at 1 Hz. The size of the samples used was ca. $36 * 14 * 3$ mm. Differential scanning calorimetric (DSC) analysis was performed on a Du Pont 2010 instrument operated at a heating rate of 5°C min^{-1} over the temperature range from 30–180°C. Thermo-gravimetric analysis (TGA) was performed using a Perkin-Elmer TGA-7 instrument operated at a heating rate of 10°C min^{-1} over the temperature range from 110–800°C.

Results and Discussion

FT-IR Analysis

The molecular structures of the DGEBA samples modified with pendent organic rigid-rod compounds are shown below:

HPHB reinforced DGEBA

HPB reinforced DDGEBA

BSPA reinforced DGEBA

NPT reinforced DGEBA
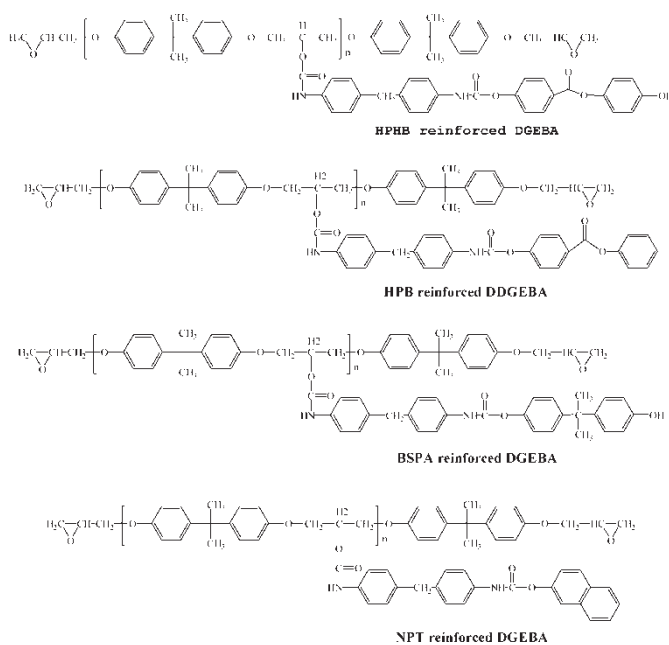
FT-IR spectra of the nanoscale HPHB-appended self-reinforced DGEBA is shown in Fig. 1. In the initial stages of the reaction between DGEBA and MDI, the signals of the

Figure 1. FT-IR spectra recorded at (a) the initial stage of the reaction between MDI with DGEBA, (b) the middle stage of the reaction between MDI and DGEBA, and (c) the final stage of the completed reaction.

hydroxyl (OH) groups (at 3500 cm^{-1}) and the isocyanate (NCO) groups (at 2270 cm^{-1}) co-existed (Fig. 1a). Up to the middle stage of the react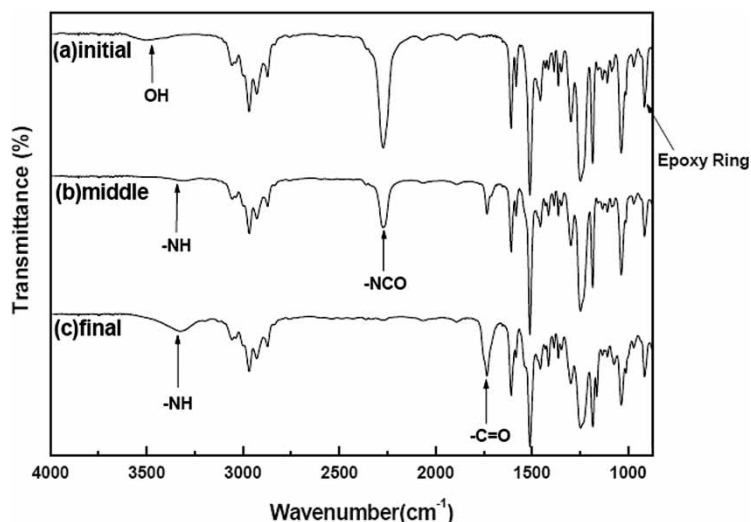ion, the signal of the OH groups gradually reduced, the peak of the NCO groups reduced to half of its original value, and a signal for the carbonyl groups (C=O) of urethane linkages (NHCOO) appeared at 1740 cm^{-1} (Fig. 1b). Finally, after HPHB was added into the DGEBA/MDI mixture, the peak of the residual NCO groups disappeared and that of carbonyl groups of the NHCOO linkages increased significantly. A signal located at 3300 cm^{-1} was present in the final spectrum (Fig. 1c), indicating that the NH groups were present in the structure of the modified polymer. The final spectra of the DGEBA samples modified with HPB, BSPA, and NPT were similar to that of the HPHB-modified sample.

