1046 *Macromolecules* **2006,** *39,* 1046−1052

Relaxation and Reinforcing Effects of Polyrotaxane in an Epoxy Resin Matrix

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Received August 29, 2005; Revised Manuscript Received December 6, 2005

ABSTRACT: Polyrotaxanes with a low threading ratio of α-cyclodextrin (α-CD) on a poly(ethylene glycol) chain effectively acted as both the relaxation and reinforcing reagents in Novolac-type epoxy resin. The polyrotaxanes were incorporated into the epoxy resin during the curing process to produce transparent and rigid epoxy resin/polyrotaxane (E/PR) alloys. From dynamic mechanical analysis (DMA) of the E/PR alloys, it was found that the polyrotaxane contributed not only as a stress-relaxation component but also as a reinforcing modifier in the epoxy resin matrix. The morphology and chemical structures of polyrotaxanes in the epoxy resin matrices were assumed to be in a nanoscale dispersion, forming an interpenetrate network structure with multi cross-linking bonds on threaded α-CDs. This assumption was made based on their transparency, differential scanning calorimetry, small-angle X-ray scattering, and DMA analyses. This is the first report on the unique properties of polyrotaxanes added in a rigid matrix.

Introduction

Cyclodextrins (CDs) are cyclic oligomers of a (1−4)-α-D-glucopyranosyl unit consisting of six, seven, and eight units termed as α, *β*, and *γ*-CD, respectively. Their dominating characteristic is their ability to include a variety of molecules.[1−3] This is because their structures have hydrophobic spaces within the inner cavities and this property allows a range of guest molecules to be incorporated into the hydrophobic spaces. During past few decades, work in this research field has been developed to include reports that CDs can form inclusion complexes with various linear polymers such as poly(ethylene glycol) (PEG),[4] poly(tetrahydrofuran),[5] poly(propylene glycol),[6] poly(*ϵ*-caprolactone),[7] and poly(3-hydroxypropionate).[8] Polyrotaxane with a supermolecular structure is obtained after capping both ends of the chain with a block group larger than the diameter of the CD's inner cavity to prevent the dethreading of the polymer chain. Recently, research on polyrotaxane has taken great strides with various potential applications expected. For example, Harada et al., after cross-linking adjacent CDs, created a molecular tube by the removal of the blocking end groups and guest polymers.[9,10] Ito et al. developed a slide-ring gel by a coupling reaction between CDs on polyrotaxanes.[11] Yui et al. demonstrated a pH-controlled molecular piston using polypseudorotaxane consisting of a triblock copolymer and CDs.[12] In these previous studies, the most advantageous characteristic of polyrotaxane is the special molecular mobility of each host and guest molecule based on its interlocking structure. As no covalent bond exists between the host and guest molecules, the polyrotaxane may exhibit this special molecular mobility even in a rigid matrix as suggested by Nagapudi et al., who prepared a linear polyurethane in the presence of crown ether, resulting in the formation of a polyurethane−rotaxane.[18] However, there is no report about the effect of polyrotaxane as a functional additive to rigid networked materials.

A typical example of one such rigid material is epoxy resin, which is widely used in high-performance protective coatings, structural adhesives, low-stress IC encapsulates, and matrix resins of composites. The epoxy resin changes into a highly cross-linked and rigid matrix after its curing process.[13−15] However, its tendency to crack easily is considered to be a serious drawback to its use in advanced and sophisticated applications, which require high performance epoxy resins capable of being manipulated through large temperature ranges. Thus far, various kinds of modified rubber particles and thermoplastics have been introduced into the epoxy resin matrices as impact resistance modifiers to help inhibit the growth of cracks.[16,17] However, these modifications tended to compromise other important properties, such as tensile modulus and glass transition temperature (T_g). This was because the modifiers introducing the flexible properties were replacing or diluting the rigid network structures of the original epoxy resins.

In this paper, effects of the polyrotaxane as an inner-stress relaxation reagent in an epoxy resin matrix are investigated. It was expected that the molecular mobility of the guest molecule in the polyrotaxane would contribute to the inner-stress relaxation of the rigid matrix and that the host molecules on the polyrotaxane would function as multi-cross-linking sites to maintain or improve the mechanical properties of the original matrix. To achieve these aims, polyrotaxanes with lower threading ratio values (*f*, %) of host molecules were synthesized from PEG and α-CD, and then incorporated into a Novolac-type epoxy resin matrix via the curing process of the resin. The effects of the polyrotaxane on the mechanical and thermal properties of the epoxy resin are discussed.

