

Preparation of *N*-Grafted Poly(*p*-phenyleneterephthalamide) and Applications to a Molecular Composite with Epoxy Resin

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ABSTRACT: To prepare the molecular composite of poly(*p*-phenyleneterephthalamide) (PPTA) and epoxy resin (Epoxy), *N*-grafted PPTA (PPTA-*g*-Epoxy) was synthesized from PPTA and Epoxy via metalation of PPTA in a solution of sodium methylsulfinylcarbanion in dimethylsulfoxide. The Characterization of PPTA-*g*-Epoxy was carried out by IR, TGA, DSC, and X-ray diffraction. Molecular composites were prepared from PPTA-*g*-Epoxy of more than 100% grafting of Epoxy, epoxy resin and triethylenetetramine as a hardener. The bending modulus of 3.0 GPa and bending strength of 164 MPa were obtained for the molecular composite, and found superior to those of epoxy resin by factors of 1.66 and 1.36, respectively. The reasons for low reinforcing effect are discussed.

KEY WORDS Poly(*p*-phenyleneterephthalamide) / Epoxy Resin / Molecular Composite / Graft Copolymer /

The basic idea of molecular composite (MC) is the extension of the principle of fiber-reinforced plastics (FRP). That is, rigid rod like molecules play a reinforcing role like fibers in FRP and flexible coil-like molecules correspond to matrix resin in FRP.¹

The advantages of MC are: (1) the aspect ratio of rod molecules is large, (2) the ideal covalent bond strength in rod molecules is usable, and (3) a blend texture is homogeneous which is desirable for removing defects and increasing strength. The preparation method of MC is to dissolve rigid rod molecules and flexible coil molecules in their common solvent and coagulate in a bath.¹

In this paper, the reinforcement of epoxy resin by PPTA molecule was studied. The difficulties were in finding a common solvent for both components. The solvent of PPTA is sulfuric acid with concentration above

97 wt%. Almost all conventional polymers are decomposed by sulfuric acid except aliphatic nylons.¹ One of the authors² found that the reagent of sodium methylsulfinylcarbanion prepared by the reaction of sodium hydride and dimethylsulfoxide (DMSO) converts PPTA to PPTA-polyanion to form a homogeneous solution of PPTA in DMSO. DMSO is strongly polar and suitable to dissolve a wide range of conventional linear polymers as matrix. Molecular composites of PPTA prepared by using a solvent of DMSO are PPTA/ABS resin,^{3,4} PPTA/NBR rubber,⁵ PPTA/polyamideimide,⁶ etc.

The process employed in the above examples was used for epoxy resin as a matrix polymer. The regeneration of PPTA-polyanion together with epoxy resin in an acidic coagulation bath was found to be impossible. The method in this paper is to prepare a series of

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grafted copolymers of PPTA at first and at the second stage, a grafted copolymer with solubility in triethylenetetramine as a common solvent was selected and the molecular composite was prepared with epoxy resin.

EXPERIMENTAL

Materials

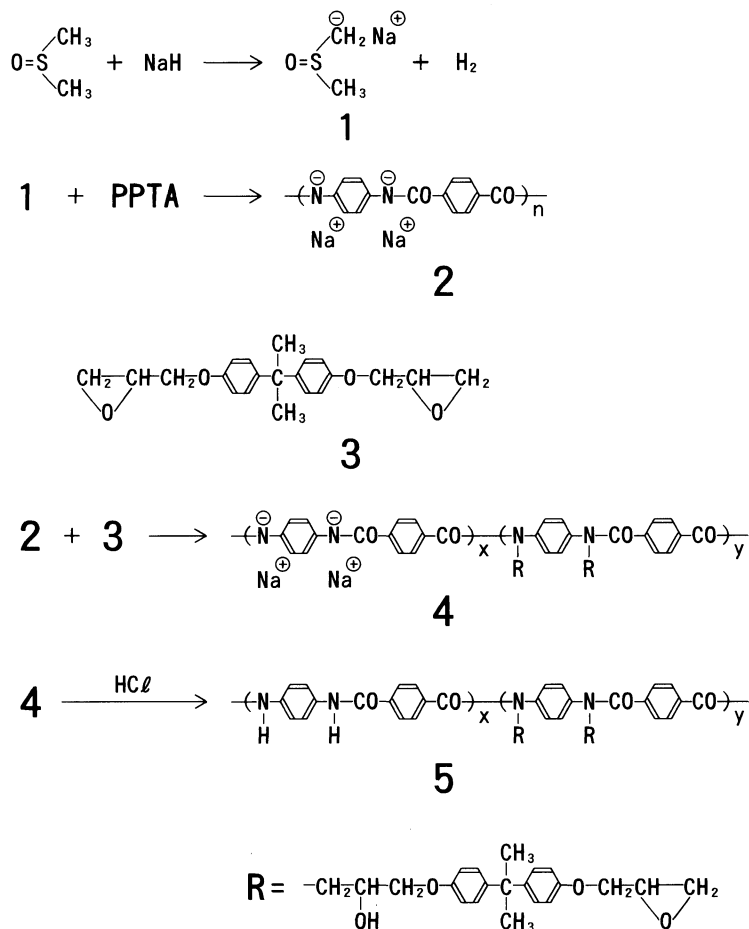
Poly(*p*-phenyleneterephthalamide) (PPTA) was obtained from Asahi Chemical Ind. Co., the weight average molecular weight of which was 2×10^4 . Epoxy resin was liquid bisphenol A type resin, DER 383 of Dow Chemical Co. (abbreviated in this paper to Epoxy), the epoxy value of which was 176–186. The