Differential Scanning Calorimetry (DSC) Analysis

Data from the DSC analysis of the HPHB-modified DGEBA is shown in Fig. 2 and Table 2. The glass transition temperature (Tg) increased with increasing HPHB content from 96°C for DGEBA up to 115°C for the sample modified with 7.49 wt.% of HPHB because of the small amounts of this pendent aromatic rigid-rod compound in the structure. This behavior is quite different from that exhibited by composites reinforced with inorganic fibers, which are incompatible materials, and which do not change the Tg of the polymer.

The values of Tg of the HPB-, BSPA-, and NPT-modified DGEBA samples exhibited similar trends to that of the HPHB-modified DGEBA (see Table 2). Each of these nanoscale rigid-rod-appended DGEBA samples exhibited a single value of Tg, strongly suggesting that these rigid-rod materials grafted onto the main chain structure were fully miscible with the homogeneous DGEBA matrix. These four nanoscale organic rigid-rod compounds were grafted onto DGEBA through urethane linkages via another rigid-rod compound (MDI) with the pendent secondary hydroxyl groups (OH) of
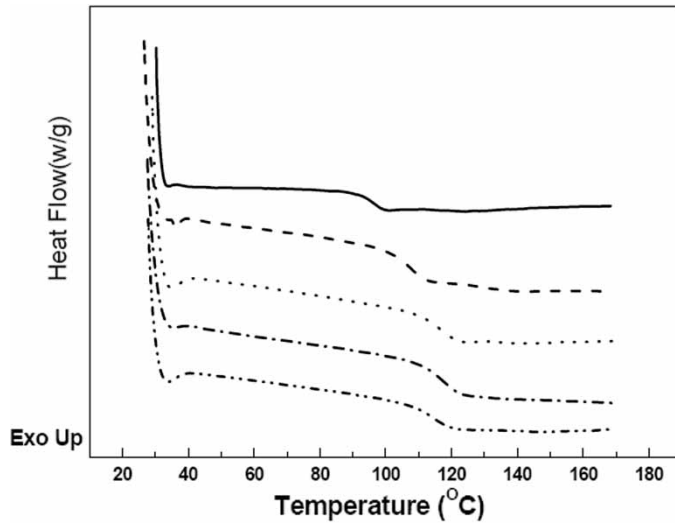
Figure 2. DSC traces of DGEBA samples modified with HPHB for contents of (·): 0 wt.%, (− − −): 1.5 wt.%, (· · · · · ·): 3.09 wt.%, (− · − · −): 5.07 wt.%, and (− ·· − ··): 7.49 wt.%.

DGEBA. The four organic rigid-rod compounds were connected via the rigid-rod MDI moieties to increase the length/diameter (L/D) ratios of the nanoscale molecular fibers; this was because they dispersed well at the molecular level in the modified DGEBA matrix and the presence of these organic rigid-rod compounds on the DGEBA side chains increased the values of Tg of the resultant nanofiber-reinforced epoxy composite polymers.