Experimental Section

Materials. Bis-amine-terminated PEG-2000 (polydispersity (PDI) = 1.37), PEG-20000 (PDI = 1.06), and PEG-35000 (PDI = 1.16) were purchased from General Science Co., Wako Pure Chemical Industries, Ltd., and Aldrich, respectively, and used without further purification. α-Cyclodextrin (α-CD) was obtained from Wako Pure Chemical Industries and used as received. Dialysis tube (fraction-

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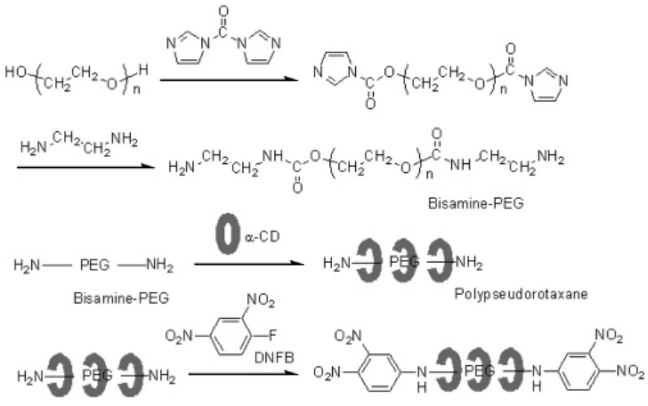
10.1021/ma051888k CCC: $33.50

Scheme 1. Preparation of Polyrotaxane



ation molecular weight: 12000) was obtained from Nihon Medical Science Inc. Novolac-type epoxy resin (EPICLON N-730-A; average epoxide equivalent weight, 174 g; average molecular weight, 415) was generously supplied from Dainippon Ink & Chemical Inc. Other chemicals, *N*,*N*′-carbonyl diimidazole, ethylenediamine, and 2,4-dinitrofluorobenzene (DNFB), and solvents, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol, DMSO-d_6, 2-ethyl-4-methylimidazole, and 1-methyl-2-pyrrolidone (NMP), were purchased from Wako Pure Chemical Industries, Ltd. and used as received.

Characterization Methods. ^{1}H NMR spectra were recorded on a Varian INOVA400 NMR spectrometer operating at 400 MHz for the proton investigation in DMSO-*d6* solution with tetramethylsilane as the internal standard. Fourier transfer infrared (FT-IR) spectra were recorded from KBr pellets on a Perkin-Elmer Spectrum One in a range of 4000−400 cm^{-1} with a resolution of 2 cm^{-1}. UV−visible spectra were recorded on a JASCO V-570 UV/visible/near-IR spectrophotometer.

Differential scanning calorimetry (DSC) measurements were carried out using a Seiko Instruments Inc. EXTAR SII-6200 DSC system. Each sample was encapsulated in an aluminum pan (5 mm in diameter) and heated from −100 to +200 °C at a heating rate of 10 °C min^{-1} in a nitrogen flow of 20 mL min^{-1}. After the sample was quenched at −100 °C, a second scanning of DSC measurement was carried out at a heating rate of 5 °C min^{-1}. Thermogravimetric analysis (TG/DTA) was conducted on a Seiko Instruments Inc. EXSTAR 6200 TG system. After thoroughly drying, samples were recorded from 60 to 500 °C at a heating rate of 10 °C min $^{-1}$ in a constant nitrogen flow 100 mL min^{-1}. Dynamic mechanical analysis (DMA) of E/PR alloys was performed on a Seiko SDM 5600 DMA 110 system.

SAXS (Small-angle X-ray scattering) measurements were performed on a Rigaku 2000 system using Cu Kα radiation at a generator power of 40 kV and 30 mA with a 2θ scan range of 0.01−5.00° at a scanning speed of 0.1° min $^{-1}$.

Preparation of Polyrotaxane. Polyrotaxanes with high molecular weights and low threading ratio values (f, %) of α-CD were synthesized from α-CD and PEGs of various molecular weight using a method similar to that well documented in the literature (Scheme 1).[9−11] A typical procedure for obtaining polyrotaxane PR-20000 from PEG-20000 is as follows:

Bis-amine-terminated PEG-20000 (bisamine-PEG-20000) was prepared from PEG-20000 by reactions first with *N*,*N*′-carbonyl diimidazole and then with ethylenediamine. PEG-20000 (5.0 g, 0.25 mmol) was dissolved in dichloromethane (50 mL) and then *N*,*N*′-carbonyl diimidazole (0.81 g, 5 mmol) was added. The reaction was carried out for 12 h at room temperature under stirring. Diethyl ether (300 mL) was added into the reaction solution to obtain a white precipitate, which was isolated by centrifugation for 5 min at 7000 rpm, then washed twice with diethyl ether (300 mL), and dried to obtain bis-imidazoylcarbonyloxy-terminated PEG-20000 in a yield of 78%. FT-IR (KBr): (cm^{-1}) 2890 (ν_{CH}, CH_2 group), 1690 ($\nu_{C=O}$, $>N-C(=O)-O-$), 1110 (ν_{C-O-C}). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.51 (s, $-CH_2CH_2-$).

Table 1. Preparation of Polyrotaxanes

		polyrotaxane			
	bisamine−PEG amination ratio (%)	yield (%)	composition of α-CD:PEG: end-capping group (wt %)	no. of α-CD threaded onto a PEG chain	threading ratio of α-CD (f, %)
PR-2000	98	11.7	55.1:37.8:7.1	3.1	13.3
PR-20000	81	10.1	51.2:47.9:0.9	21.7	9.7
PR-35000	80	6.3	50.4:49.1:0.5	37.2	9.3

The bis-imidazoylcarbonyloxy-terminated PEG-20000 (3.45 g, 0.17 mmol) was dissolved in dichloromethane (50 mL), then ethylenediamine (10 mL, 166.45 mmol) was added dropwise at room temperature. After stirring for 2 h, diethyl ether (300 mL) was added into the reaction solution to obtain a white precipitate. The precipitate was dissolved in distilled water (100 mL) and purified by using a dialysis tube to eliminate low molecular weight materials weighing less than 12000. After the dialysis, water was evaporated to obtain bisamine-PEG-20000 (2.6 g, yield 52.4%). The characterization data of bisamine-PEG-20000 were as follows: FT-IR (KBr): (cm^{-1}) 3440, (ν_{NH}, amino group), 2890 (ν_{CH}, CH_2 group), 1110 (ν_{C-O-C}). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.51 (s, $-O-CH_2CH_2-$).