hardener for Epoxy was triethylenetetramine (TETA).

Metalation of PPTA to form polyanion of PPTA was carried out by sodium hydride and dimethylsulfoxide (DMSO) at 343 K. Sodium hydride is a market product, in which 60 wt% of NaH is dispersed in liquid paraffin.

Preparation of *N*-Grafted PPTA (PPTA-*g*-Epoxy)

The metalation reaction of PPTA was carried out in DMSO. Sodium methylsulfinylcarbanion (the reagent **1**) was synthesized in DMSO, followed by adding PPTA, and a homogeneous solution of PPTA-polyanion resulted.² 3 mmol of sodium hydride (0.12 g



Scheme 1.

Table I. Preparation of conditions and analysis of PPTA-g-Epoxy^a

Code	Graft reaction time/h	Yield	Elemental analysis (found: %)			Grafting
		(%)	H	C	N	mol%
G-1	3	28	4.97	47.10	8.26	14.8
G-2	6	28	5.95	72.55	5.96	37.4
G-3	16	37	5.24	67.33	6.66	26.8
G-4	20	72	6.05	65.74	2.37	138.8
G-5	30	—	6.42	66.57	2.13	158.4
G-6	20	25	6.23	66.32	2.06	165.0

^a 3.0 mmol of NaH, 2.5 mmol of PPTA, and 1.0 g of Epoxy; reaction temperature, 323 K.

of NaH suspended in liquid paraffin) and 150 ml of DMSO were reacted in a flask under nitrogen atmosphere by stirring, and the flask was heated to 343 K after 20 min, and held for 40 min. The solution was cooled to 303 K. 0.25 g of PPTA (2 mmol of amide unit) was added to the solution with stirring. PPTA was dissolved to give a transparent dark red colored solution by forming PPTA-polyanion (**2**). The reaction scheme is given by Scheme 1. Epoxy (epoxy resin DER 383), **3**, was added to the DMSO solution of PPTA-polyanion. Graft copolymerization took place between **2** and **3** to give **4**, where *R* is the ring-opened Epoxy. The conditions of the graft copolymerization are listed in Table I. The reaction solution was, with stirring, poured into an aqueous solution of hydrochloric acid which was equivalent to the moles of sodium hydride originally employed. The product of **4** was neutralized and PPTA was regenerated to give the final product, **5**. The precipitate obtained after filtration was washed with water, acetone and a mixed solution of hexane-benzene of 1:1 and dried under vacuum to obtain a powdery sample. Table I lists the yield and elemental analysis, from which the degree of grafting in mol% was calculated. Nitrogen content was used to evaluate the degree of grafting, since the nitrogen atom is included only in the PPTA-g-Epoxy and the hardener of TETA is not added at this stage.

Characterization of PPTA-g-Epoxy

Infrared absorption spectra were measured by the KBr method using a Nihon Bunkou A-202. Elemental analyses were conducted by a Yanagimoto CHN Corder of MT-3. Thermogravimetric analyses (TGA) and differential scanning calorimetries (DSC) were carried out using a Rigaku Denki TG-8111 and DSC-8230, respectively. X-Ray diffraction intensities were recorded by a Rigaku Denki's Geigerflex RAD-III A using Cu-*K_α* beam.

