Mechanical Properties and Intermolecular Interactions in Molecular Composites Composed of Wholly Aromatic Polyamide and Poly-(Amide-Imide)

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MECHANICAL PROPERTIES AND INTERMOLECULAR INTERACTIONS IN MOLECULAR COMPOSITES COMPOSED OF WHOLLY AROMATIC POLYAMIDE AND POLY-(AMIDE-IMIDE)

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ABSTRACT

Poly(p-phenylene-3,4'-oxydiphenylene terephthalamide) (PPOT) and poly(4,4'-oxydiphenylene-4-carbonamidephthalimide-N-yl) (PAI) are compatible. Molecular composites were prepared by solution blending and subsequently solvent casting. The glass transition temperature of the composite increased with increasing fraction of PPOT. Intermolecular interactions between the two components increase due to formation of hydrogen bonds between the amide linkages of the component polymers. The elastic modulus of the composite was always higher than the modulus predicted on the basis of the additivity. Similar deviations from additivity were observed for the bulk density. These desirable results arise from an increase of the packing density of molecules due to the additional hydrogen bonding also shown by the infrared spectra.

INTRODUCTION

Wholly aromatic polyamides, such as poly(p-phenylene terephthalamide) are rigid polymers and have high strength, high modulus, and excellent heat resistance. It is expected that the mechanical properties of conventional flexible polymers can be improved by dispersing finely and uniformly rigid molecules in them that reinforce them [1-3]. These novel blend polymers are generally designated as "molecular composites."

The compatibility of the rigid polymer and the flexible matrix polymer are the most important factors in producing mechanical properties superior to those of the unreinforced matrix polymer. For example, in the case of compatible glassy polymer blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and atactic polystyrene (PS), the elastic modulus of each blend composition was higher than that calculated on the basis of the additivity law [4]. A strong correlation between the packing density and modulus was shown by the (PPO + PS) blend [4]. The van der Waals interaction between the phenyl ring of PS and the phenylene ring of PPO is quite strong and responsible for the blend compatibility [5].

The molecular composite composed of poly(p-phenylene terephthalamide) (PPTA) and poly(4,4'-oxydiphenylene-4-carbonamidephthalimide-N-yl) (PAI) was studied to investigate the relationship between the mechanical properties and the state of molecular aggregation [6]. Very small PPTA molecular bundles were finely and uniformly dispersed in the PAI matrix on a photomicroscopic scale as long as the content of PPTA was below 5 wt%. The elastic modulus of PAI blended with 3 wt% PPTA was 3.9 GPa compared to 2.6 GPa for PAI. However, macroaggregates of PPTA were formed when the PPTA content was above 5 wt% and, therefore, the reinforcing ability of PPTA decreased greatly. The cohesive force between the PPTA molecules is relatively strong both because of good packing of the benzene rings and of hydrogen bond formation between the amide groups. An actual molecular composite may be realized by copolymerization of both flexible and rigid segments, since the mutual solubility of the polymers might be increased even if the cohesive force of the rigid segments in the co-polymer may be decreased in the composite.

In this work, so-called molecular composites composed of a wholly aromatic polyamide, poly(p-phenylene-3,4'-oxydiphenylene terephthalamide) (PPOT), and PAI were prepared by solvent casting from an isotropic ternary solution, and the relationships between the state of molecular aggregation and the mechanical properties were investigated.

EXPERIMENTAL

Preparation of Molecular Composites

Figure 1 shows the chemical structures of PPOT, of poly(amic acid) [poly-(4,4'-oxydiphenylene-3-(carboxylic acid)terephthalamide) (PAA)], and of PAI. PPOT was supplied by Teijin Co. PAA was Torlon 4000T supplied by Mitsubishi Chem. Ind. Co. PAI was obtained by curing PAA *in vacuo* at 533 K for 12 h.