Dynamic Mechanical Analysis (DMA) Analysis

The loss tangent (tan δ), as measured through DMA, of the DGEBA samples modified with HPHB, HPB, BSPA, and NPT, respectively is illustrated in Figs. 3–6. Considering the DGEBA modified with HPHB as a sample, the neat DGEBA sample exhibited

Table 2
Glass transition temperatures (Tg) obtained from DSC analyses of
DGEBA samples presenting pendent rigid rod

	Content (wt.%)				
Rigid-rod compound	0	1.50	3.09	5.07	7.49
Tg values (°C)					
HPHB	96	108	117	117	115
HPB	96	105	109	109	109
BSPA	96	102	104	109	113
NPT	96	108	113	—	—
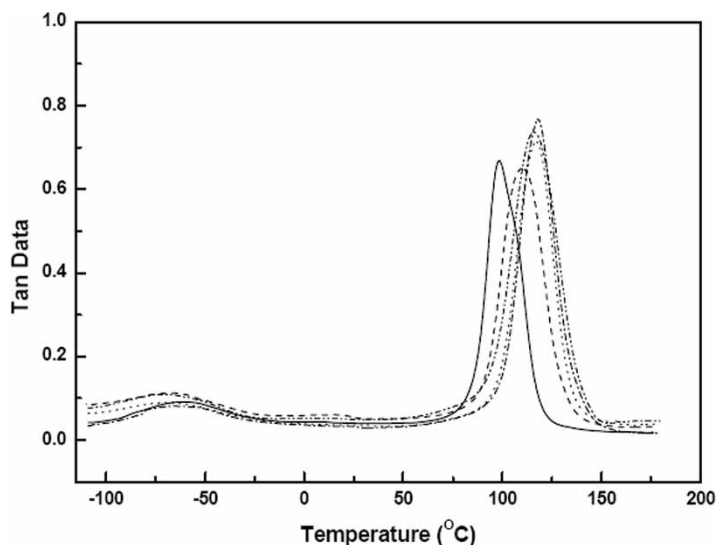
Figure 3. Plots of tan δ from the DMA of DGEBA samples modified with HPHB for contents of (·): 0 wt.%, (−−−): 1.5 wt.%, (······): 3.09 wt.%, (−·−·−): 5.07 wt.%, and (−··−··): 7.49 wt.%.

(Fig. 3) two temperature relaxation regions. The first peak (low loss tangent) appeared at −60°C, corresponding to the low temperature relaxation region (β) due to short segment motion of DGEBA. The other peak (high loss tangent), at 100°C, represents the high temperature relaxation region (Tg) and is related to the long segment motion of DGEBA. The high temperature relaxation region (Tg) increased to 115, 109, and 113°C upon increasing the contents of HPHB, HPB and BSPA to 7.49 wt.%, respectively, in the DGEBA matrix;
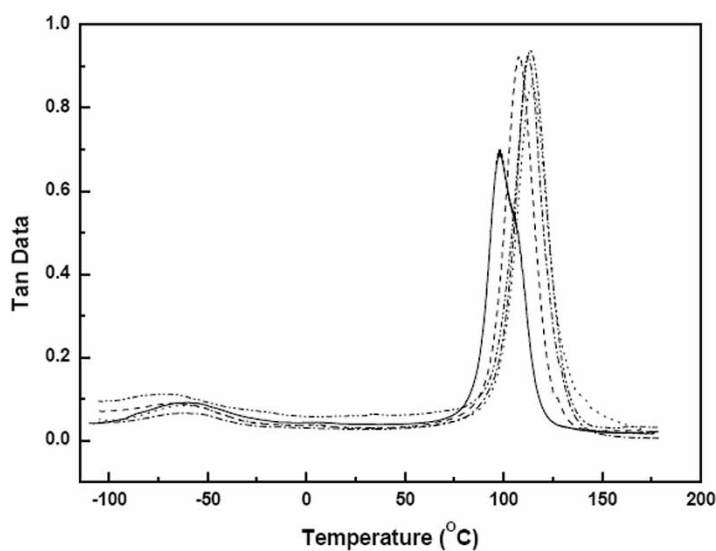
Figure 4. Plots of tan δ from the DMA of DGEBA samples modified with HPB for contents of (·): 0 wt.%, (−−−): 1.5 wt.%, (······): 3.09 wt.%, (−·−·−): 5.07 wt.%, and (−··−··): 7.49 wt.%.