Preparation of Molecular Composites and Measurements of Their Physical Properties

Two molecular composites, MC-1 and MC-2, were prepared from a homogeneous solution in a common solvent of TETA for PPTA-g-Epoxy and Epoxy DER 383.

The MC-1 sample was prepared as follows. 0.21 g of G-5 (Table I) was dissolved in 0.74 g of TETA, to which 5.00 g of Epoxy were added. The solution was well mixed and poured into a mold. The curing process was to keep it at room temperature for 24 hours, at 353 K for 7 hours, at 373 K for 48 hours, and finally at 433 K for 2 hours. The net content of PPTA in the MC-1 sample was 0.6 wt%.

The MC-2 sample was prepared by adding 5.00 g of Epoxy DER 383 to the acetone solution of 2.0 g of G-6 (Table I) and acetone was removed by evaporation under vacuum

at 343 K, to which 0.78 g of TETA at 323 K was added with stirring. The mixture was poured into a mold and cured at 353 K for 2 hours, at 373 K for 3 hours, and at 433 K for 2 hours. The net content of PPTA in the MC-2 sample was 4.5 wt%.

Viscoelasticity was measured at 110 Hz with a heating rate of 1 K min^{-1} using Orientec's Rheovibron DDV-III-C over the temperature range from 290 K to 440 K. Bending modulus and bending strength were measured using Orientec's tensile tester, Model STM-50 BP, following the JIS K7203.

RESULTS AND DISCUSSION

Characterization of PPTA-g-Epoxy

Figure 1 shows the infrared spectra of PPTA(A), G-1(B), and G-4(C). In the spectra of B and C, the C–H stretching vibration of epoxy ring was found at 2975 cm^{-1} . The amide I, II, and III absorptions of PPTA were found at 1650 cm^{-1} ($\nu_{\text{C=O}}$), 1550 cm^{-1} (δ_{CONH}) and 1320 cm^{-1} (CONH). The absorption of hydrogen bonded N–H was at 3330 cm^{-1} .

The absorption at 2975 cm^{-1} increases with grafting (refer to Table I), and the absorptions of 1550 cm^{-1} and 1320 cm^{-1} decrease. As for

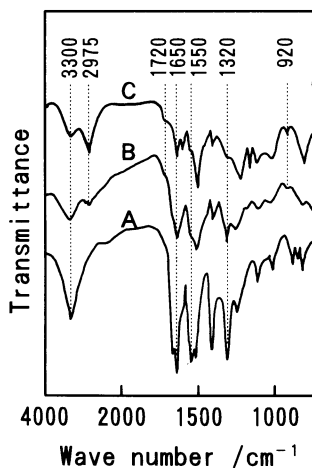


Figure 1. Infrared spectra of (A) PPTA, (B) G-1, and (C) G-4.

the epoxy group, the characteristic absorption of epoxy group is found at 920 cm^{-1} as a minor absorption, while the absorption in the range of 1720 cm^{-1} appearing as a shoulder suggests the partial disappearance of epoxy group by ring opening. The reaction product of PPTA–polyanion and phenylglycidylether as a model compound showed the same shoulder in its IR absorption spectrum, from which the 1720 cm^{-1} absorption is considered to be associated with the ring opening of epoxy group.

Figure 2 shows TGA and DSC curves for the samples of PPTA-g-Epoxy with different degrees of grafting. Table II lists the temperature at 10 wt% decrease in weight and the

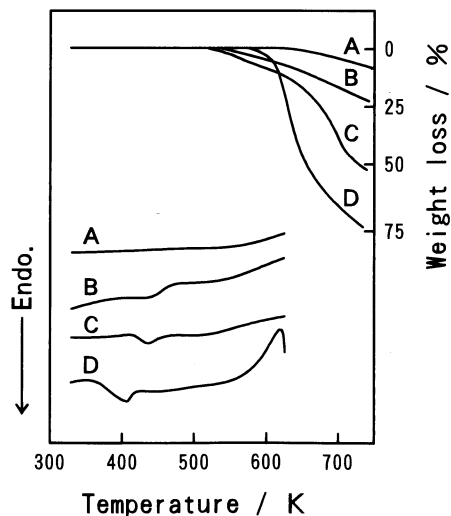


Figure 2. TGA and DSC curves of (A) PPTA, (B) G-1, (C) G-4, and (D) Epoxy.