Figure 2 shows the scheme for the preparation process of the PPOT/PAI molecular composite. PPOT was dissolved at 303 K in *N*-methyl-2-pyrrolidone (NMP) to which 1.2 mol% calcium chloride had been added. PAA was also dissolved in NMP at 303 K. The PPOT and PAI solutions were mixed at 303 K and stirred for 8 h to give a red, isotropic, transparent solution. The mixture was solvent-cast *in vacuo* at 343 K for 8 h to obtain a film of the molecular composite and then washed with pure water for 48 h in order to remove the organic solvents and inorganic salt. The PPOT/PAA composite film was dried *in vacuo* at 393 K for 12 h. The PPOT/PAA composite film was cured *in vacuo* at 533 K for 12 h to obtain the final PPOT/PAI composite film. The weight ratios of PPOT/PAI were 10/90, 30/70, and 50/50.
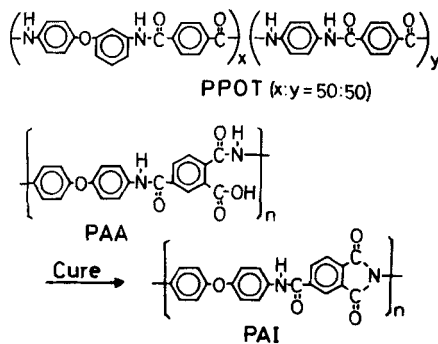
PPOT ($x:y = 50:50$)

PAA

Cure →

PAI

FIG. 1. Chemical structures of poly(*p*-phenylene-3,4'-oxydiphenylene terephthalamide) (PPOT), poly(4,4'-oxydiphenylene-3-(carboxylic acid) terephthalamide) (PAA), and poly(4,4'-oxydiphenylene-4-carbonamide-phthalimide-*N*-yl) (PAI).
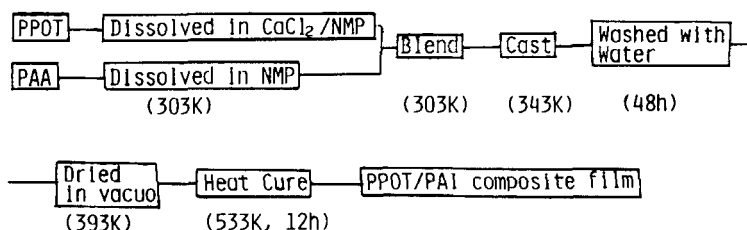
PPOT ── Dissolved in CaCl₂/NMP ┐
                                ├ Blend ── Cast ── Washed with Water ──
PAA ── Dissolved in NMP ────────┘
        (303K)   (303K) (343K)   (48h)

── Dried in vacuo ── Heat Cure ── PPOT/PAI composite film
    (393K)   (533K, 12h)

FIG. 2. Scheme of preparation process for PPOT/PAI molecular composite.

Measurements of Structure and Properties of the Molecular Composites

Optical anisotropy in the composite films was observed with a POH polarizing optical microscope (Nippon Kogaku Co.) under crossed nicols.
- Change of weight loss due to thermal degradation was measured with a Shimazu DT-30 thermal analyzer (Shimazu Co.) at a heating rate of 20 K/min in a nitrogen atmosphere. The glass transition behavior was measured with a Unix differential scanning calorimeter (Rigaku Co.) at a heating rate of 10 K/min.

The temperature dependence of the dynamic viscoelastic properties was measured at 11 Hz in a nitrogen atmosphere with a Rheovibron DDV-IIC dynamic viscoelastomer (Orientec Co.). Stress-strain measurements were obtained at an initial strain rate of 33%/min with a Tensilon UTM-III 500 tensile tester (Orientec Co.).

The density was measured at 303 K by a flotation method using a xylene-tetrachloromethane mixture. Also, infrared (IR) spectra were measured with an FT/IR-3 Fourier transform infrared spectroscope (JEOL Co.) to elucidate changes in the wavelength and intensity of the C=O stretching band on blending PAI with PPOT. The wavenumber resolution was 2 cm⁻¹.

RESULTS AND DISCUSSION

State of Mixing of PPOT and PAI in Composite Films

According to polarizing optical microscopic observation, PPOT films are optically anisotropic, whereas PAI films are optically isotropic. PPOT/PAI composite films showed a homogeneous birefringent image, and distinctive anisotropic domains could not be detected. This indicates that PPOT mole-
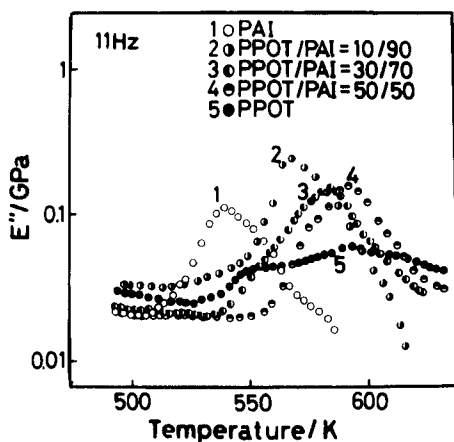
FIG. 3. Temperature dependence of loss modulus E'' at 11 Hz for PAI, PPOT, and PPOT/PAI composites.

cules are homogeneously dispersed in the PAI matrix on the photomicroscopic scale, even in the case of 50 wt% PPOT.