Figure 5. Plots of tan δ from the DMA of DGEBA samples modified with BSPA for contents of ($\cdot$): 0 wt.%, (—): 1.5 wt.%, (. . . . .): 3.09 wt.%, (– – –): 5.07 wt.%, and (– –): 7.49 wt.%.
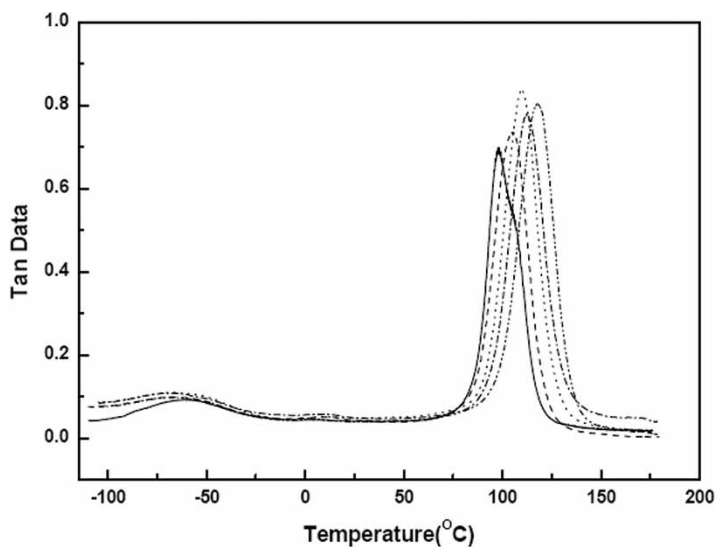
these tendencies of other three organic rigid-rod compounds in DGEBA systems are consistent with the shifts in the values of Tg that we observed in our DSC analyses (Table 2). In contrast, the peak temperatures of the low temperature relaxation region (β) at $-60°$C, dropping slightly (i.e., without significant change), indicate that the introduced organic rigid-rod compounds increased the free volume and permitted the short segments of DGEBA to move at lower temperatures. In other words, the significant increase in the
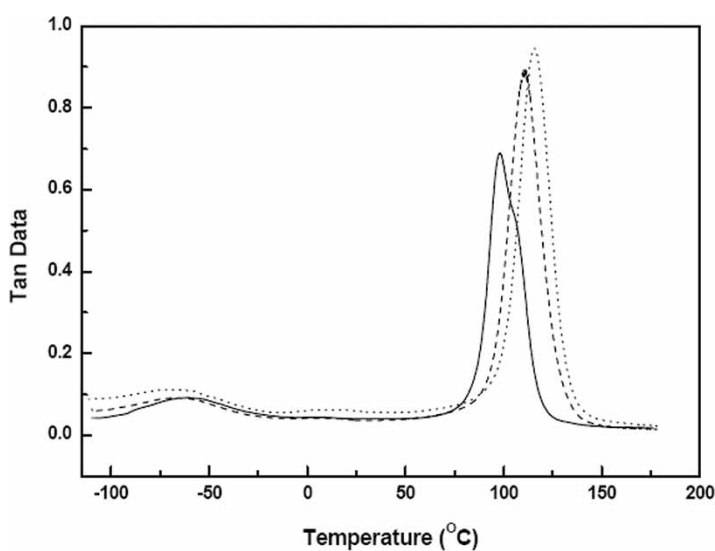
Figure 6. Plots of tan δ from the DMA of DGEBA samples modified with NPT for contents of ($\cdot$): 0 wt.%, (– – –): 1.5 wt.%, and ($\cdot\cdot\cdot\cdot\cdot$): 3.09 wt.%.

value of Tg after appending the rigid-rod compounds onto DGEBA indicates that the nanoscale rigid-rod, fiber-like materials were dispersed in the DGEBA, possibly increasing the free volume. Thus, the nanoscale organic rigid-rod compounds self-reinforced the DGEBA, resulting in clearly increased peak temperatures for the high temperature relaxation.

In polymer blends, in general, the presence of heterogeneous or phase-separated domains causes multiple loss tangents to appear in DMA measurements. Because we observed that no additional loss-tangent peaks were generated, it indicates that the organic rigid-rod compounds are dispersed well on the molecular (nano) scale within the DGEBA. The relaxation due to the rigid-rods, which are relatively short and thus could rotate at low T and are at low concentration, was not observed.