The amination ratio of the bisamine-PEG-20000 was evaluated by the well-defined method of substituting an amino group with 2,4-dinitrofluorobenzene (DNFB). A solution of bisamine-PEG-20000 (0.1 g, 0.005 mmol) in dichloromethane (10 mL) was mixed with DNFB (0.0046 g, 0.025 mmol) and stirred for 2 h at room temperature. After the reaction, the solution was added into diethyl ether (50 mL) to obtain a yellowish precipitate. The precipitate was isolated by filtration and vacuum-dried at room-temperature overnight in vacuo. The amination ratio was calculated by comparing the absorption intensity at 345 nm in a UV spectrum with a calibration curve. This calibration curve employed a standard material synthesized from the reaction product of 2,2′-(ethylenedioxy)bis(ethylamine) with DNFB.

Bisamine-PEG-20000 (1.0 g, 0.05 mmol) and α-CD (0.388 g, 0.40 mmol) were dissolved in distilled water (20 mL) under vigorous stirring for 1 h at 80 °C and kept overnight in a refrigerator at below 10 °C to give polypseudorotaxane as a white precipitate. The polypseudorotaxane was isolated by filtration and vacuum-dried to remove the water completely. Then, after it had been suspended into DMF (10 mL), end-capping reagent DNFB (2.4 g, 12.9 mmol) was added into the solution to cap the Bisamine termini with the bulky 2,4-dinitrobenzyl group. After the suspension had been stirred for 2 h at room temperature, the reaction mixture was dissolved completely by pouring it into DMSO (50 mL), after which water (300 mL) was added to give a yellow precipitate. The precipitate was isolated by centrifugation and washed twice by water and methanol. Finally, the product was vacuum-dried overnight at 80 °C to yield polyrotaxane PR-20000 (0.21 g, 10.1% yield based on bisamine-PEG-20000).

Other polyrotaxanes, PR-2000, and PR-35000 were also synthesized in the same way as PR-20000. Characterization of the polyrotaxanes; PR-2000, -20000, and -35000, was performed with ^{1}H NMR and FT-IR. The average number of α-CD threaded into a PEG chain was estimated by comparing the integral values of the corresponding signals in ^{1}H NMR spectra, using the signals of $C(1)-H$ of α-CD and $-O-CH_2-CH_2-$ of PEG. The % f value of α-CD was calculated from the stoichiometry, in which two methylene units of PEG were assumed to be equal to the depth of the α-CD inner cavity (ca. 7.9 Å). Characterization results are listed in Table 1.

Preparation of Epoxy Resin/Polyrotaxane Alloy (E/PR Alloy). Novolac-type epoxy resin was cured in the presence of polyrotaxane with 2-ethyl-4-methylimidazole as a curing agent to prepare an epoxy resin/polyrotaxane (E/PR) alloy. A typical preparation procedure of E/PR-20000 is as follows:

A solution of PR-20000 (0.1 g) in DMSO (1 mL) was added into the Novolac-type epoxy resin (1 g) at 60 °C and then the mixture was stirred for 10 min to obtain a clear solution. To this solution, a solution of 2-ethyl-4-methylimidazole (0.02 g) as a curing agent in 1-methyl-2-pyrrolidone (0.2 mL) was added. After evaporating the solvents at 80 °C for 30 min in vacuo, the solution mixture was poured into a mold (100×10 mm^2 in area and 0.5 mm in depth). Curing was performed at 145 °C for 3 h to obtain a uniform and transparent sheet material. This material was subjected to further heating for 2 h at 220 °C under 1.33 kPa to complete the curing and the removal of the residual solvents and water, resulting in a transparent product E/PR-20000 (10 wt %). Other E/PR alloy sheets and a reference sample sheet of neat epoxy resin were also prepared in the same way; the former with and the latter without the corresponding polyrotaxanes.

Dynamic Mechanical Analysis of E/PR Alloys. DMA of E/PR alloys was performed on a Seiko SDM 5600 DMA 110 system. The E/PR alloy sample sheet, after molding to give a regulated area of 20×5 mm^2 and thickness of 0.5 mm, was used for DMA measurements, in which the mechanical properties: storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were monitored in a temperature range of -100 to $+200$ °C at a heating rate of 2 °C min^{-1}. The DMA measurements were carried out in a tensile mode under a low tension load of 5 gf and amplitude of 5 μm at frequencies of 0.5, 1, 2, 5, and 10 Hz. Obtained tan δ profiles were simulated by a computer simulation method with a commercial software, PeakFit version 4, to separate each component into its independent energy dispersion mode. Transition temperature was taken as the temperature at the top of the peak in the tan δ profile. Activation energy (E_a) of each dynamic dispersion mode was calculated from the Arrhenius plot using the relation[19-21]

$$f \approx \exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

where f, R, and T are the applied frequency, the gas constant, and absolute temperature, respectively.