Figure 3 shows the temperature dependence of the loss modulus, E''. The absorption peak around 540 K is associated with micro-Brownian motion corresponding to the glass-transition behavior of PAI, since a change of specific heat was clearly detected around 540 K upon DSC measurement. The E'' peak of the PPOT/PAI composites increased with increasing PPOT content to the temperature of the E'' peak of PPOT. Hardly any broadening of the E'' peaks was observed on blending PAI with PPOT. Such behavior indicates that PPOT molecules are finely dispersed in the PAI matrix without any phase separation. The E'' behavior corresponds to an increment of the T_g of PAI due to depression of the micro-Brownian motion of the PAI molecules by the finely dispersed PPOT molecules.

Mechanical Properties

Figure 4 shows the stress-strain curves. The initial modulus E, strength σ_b, and ultimate elongation ϵ_b were increased by the dispersed PPOT molecules in the PAI matrix. The values of E, σ_b, and ϵ_b in Table 1 tend to increase with increasing PPOT content, and this result suggests that the PAI is reinforced by the PPOT.
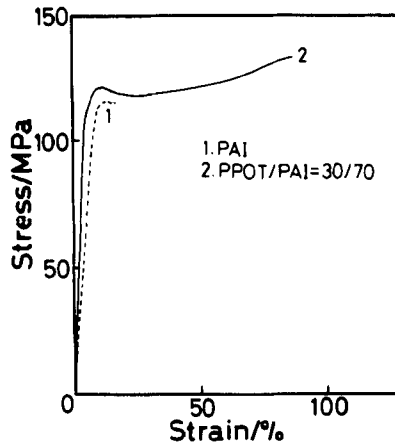
FIG. 4. Stress-strain curves at room temperature for PAI and the composite of PPOT/PAI (30/70).

The broken line shown in Fig. 5, which shows the modulus, is drawn on the assumption of additivity of the modulus, i.e., the modulus of the composite, E_c, is given by

$$E_c = E_1\phi_1 + E_2\phi_2, \tag{1}$$

TABLE 1. Elastic Modulus E, Strength σ_b, and Ultimate Elongation ϵ_b for PAI, PPOT, and the Composites of PPOT/PAI

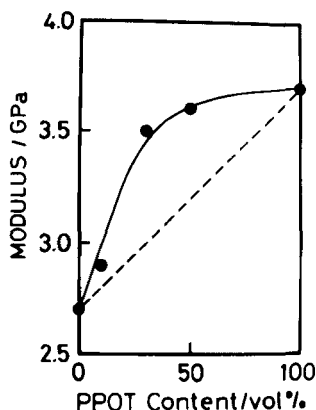| Sample	E, GPa	σ_b, MPa	ϵ_b, %
PAI	2.7	115	17
PPOT/PAI:			
10/90	2.9	98	26
30/70	3.5	133	86
50/50	3.6	130	90
PPOT	3.7	124	120

FIG. 5. Elastic modulus at room temperature as a function of the PPOT content.

where ϕ_1 and ϕ_2 are the volume fractions and E_1 and E_2 are the moduli of PPOT and PAI, respectively. The measured values of the modulus for the composites were always higher than those evaluated from Eq. (1). This deviation from additivity is not observed for a completely phase-separated system. Therefore, it is concluded that the present composites are well mixed with an additional intermolecular interaction between the two components. This conclusion is supported by density measurements and an infrared absorption study, discussed next.