Thermal Gravimetric Analysis (TGA)

The TGA was used to determine the thermal degradation temperatures (Td) and the char yields of the resultant epoxy materials (Figs. 7 and 8). Consider the DGEBA modified with NPT as a sample (Fig. 7). The neat DGEBA polymer exhibited three thermal degradation regions. Upon increasing the NPT content in the DGEBA sample, the heat degradation temperature curve shifted to higher temperature, indicating that the presence of the organic rigid-rod compound improved the thermal stability of the DGEBA polymer. Table 3 lists the first thermal degradation temperatures of the four rigid-rod-modified self-reinforced DGEBA samples. The values of Td of the HPHB- and BSPA-modified self-reinforced DGEBA samples were similar to that of the NPT-modified polymer. For these three rigid-rod-reinforced DGEBA samples, the thermal degradation temperatures were increased by 20–30°C when 7.49 wt.% of the organic rigid-rod compounds had been added into the DGEBA matrix.

As indicated in Fig. 8, we found that the HPB-modified DGEBA systems exhibited only one thermal degradation region, with the thermal degradation temperature increasing
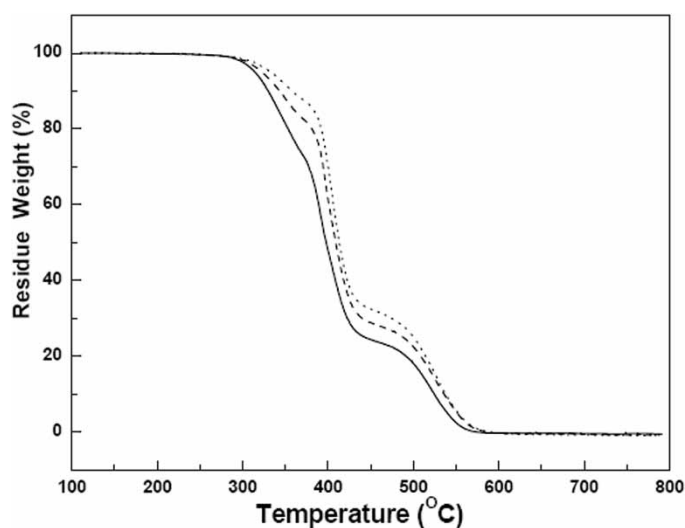
Figure 7. TGA traces of DGEBA samples modified with NPT for contents of (·): 0 wt.%, (– – –): 1.5 wt.%, and (·····): 3.09 wt.%.
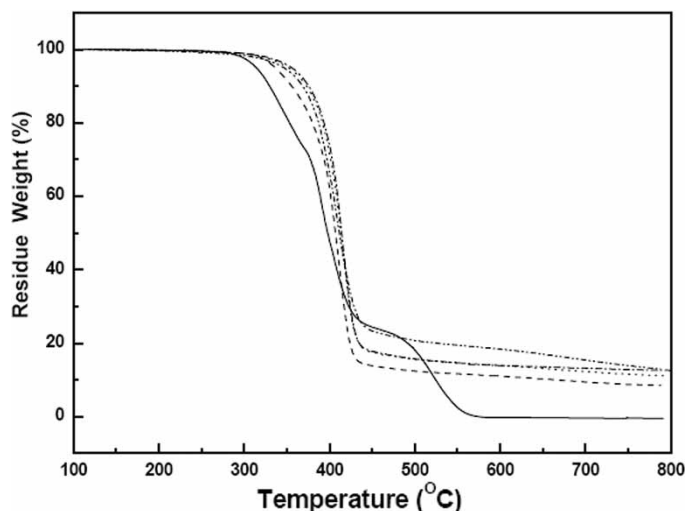
Figure 8. TGA traces of DGEBA samples modified with HPB for contents of (·): 0 wt.%, (—): 1.5 wt.%, (······): 3.09 wt.%, (−·−·−): 5.07 wt.%, and (−··−··): 7.49 wt.%.

upon increasing the HPB content in the DGEBA matrix. The thermal stabilities of the DGEBA samples were improved greatly after the introduction of the HPB organic rigid-rod compounds.