Results and Discussion

Synthesis of Polyrotaxanes with Low Threading Ratio Values of α-CD. To improve the sensitivity of epoxy resins to thermal and mechanical stresses, epoxy resin/polyrotaxane (E/PR) alloys were prepared. The polyrotaxane is expected to act so as to reduce the inner-stress in the E/PR alloys at the same time as achieving or maintaining other functions such as improving or maintaining the original mechanical and thermal properties of the matrix resins. For these desired functions to be effectively exhibited, domains of the polyrotaxane need to be dispersed finely and homogeneously throughout the matrix.

To secure the mobility of guest molecules and to maintain the mechanical properties of the matrix, the threading ratio value (f, %) of α-CD on the guest molecule should be reduced and the guest molecule should be of a higher molecular weight (MW). Most of the previously reported polyrotaxanes had a high % f of CD of more than 50% on oligomeric guest molecules (MW $<$ 4000), because the aim was to prepare a tubular supermolecule and a molecular necklace etc.[9,10] The least % f of α-CD previously reported was 19% on PEG-2000 as the guest molecule,[22] which means that the weight ratio PEG:α-CD was 32.3:67.7 (w/w). Even in the case of the polyrotaxane with the least % f, the guest molecule's mobility must be restricted by the host molecules.

To synthesize the polyrotaxane with low % f, the complexation was carried out under conditions of a lower feed ratio of α-CD to bisamine-PEG to prepare polypseudorotaxane as an intermediate (Scheme 1). For the amination of the hydroxyl termini of PEG, carbonyl diimidazole and ethylenediamine were employed as effective reagents in preparing bisamine-PEG with a high amination ratio value (Table 1).[23] Finally, the end-capping of polypseudorotaxane was achieved by a reaction with 2,4-dinitrofluorobenzene (DNFB),[4] which was used for the quantification of the amino group. Results of the amination ratio, yield of polyrotaxane, number of threaded α-CD on a PEG chain, weight ratio of components [α-CD:PEG:end-capping group], and % f are listed in Table 1. Though the amination ratio was high enough to guarantee producing the rotaxane structure, the measured values of less than 1.0 suggest that other reactions, such as dimerization and cyclization of PEG chains, occurred during the reactions with carbonyl diimidazole and ethylenediamine. The % f and weight ratio of α-CD resulted in ranges of 9.3−13.3% and 50.4−55.1 wt %, respectively. As a consequence, preparation of the high molecular weight polyrotaxanes, PR-20000 and PR-35000 with a lower % f of around 10% was achieved, although the yield was decreased by around 10%. However, such yields of the polyrotaxanes with the low % f may be reasonable when compared to the previously reported values of 28 and 18% in yield for polyrotaxanes from PEG-20000 with $f = 28$ and 19%, respectively.[10,11,22]

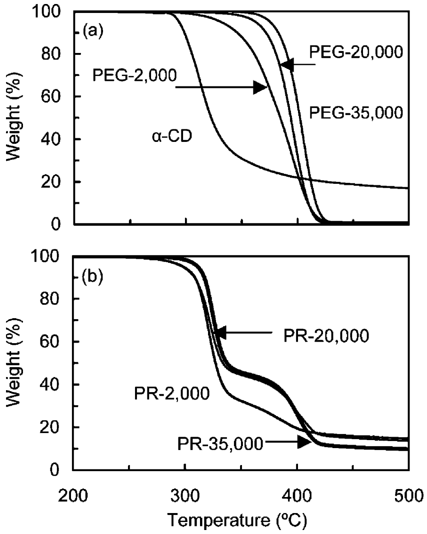


Figure 1. TG profiles of α-CD, PEGs, and polyrotaxanes.

It is generally accepted that the interaction between α-CD and PEG, as the host and guest molecules, respectively, plays a key role in favoring polyrotaxane formation. Such an interaction is based on the hydrophobic property of the inner cavity of α-CD to form the inclusion complex.[8,24] The inclusion complex formation of α-CD and PEG as the polyrotaxane was determined by ^{1}H NMR analysis, with a spectral shift in δ values and a broadening of signals observed on the signals of C(2)−O*H*, C(3)−O*H*, and C(6)−O*H*. These δ values were the same or very closely approximated to those of previously reported polyrotaxanes.[4] These results indicate that the α-CDs in the obtained polyrotaxanes were tethered noncovalently on the end-capped PEG chains.

Thermal Properties of Polyrotaxanes and E/PR Alloys. The E/PR alloys were prepared via the curing and solvent/water elimination processes at high temperatures of 145 and 220 °C, respectively. It is important, therefore, to examine the thermal resistance and degradation behavior of each constituent of the polyrotaxanes. In Figure 1, results of thermal gravimetric analysis (TG) of α-CD, PEGs, and polyrotaxanes are illustrated. No weight loss was detected in a temperature range of 60−200 °C for all the polyrotaxanes. α-CD showed a rapid decrease in weight over 290 °C and left approximately 20 wt % in weight as residue at 500 °C. All the TG profiles of the PEGs showed similar curves, in which complete degradation was achieved in a range of 300−420 °C, with the profiles of PEGs starting the