Table II. Thermal properties

Code	Grafting	Temperature of 10% weight loss/k	T_g
	mol%		K
G-1	14.8	633	—
G-4	138.8	618	418
G-5	158.4	614	417
G-6	165.0	575	406
Epoxy sheet	—	618	390
PPTA	—	809	—

glass transition temperature for the PPTA-g-Epoxy samples, Epoxy and PPTA. The thermal stability of PPTA-g-Epoxy decreases with increasing degree of grafting by Epoxy as seen in Figure 2 and Table II. The glass transition temperature appeared in the DSC curve for the sample highly grafted by Epoxy and lowered with increasing degree of grafting. The substitution of amide proton of PPTA by epoxy resin makes the plane of the amide group fixed by resonance broken and solution viscosity decreases by substitution due to the loss of the rigid rod like nature of PPTA. The lowering of decomposition temperature in TGA curves is considered to be caused by substituting the proton of amide group with alkyl group. The single bond between carbon and nitrogen atoms in the substituted amide group is weaker than the unsubstituted amide C–N bond and thermal endurance is lowered by substitution.

Figure 3 shows the X-ray diffraction intensity curves. The scattering angles of 20.3° , 22.5° , and 27.8° correspond to diffraction from the crystal planes of (110), (200), and (004) of PPTA crystal.⁷ For the samples of

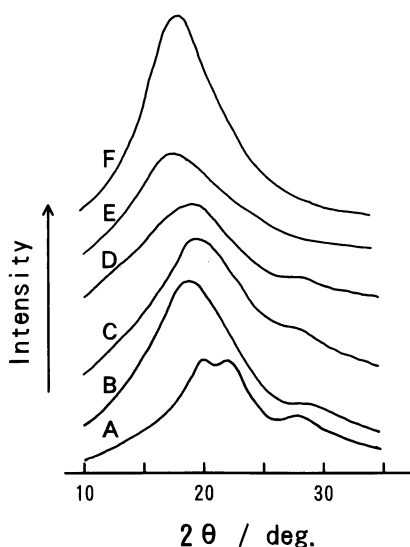


Figure 3. Intensity curves of wide-angle X-ray diffraction: (A) PPTA, (B) G-1, (C) G-3, (D) G-2, (E) G-5, and (F) G-6.

PPTA-g-Epoxy, these peaks broadened with increasing degree of grafting, and both peaks located around 20° unite and shift to the low angle side. The (004) peak disappears for samples with the degree of grafting over 100%. The (004) diffraction corresponds to the regularity of PPTA along the molecular axis and indicates the existence of a stiff chain sequence which is effective for reinforcement of flexible coil-like chains. Based on these considerations, PPTA-g-Epoxy with low grafting still retains the stiff chain sequences expected to be effective in reinforcement. The polymers with high degree of grafting more than 100% lose the intramolecular regularity, which accompanies the loss of rigidity and results in an amorphous state. This accords with the appearance of the glass transition temperature associated with the epoxy group in the DSC curves in Figure 2.

Mechanical Properties of Molecular Composites

Figure 4 shows the dynamic viscoelasticity at 110 Hz as a function of temperature for samples of MC-1 (open square) and MC-2 (open circle) and unmodified epoxy resin (filled circle). The $\tan \delta$ peak located at about 420 K for Epoxy is the primary relaxation of the network chain including bisphenol A in the network formed by a hardener of TETA, which is related to the glass transition of Epoxy. The small shoulder located at the lower temperature side of the α peak of Epoxy might be assignable to the relaxation caused by the thermal motion of flexible linear chain, being called the α' peak. This notation was proposed by Ochi *et al.*⁸ for some systems of epoxy resins hardened by amines different from DER 383 and TETA in this paper.

Another explanation for the α peak and α' peak is that the system is essentially a two-phase structure composed of phases with different cross-linked densities.⁹ The primary peaks of the MC-1 and MC-2 samples in loss-tangent curve are seen to be roughly

single. A more detailed inspection of the primary peak of MC-2 reveals, however, a shoulder at the high temperature side of the large primary peak, which accords with the temperature location of the primary peak of Epoxy. Compared with the shape of $\tan \delta$ peak of MC-2, the shape of $\tan \delta$ peak of MC-1 is close to be single, in the absence of subpeak. It should be noticed that both primary peaks of the molecular composites are located at the temperatures lower than the primary peak of Epoxy.