Intermolecular Interactions in the Composite

Figure 6 shows the density as a function of the PPOT content. The broken line represents the density ρ_c calculated by the following additivity law:

$$\rho_c = \rho_1\rho_2/(w_1\rho_2 + w_2\rho_1),\tag{2}$$

where ρ_1 and ρ_2 are the densities of PPOT and PAI homopolymers, and w_1 and w_2 are the weight fractions of PPOT and PAI, respectively. The experimental values of ρ_c are always greater than the calculated ones. The packing density, ρ^*, can be calculated as the ratio of the van der Waals volume V_w to the molar volume V as follows [4, 7] :

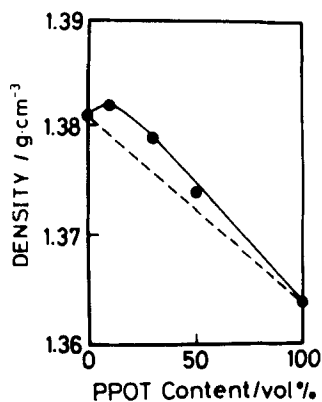$$\rho^* = V_w/V = \rho V_w/M,\tag{3}$$

FIG. 6. Density as a function of the PPOT content.

where ρ is the density of the sample and M is the molecular weight. V_w is calculated from bond distances and the van der Waals radii for the PAI and PPOT repeating units [7]. The solid curve in Fig. 7 shows the packing density calculated from the experimental density, the broken curve that calculated from the density estimated by Eq. (2). The experimental packing density is always slightly greater than the calculated one. It is reasonable to assume
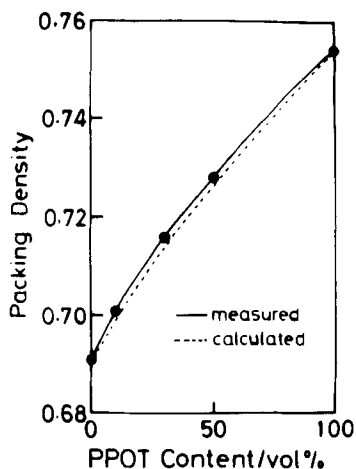

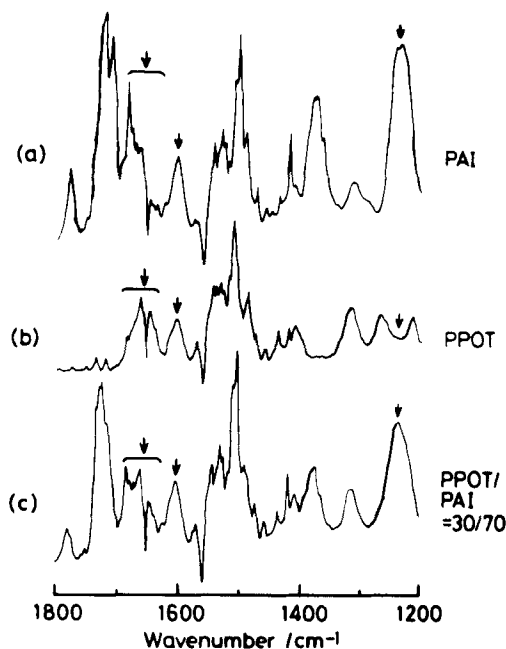FIG. 7. Packing density as a function of the PPOT content.

FIG. 8. Infrared absorbance spectra of (a) PAI, (b) PPOT, and (c) the composite of PPOT/PAI (30/70).

that the excess of the measured packing density in Fig. 7 is related to the fact that the modulus deviates from additivity, as shown in Fig. 5.

The intermolecular hydrogen bond between PAI and PPOT was investigated by means of infrared (IR) absorption measurements (see Fig. 8). In the PPOT spectrum, the C=C stretching band of the benzene ring appears at 1600 cm^{-1}. In the PAI spectrum, the C–O–C asymmetric stretching band of diphenyl ether and the C=C stretching band of benzene ring are located at 1230 and 1600 cm^{-1}, respectively. The Amide I band, which is mainly associated with the C=O stretching mode, appears in the wide range from 1630 to 1690 cm^{-1} for both homopolymers. This wide range may be explained as follows.