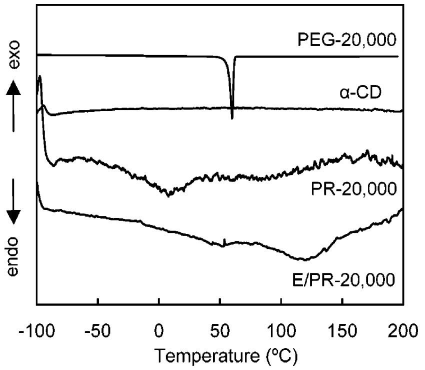


Figure 2. DSC profiles of PEG-20000, α-CD, PR-20000, and E/PR-20000 (10 wt %) alloy.

degradation at a lower temperature in accordance with their lower molecular weight. On the other hand, TG profiles of the polyrotaxanes produced a two-stage weight-loss pattern consisting of the degradation of the α-CD and PEG parts in temperature ranges of 280−350 and 350−410 °C, respectively. The weight-loss in each step corresponded to the degradation of the α-CD and PEG parts. These results reflect the % *f* value of polyrotaxanes. It is worth noting that the polyrotaxanes are thermostable at the temperatures experienced during the curing and solvent elimination processes.

Figure 2 shows DSC profiles of PEG-20000, α-CD, PR-20000, and E/PR-20000 (10 wt %) in a range of −100 to +200 °C, with the second scanning carried out just after rapid quenching was employed. The profile of PEG-20000 exhibited a sharp melting peak of crystalline at 61.3 °C, while α-CD showed no clear transition point in this temperature range. The profile of PR-20000 showed broad transition modes around 0 °C and in a range of 50−150 °C. Similar results were obtained using the other polyrotaxanes. These results indicate that the threaded α-CDs interfere with the PEG parts in the polyrotaxanes causing them to aggregate and crystallize, despite their low % *f*.

In the profile of the E/PR-20000 alloy, two broad transition modes appeared around 50 and 125 °C. These two modes may be assigned to a dynamic dispersion mode of PEG chains in the polyrotaxanes and the glass transition of the epoxy resin matrix, respectively. In a DSC profile of original cured epoxy resin, a transition mode at the lower temperature was not observed. Thus, some parts of the PEG chain in the E/PR-20000 alloy must retain molecular mobility even under the restriction imposed by the threaded α-CDs and the epoxy resin matrix. Such flexible PEG parts may be formed during the curing process of the epoxy resin at the high temperatures.

Dynamic Mechanical Properties of E/PR Alloys. Dynamic mechanical properties of E/PR alloys with various contents (5, 10, and 20 wt %) of the polyrotaxanes were evaluated with DMA in a temperature range of −100 to +200 °C at various frequencies (0.5, 1, 2, 5, and 10 Hz) of the sinusoidal wave loading. DMA results at a frequency of 10 Hz are illustrated in Figure 3, which compares the dynamic mechanical properties of three E/PR (10 wt %) alloys against the original cured epoxy resin sample as a reference. DMA profiles of E/PR-20000 with various PR content (5, 10, and 20 wt %) alloys are shown in Figure 4.

Figure 3 shows the temperature dependence of the dynamic viscoelastic properties: storage modulus E', loss modulus E'', and loss tangent tan δ. All the E/PR alloy samples had two main relaxation modes in the ranges of −100 to −50 °C and 100 to 150 °C attributed to the molecular motions of the original epoxy resin matrix part described in terms of the β- and main dispersion modes, respectively. Interestingly, for E/PR-20000 and E/PR-35000 alloys, an additional relaxation mode in a range of 30−100 °C was clearly exhibited in the E'' and tan δ profiles. E/PR-2000 alloy also gave a weak molecular motion in the same temperature range of 30−100 °C, while the original cured epoxy resin showed no molecular motion. These results agreed with the endothermic broad peaks in the DSC profile of E/PR-20000 alloy as shown in Figure 2.

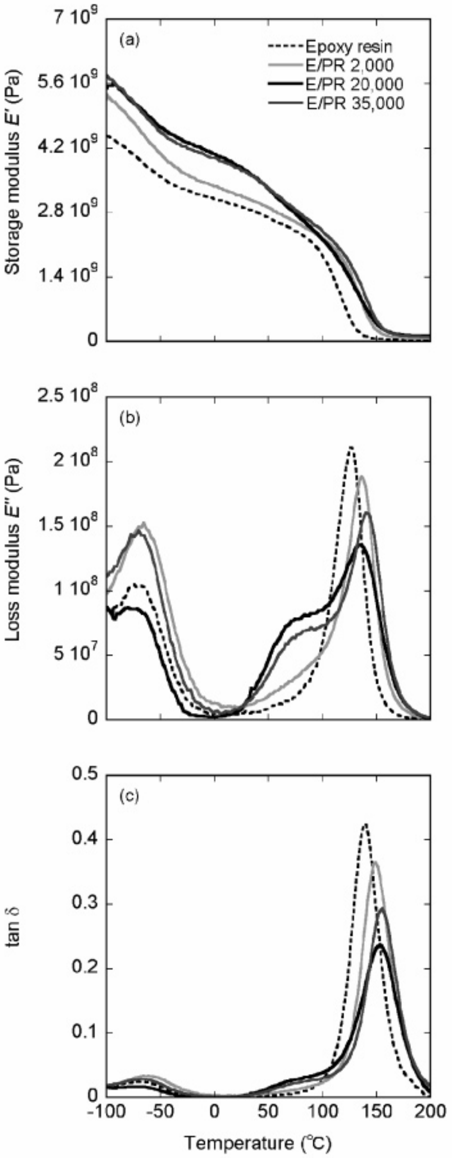


Figure 3. DMA profiles of E/PR (10 wt %) alloys: (a) storage modulus E', (b) loss modulus E'', and (c) loss tangent tan δ profiles.