Differential analysis of the TGA curves allowed us to determine the dependence of the residual weights of the epoxy on the temperature. Figure 9 presents the differential analysis of the NPT-modified self-reinforced DGEBA sample shown in Fig. 7. The neat DGEBA material (solid line) exhibited three thermal degradation regions. With increasing amounts of NPT, the area of the first thermal degradation region (ca. 340°C) decreased (Fig. 9). Conversely, the areas of both the second (ca. 390°C) and third (ca. 520°C) thermal degradation regions increased upon increasing the NPT content. Thus differential analysis of the TGA curves also indicates that the presence of the organic rigid-rod compounds improved the thermal stability of the DGEBA material. The trends in the thermal degradations of the

Table 3
Thermal degradation temperatures (Td) obtained from TGA analyses of DGEBA samples presenting pendent rigid-rod moieties

	Content (wt.%)				
Rigid-rod compound	0	1.50	3.09	5.07	7.49
Tg values (°C)					
HPHB	314	321	338	342	335
HPB	314	337	352	356	346
BSPA	314	321	325	325	336
NPT	314	322	333	—	—
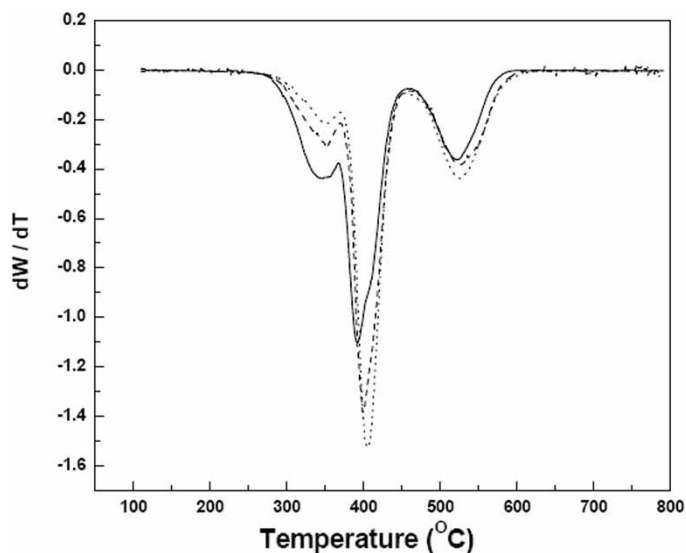
Figure 9. Differential residual weight diagrams of DGEBA samples modified with NPT for contents of (·): 0 wt.%, (– – –): 1.5 wt.%, and (· · · · · ·): 3.09 wt.%.

HPHB- and BSPA-modified self-reinforced DGEBA samples were both similar to that of the NPT-modified polymer. Thus, we conclude that the incorporation of each of these three rigid-rod compounds into the DGEBA system can improve its thermal stability.

In contrast, the HPB-modified self-reinforced DGEBA sample exhibited varied results in its differential analysis (Fig. 10). The introduction of HPB into DGEBA led
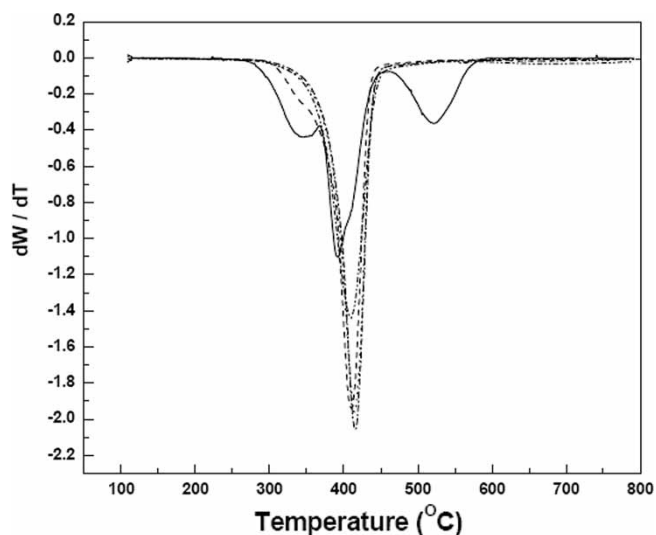
Figure 10. Differential residual weight diagrams of DGEBA samples modified with HPB for contents of (·): 0 wt.%, (– – –): 1.5 wt.%, (· · · · · ·): 3.09 wt.%, (– · – · –): 5.07 wt.%, and (– ·· – ··): 7.49 wt.%.

to only one thermal degradation region, which means the thermal stabilities of the DGEBA samples were improved greatly after the introduction of the HPB organic rigid-rod compounds. Therefore, the presence of all four of the organic rigid-rod compounds did indeed improve the thermal stabilities of their modified DGEBA systems.