Thus, the effect of introduction of PPTA-g-

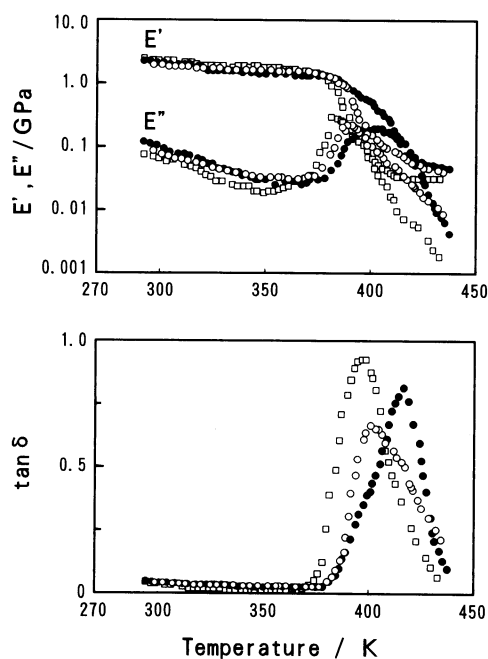


Figure 4. Dynamic mechanical properties, E' , E'' and $\tan \delta$ as a function of temperature for (●) Epoxy, (□) MC-1, and (○) MC-2.

Epoxy on the texture of epoxy resin, which is composed of the networks of dense and loose cross-link densities,⁹ is to loosen the two-phase structure and homogenize the texture of hardened epoxy resin as a whole. It is an interesting subject for the future to clarify the fact that the substituted PPTA sequence appearing in the *N*-grafted PPTA chain hinders the localization of network densities during curing, due to the expanding substituted PPTA chain in 3-dimensional space.

Bending Stress-Bending Strain Curves

Figure 5 shows the bending stress-strain curves for sheets of Epoxy(A), the MC-1(B), and the MC-2(C). There is no distinctive difference between the curves of A and C, whereas the curve B of the MC-1 sample is stiffer and stronger than the others. Table III

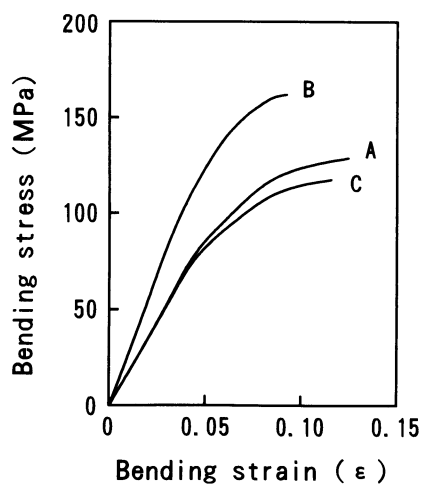


Figure 5. Bending stress-bending strain curves of (A) Epoxy, (B) MC-1, and (C) MC-2.

Table III. Bending modulus and bending strength

Code	Net PPTA content	Bending modulus	Bending strength	Ultimate elongation	Density
	wt%	GPa	MPa	%	g cm ⁻³
MC-1	0.6	3.0	164	9	1.193
MC-2	4.5	1.9	117	12	1.190
Epoxy sheet	0	1.8	121	10	1.185

lists the modulus, strength and elongation-at-break. The densities at room temperature are also listed in Table III. The density of MC-1 is 1.193 g cm^{-3} , which is the highest among the samples, indicates improved homogeneity of network densities and the lowering of stress-concentration to the defects. Based on these considerations, the texture of Epoxy has both dense and loose regions, the density of which is as a whole low, although the density of the densely packed region is high. Lower modulus and strength of Epoxy might be due to the heterogeneous texture. The low density, lower cross-linked region forms the weak points.

CONCLUSION

The structure of *N*-grafted PPTA prepared by the reaction of sodium methylsulfinyl-carbanion and epoxy resin was identified by infrared absorption spectra. Thermal stability of PPTA-*g*-Epoxy was lowered by increasing the degree of grafting, thus losing crystallinity finally to give an amorphous state. Variation of the glass transition temperature accords with this tendency. The broadening and missing of the (004) diffraction indicates a loss of molecular stiffness of PPTA, resulting in decreased reinforcement.

The molecular composites prepared by PPTA-*g*-Epoxy with high degree of grafting and Epoxy in the presence of hardener showed 3 GPa of bending modulus and 164 MPa of bending strength for net content of 0.6 wt% PPTA. Although lowering of grafting is expected to increase the reinforcing effect, the realization of homogeneous texture becomes difficult due to immiscibility between both components.

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