In Figure 4, the additional molecular motion varied with the content of PR-20000. In these samples, in contrast to the 5 and 10 wt % samples, E/PR-20000 (20 wt %) was opaque and not transparent, due to the phase separation of polyrotaxane in the matrix. The increase in the PR-20000 content from 5 to 10 wt % led to the increases in E'' and tan δ in the temperature range of 30−100 °C (Figure 4, parts b and c). In contrast, however, the increase in the amount to 20 wt % caused decreases in the same properties when compared with those of E/PR-20000 10 wt %. These irregular changes in the properties of E/PR (20 wt %) alloy may be caused by its phase separation as distinct from the transparent alloys with 5 and 10 wt % of PR-20000. This phase separation of PR in the matrix caused the broadening of

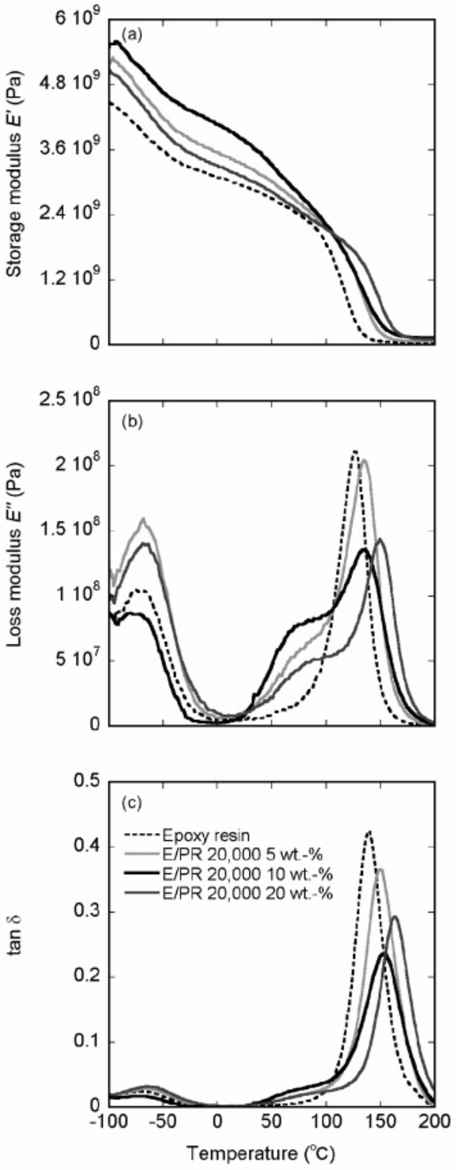


Figure 4. DMA profiles of E/PR-20000 (5, 10, and 20 wt %) alloys: (a) storage modulus E', (b) loss modulus E'', and (c) loss tangent tan δ profiles.

the temperature range of the additional molecular motion, particularly to higher temperatures than 100 °C, resulting in the apparent decreases in E'' and tan δ intensities in the temperature range of 30−100 °C. It appears from these results that the added PR-20000 and PR-35000, or, more precisely, the PEG-20000 and PEG-35000 chains in the polyrotaxanes, must contribute to the molecular motion. On the other hand, it is considered that the PEG-2000 chains in PR-2000, because of their short chain length and bulky end-capping groups, did not have enough flexibility to show any additional molecular motion.

In Figure 3a and 4a, E' profiles of E/PR alloys exhibited significant increases in the storage modulus in comparison with the reference profile. Moreover, the main-chain relaxation peaks in E'' and tan δ profiles of E/PR alloys steadily shifted to higher temperature ranges as a function of PEG-chain length and content of the polyrotaxane. These results indicate that the polyrotaxane contributed as a reinforcing modifier in the epoxy resin matrix.

To clarify the contribution of polyrotaxanes to the dynamic mechanical properties of E/PR alloys, a mixture of components: α-CD and DNFB-end-capped PEG-20000 was added into the epoxy resin using the same amounts of the components as those in E/PR-20000 (10 wt %). Results are shown as the E'' profile and compared with E/PR-20000 alloy and the reference in Figure 5. In the E'' profile, slight additional molecular motion in the range of 30−100 °C and a small increase in the main-chain relaxation peak temperature were observed when compared with those of the reference. A slight increase in E' value was also observed. These changes in the dynamic mechanical properties of the mixture alloy were considerably less than those of the E/PR alloys, because each component in the mixture alloy was unable to function alone.