Stress-Strain Properties

The results of the stress-strain properties of the various organic-rigid-rod-modified DGEBA samples are given in Fig. 11. The four different modified DGEBA resins exhibited the same trend for their tensile strengths increasing upon increasing their organic rigid-rod component in the DGEBA matrices.

   The stress-strain properties of the various organic-rigid-rod-modified DGEBA resins also depended greatly on the choice and amount of the organic rigid-rod compounds. Taking the HPHB and HPB systems as an example, the former system exhibited lower tensile strengths than the later, even though they have similar rigid-rod structures. Presumably, the effect arises because of the different end groups of these systems, and brings different interactions between the OH end groups and the polar groups in DGEBA.

   For the BSPA system, the addition of a small amount of BSPA (up to 3.09 wt.%) increased the tensile strength significantly; further addition of BSPA to the DGEBA resin (>3.09 wt.%) led to the tensile strength remaining unchanged. It is possible that the constant tensile strength upon adding BSPA may be a consequence of the structural similarity between BSPA and DGEBA, e.g. the presence of methyl groups in both BSPA and DGEBA resulting in their excellent compatibility.

   For the NPT-modified system, i.e. with naphthalene groups present from the side chains of the DGEBA resin, the tensile strength also increased upon increasing the content of NPT in the DGEBA matrix. The improvement of the tensile strength of the
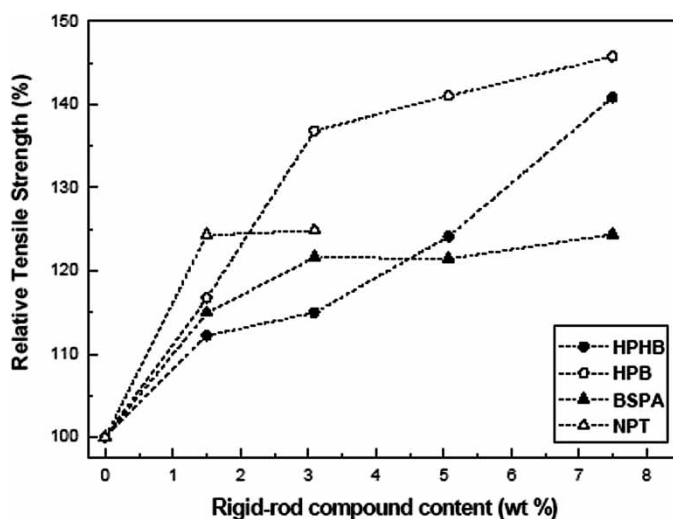
Figure 11. Effects of the organic rigid-rod compounds on the tensile strengths of the modified DGEBA resins relative to nonmodified DGEBA. The solid circles, hollow circles, solid triangles, and hollow triangles refer to the HPHB-, HPB-, BSPA-, and NPT-modified DGEBA systems, respectively.

NPT-modified DGEBA was more significant than those of the HPHB-, HPB-, and BSPA-modified DGEBA samples at a low rigid-rod content (1.50 wt.%) because of NPT's possessing the most rigid structure.

Conclusions

Four pendent organic rigid-rod compounds grafted onto the secondary hydroxyl groups of epoxy resin serve as nanoscale organic molecular fibers. The reinforcement effect was similar to the fiber reinforced polymer composites, but these were more miscible in the form of molecular composites. These molecular composites increase Tg and improve the thermal stability of the resultant polymer matrix. Unlike fiber reinforced polymer composites, these molecular composites behave as self-reinforced epoxy resins.

Acknowledgments

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