According to Randall et al. [8], the Amide I band of the secondary amide group in the solid state appears around 1640 cm^{-1} and shifts to 1680 cm^{-1} if the secondary amide group is diluted with an inert solvent due to dissociation of the hydrogen bonds, which existed in the solid state, in the inert sol-

vent. Therefore, in polypeptides, the wavelength of the Amide I band depends on their secondary structures [9]. For crystalline polycaprolactam, it is at 1640-1650 cm^{-1}, whereas for amorphous polycaprolactam, it is at 1650-1680 cm^{-1} [10]. This result indicates that the force constant of hydrogen-bonded amide linkages in amorphous polycaprolactam is lower than that in the crystalline form. It is concluded that the IR absorption around 1680 cm^{-1} in our spectra arises from amide linkages without hydrogen bonding, whereas that at 1630-1640 cm^{-1} comes from hydrogen-bonded amide linkages.

These assignments are also supported by the change in the wavelength of the Amide A band, which is associated with N—H stretching. The wavelength depends on whether the amide linkages are hydrogen-bonded or not. When nylon 6 was treated with iodide, the wavelength of Amide A was shifted from 3290 to 3350 cm^{-1} [11]. Since iodides form complexes with C=O groups, this indicates that hydrogen bonds between amide linkages are dissociated so that the N—H groups become free. The Amide A bands for PAI and PPOT are observed at 3364 and 3320 cm^{-1}, respectively. It is reasonable to deduce from the chemical structures of PPOT and PAI that the fraction of hydrogen-bonded amide linkages of PPOT is greater than that of PAI. The Amide I band at 1686 cm^{-1} may be associated with the C=O stretching band in nonhydrogen-bonded amide linkages because the absorbance of PAI at 1686 cm^{-1} is much higher than that of PPOT.

Figure 9 shows the IR difference spectrum obtained by subtracting the IR absorbance spectra of both homopolymers from that of the composite. The
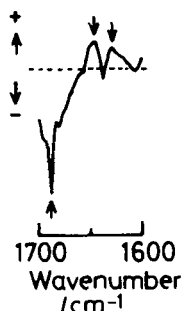

FIG. 9. Infrared difference spectrum obtained by subtracting the absorbance spectra of both PPOT (Fig. 8b) and PAI (Fig. 8a) homopolymers from that of the composite of PPOT/PAI (30/70) (Fig. 8c).

absorbances of 1230 cm^{-1} of the C−O−C asymmetric stretching band of diphenyl ether and 1600 cm^{-1} of the C=C stretching band of benzene ring were used as reference for this subtraction. The absorbance peak of 1686 cm^{-1} is negative, whereas those at 1627 and 1643 cm^{-1} are positive. Figure 9 indicates that the fraction of hydrogen-bonded amide linkages increased on mixing PPOT and PAI. This must be associated with the deviations of the density and the packing density from the additivity law (Figs. 6 and 7). Thus it is confirmed that increased intermolecular interaction between the PPOT and PAI molecules is induced by an increased hydrogen bonding on blending PPOT and PAI and, therefore, results in positive deviation from the additivity law for both the packing density and the modulus.

The storage modulus, E', of the composite was higher than that of PAI over the whole temperature range (Fig. 10). The temperature of 560 K, above which E' of the composite decreased markedly, corresponds to T_g and is higher than that of PAI. Also, E' of the composite was greater between 450 and 580 K than that of PPOT, which acts as a reinforcement. This indicates that the additional intermolecular interactions induced by blending PAI and PPOT enhanced the thermal stability, resulting in an E' of the composite that is larger than those of the unblended homopolymers. Figure 10 suggests that intermolecular interactions between the components
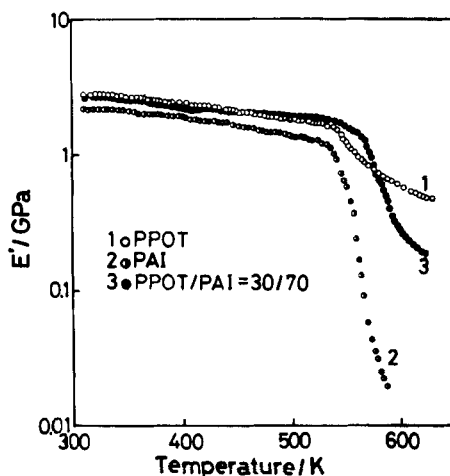

FIG. 10. Temperature dependence of storage modulus E' at 11 Hz for PPOT, PAI, and the composite of PPOT/PAI (30/70).

in the composite are largely responsible for the excellent mechanical and thermal properties of the composite, which are superior to those of the homopolymers.

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