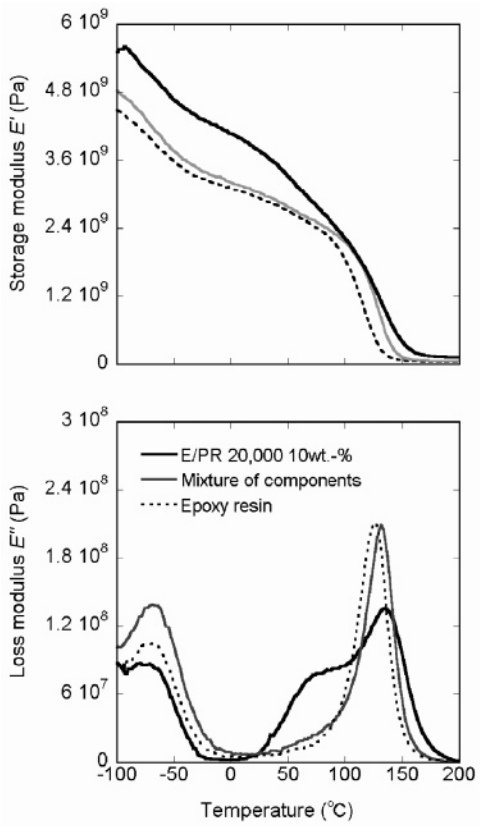


Figure 5. Storage modulus E' and loss modulus E'' profiles of a mixture of components: epoxy resin/α-CD/DNFB-end-capped PEG-20000, compared with E/PR-20000 10 wt % alloy and cured epoxy resin matrix as reference.

This result means that the additional molecular motion and the increase in the main-chain dispersion peak temperature can be attributed to the components in the polyrotaxanes, but not when these components are isolated. Therefore, it is concluded that the polyrotaxane can function not only as a relaxation agent, but also as a reinforcing and heat-resisting modifier of the epoxy resin.

Morphology and Chemical Structure of E/PR Alloys. It is expected that the improved dynamic mechanical and thermal properties of E/PR alloys are due to their special morphology and chemical structure, for example, the flexible molecular motion of the PEG chains, dense cross-linking structure around the polyrotaxane, and fine dispersion in the epoxy matrix.

The dispersion state of polyrotaxane in the epoxy matrix was evaluated with SAXS. According to Guinier's method, the radius of gyration R can be calculated from the SAXS intensity of the E/PR alloys using the exponential function:

$$\ln(I_{(q)}) = \ln(I_e M n^2) - \frac{R^2}{3} q^2 \qquad (2)$$

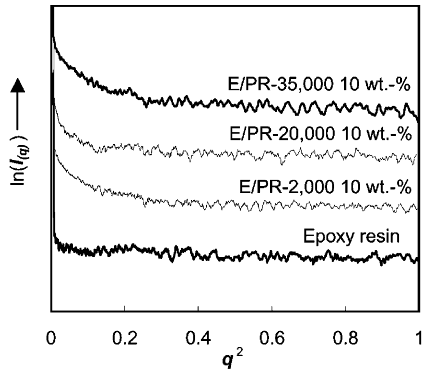
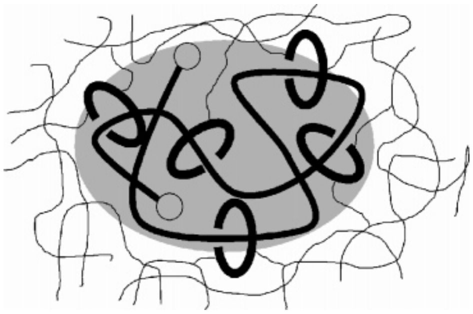


Figure 6. Plots of $\ln(I_{(q)})$ vs s^2 on SAXS analysis of E/PR alloys.

Table 2. Results of SAXS Analysis of E/PR Alloys

sample	calculated diameters of domains (nm)
E/PR-2000 (10 wt %)	19−81
E/PR-20000 (10 wt %)	35−96
E/PR-35000 (10 wt %)	23−115

Scheme 2. Schematic Model of Polyrotaxane Domain Dispersed in an Epoxy Resin Matrix



where I_e is the intensity scattered by a single electron, M the number of particles, n the number of electrons in a particle, and q the magnitude of the scattering vector. The plots of $\ln(I_{(q)})$ vs q^2 for three E/PR (10 wt %) alloys and the original cured epoxy resin are illustrated in Figure 6. In the case of the reference, the plot was totally flat, suggesting no particle was present in the matrix. On the other hand, the plots of the E/PR alloys could be correlated by some of the lines and/or curves, indicating that the E/PR alloys comprised a series of particles with a radius of gyration in a range of 10 to ≈50 nm.

In this study, the particle size will be regarded as a domain size derived from the polyrotaxane dispersed in the epoxy matrix. The plots in Figure 6 were approximated by two tangents according to Fankuchen's method,[25] from which the apparent domain sizes were calculated. Results are listed in Table 2. It was found that the domains of polyrotaxanes in the E/PR (10 wt %) alloys were apparently in a range of 19 to 115 nm in diameter. Considering actual domain dimensions of molecularly dispersed PEG-2000, -20000, and -35000, the measured domain sizes may be reasonable and suggest that many polyrotaxanes in the E/PR alloys have dispersed to form one or more domains that have originated from one polyrotaxane molecule as shown in Scheme 2.

In Scheme 2, an expected schematic model of the E/PR alloy is illustrated. This model shows a molecular domain of polyrotaxane dispersed in the epoxy resin matrix, which consists of α-CDs covalently bonded to the matrix chains at multisites and a mobile PEG chain tethered by the α-CDs and the epoxy resin matrix. Many OH groups on α-CDs tethered to a polyrotaxane are able to function as chain-transfer reaction sites during the curing reaction of the epoxy resin (Scheme 3). Thus, the α-CDs threaded on a PEG chain are regarded as multifunctional cross-linking agents, resulting in the formation of a dense cross-linked network area, which must contribute to the improvement in the heat-resistance and mechanical properties of the epoxy resin matrix. The PEG chain as a flexible guest molecule is able to move in the space formed by the cavities of the threaded α-CDs and the surrounding epoxy resin matrix to show the additional molecular motion evident in the DMA profiles. The polyrotaxane with a longer PEG chain part showed more marked relaxation and reinforcing effects, because the longer PEG chain can move in the space subject to less influence from the bulky terminal groups.

So far, it has been well established that the relationship between the relaxation and reinforcing effects of additives tend to have a simple relationship of mutual exclusion that requires compromise. In this study, we exhibited that both the effects are achievable at the same time due to the specific morphology and chemical structure of the E/PR alloy. However, it is noteworthy that, even in the E/PR alloy, the relaxation and reinforcing effects are in a mutually excluding relationship as a function of the % *f*. The higher the % *f* became, the more the reinforcing effect increased, but the less the relaxation effect functioned. However, manipulating the E/PR alloys to exhibit both effects was easy. This was because the polyrotaxanes have low % *f* (9.3−13.3%), which are effective in moving the PEG chains and sufficient to construct the cross-linkages between α-CDs and the matrix, in comparison to those earlier reported.

Therefore, the polyrotaxane domains must be absorbing the stresses by changing them into the motive energy of PEG chains and/or resisting strain by their dense cross-linking structure.

Activation Energy of Additional Molecular Motion. Apparent activation energy, E_a, of the additional molecular motion of E/PR alloys was evaluated from the relationship between the applied frequencies (0.5, 1, 2, 5, and 10 Hz) and the reciprocal of the peak top temperature in the tan δ profile, in which, prior to the analysis, different dispersion modes were separated from each other by a computer simulation technique. Results are listed in Table 3. The estimated E_a value was in a range of 130−160 kJ mol^{-1}. These E_a values were larger than $-\Delta H = 8-12$ kJ mol^{-1} for the melt of PEG crystalline.[26] They

Scheme 3. Chain-Transfer Reaction and Resulting Formation of Multicovalent Bonds with an Epoxy Resin Matrix

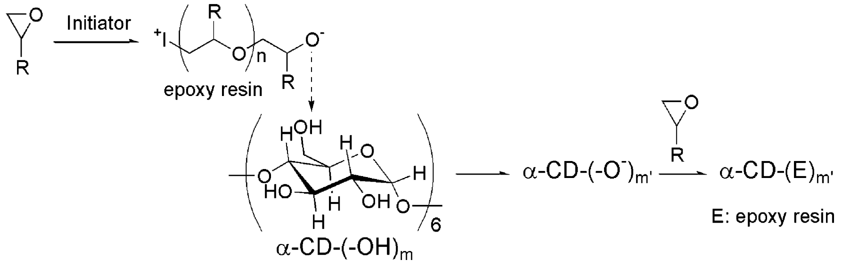


Table 3. Apparent Activation Energy E_a of Additional Molecular Motion of E/PR Alloys

sample	E_a (kJ mol^{-1})
E/PR-2000 (10 wt %)	160.2
E/PR-20000 (10 wt %)	130.1
E/PR-35000 (10 wt %)	139.9

show that the mobility of PEG chains in the polyrotaxane was restricted by the tethered α-CDs and epoxy resin matrix, suggesting the formation of a interpenetrated structure of the PEG chain part and epoxy resin matrix. E/PR-2000 alloy showed a value: $E_a = 160$ kJ mol^{-1}, higher than those of E/PR-20000 and E/PR-35000 alloys, because its shorter chain length of PEG-2000 allows the bulky termini to have a more significant influence.

The morphology and chemical structures of the E/PR alloys are not yet clear, however, the transparency and the analytical results with DSC, SAXS, and DMA suggest that the E/PR alloys have nanoscale dispersed domains in the epoxy resin matrix. Moreover, such domains must be bound covalently with the epoxy resin matrix. The unique morphology and chemical structures of E/PR alloys consist of the synthesized polyrotaxanes with a high molecular weight PEG chain and low % *f* of α-CD, resulting in the addition of both the effective relaxation and reinforcing functions to the epoxy resin matrix.

Conclusions

The polyrotaxanes with low % *f* were synthesized under the conditions of lower feed ratios of α-CD to PEG, via bisamine-PEGs and polypseudorotaxanes as intermediates. Epoxy resin/polyrotaxane (E/PR) alloys were prepared via the curing process of the Novolac-type epoxy resin, resulting in transparent rigid materials. From their transparency, DSC, SAXS, and DMA analytical results, the morphology and chemical structures of polyrotaxanes in the epoxy resin matrices were assumed to be of nanoscale dispersed domains tethered by the matrix. These unique morphologies and chemical structures made it possible to add both the effective relaxation and reinforcing functions to the epoxy resin matrix.

Acknowledgment. The authors are extremely grateful to Dr. Masahiro Yamaguchi, Dr. Kazumasa Yoshikai, and Dr. Akemi Tsuchiyama in Fukuoka Industrial Technology Center for their generous support during the DMA and SAXS measurements.

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MA051888K