

# Preparation of Poly(*p*-Phenylene Terephthalamide)/Poly(vinyl Chloride) Molecular Composite and Its Thermal and Mechanical Properties

KENJI YAMADA, MASAFUMI UCHIDA, and MOTOWO TAKAYANAGI, *Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan* and KOHEI GOTO, *Japan Synthetic Rubber Co., Ltd., Kawasaki 214, Japan*

## Synopsis

Poly(*p*-phenylene terephthalamide) (PPTA) was blended with poly(vinyl chloride) (PVC) by solution-blending method. PPTA was metalated for dissolving in dimethyl sulfoxide. Dimethyl sulfoxide was used as a common solvent. In PPTA/PVC composite, PPTA accelerated the thermal degradation of PVC. PPTA molecules are aggregated as microfibrillar form in PVC matrix. Such microfibrils are dispersed homogeneously in PVC matrix, according to polarizing microscopic observation. The average diameter of the microfibrils becomes smaller in the composite with lower content of PPTA. In the surface region of PPTA microfibrils the intermolecular hydrogen bonds between C—Cl of PVC and N—H of PPTA are formed. Young's modulus and the yield stress at room temperature were higher in the composites than those in PVC. The modulus of the composites was higher, especially at the high temperatures above their glass transition temperatures, than that in PVC. The temperature dependence of modulus can be calculated by using the mechanical model equivalent to the quasi-3-dimensional microfibrillar model which will be approximately applied to the composite structure. It becomes apparent that the modulus of the PPTA microfibrils evaluated by using the mechanical model is higher in the higher molecular weight PPTA.

## INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) fiber has very high strength, modulus, and heat endurance. PPTA molecule is rigid and cannot fold for the high rotational barriers of N-benzene bonds, C(O)-benzene bonds, and the amide C—N bonds.<sup>1</sup> It will be expected that the mechanical properties of conventional polymers are improved if rigid-rod PPTA molecules as reinforcements are dispersed finely and uniformly in the matrix.<sup>2</sup> Such a "molecular composite" is a new type of composite, which belongs to plastics reinforced by the rigid molecules or their fine fibrillar aggregates.<sup>2</sup>

In previous work,<sup>2</sup> it was shown that PPTA microfibrillar aggregates effectively reinforce the aliphatic polyamides even when several weight percentage of PPTA when PPTA and the flexible polymer are blended. Due to blending PPTA with nylon 6, the spherulitic texture of nylon 6 disappeared and a birefringent homogeneous texture was observed. It was revealed by electron microscopic observation that PPTA microfibrils with diameters of 15–30 nm were dispersed in a fracture surface of the composite.

W.-F. Hwang et al.<sup>3</sup> demonstrated the feasibility of processing the rigid rod/flexible coil polymer mixtures into molecular composites. Poly-*p*-phenylenebenzobisthiazole(PBT) and poly-2, 5(6)benzimidazole(ABPBI) were used as the rigid rod polymer and the flexible coil polymer, respectively.

In this work, the composite of PPTA/poly(vinyl chloride) (PVC) was prepared by coprecipitation from isotropic mixture of polymer solutions. In the composite the intermolecular interaction between PPTA and PVC is expected by the formation of hydrogen bond between N—H and C—Cl. This interaction may be more effective when PPTA molecules are more finely dispersed in PVC matrix. The thermal and mechanical properties of the composites are measured and the relationships between their properties and the dispersion state of PPTA in PVC matrix are investigated.

## EXPERIMENTAL

### Preparation of PPTA/PVC Composites

The viscosity average molecular weights of PPTA were 4,900, 13,000, and 25,000. The viscosity average molecular weight of PVC was 44,000. PPTA cannot be dissolved in dimethyl sulfoxide (DMSO), whereas metalated PPTA can be done in DMSO which is a good solvent of PVC. Figure 1 shows the metalation reaction of PPTA. Its reaction was carried out at 343°K for 4 h with the solution of sodium methylsulfinylcarbanion in DMSO, which was formed from reaction of powdered sodium hydride with excess dry DMSO.<sup>4</sup> The reaction of the sodium hydride was done at 343°K for 40 mins. The number of moles of sodium hydride was the same as that of amide group in PPTA and, therefore, the release of hydrochloric acid from PVC may be

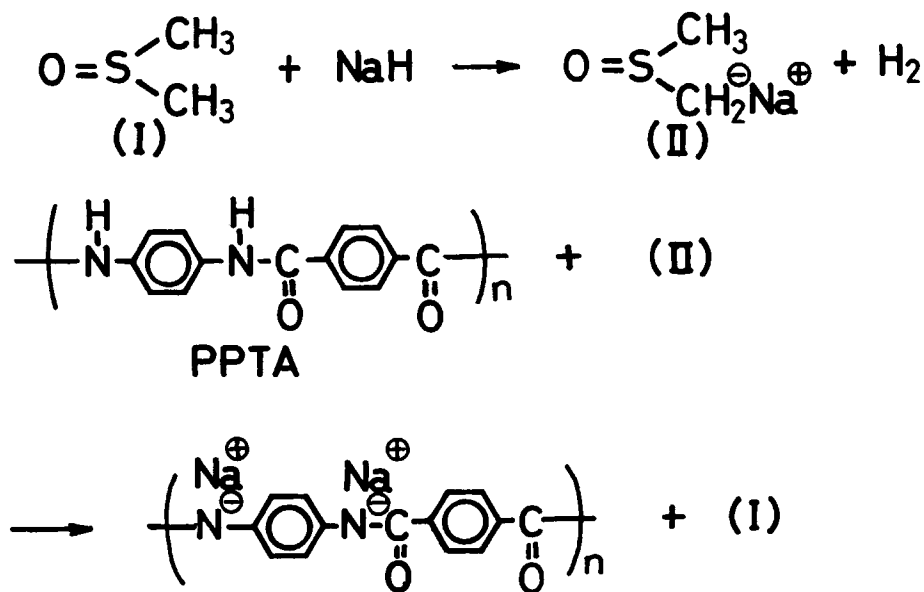


Fig. 1. Metalation reaction of PPTA.

avoided during mixing metalated PPTA solution with PVC solution. The concentration of the metalated PPTA solution was 1 to 2 wt%.

PVC was dissolved in DMSO at 333°K for 3 h under stirring and then cooled to room temperature. The concentration of the PVC solution was 5 wt%. The DMSO solutions of PVC and metalated PPTA were mixed at room temperature for 30 min under stirring. The mixed solution was homogeneous, transparent, and isotropic. The mixed solution was dropped into the large quantity of weak acid solution under stirring for transformation of metalated PPTA to PPTA. Furthermore, the flocky state of PPTA/PVC coagulations in the weak acid solution was thoroughly washed with the fresh weak acid solution for the complete transformation and then with methanol to remove DMSO and inorganic salt. The content of sodium in the dried coagulations was less than 0.1 wt%. The weight ratios of PPTA/PVC for the coagulations were 0.5/99.5, 5/95, 10/90, and 30/70.

For compounding dibutyltin maleate as stabilizer with PVC homopolymer and PPTA/PVC coagulations prepared above, the coagulations were immersed into tetrahydrofuran/methanol(=40/60) mixture containing 0.25 wt% dibutyltin maleate for one day at room temperature and then vaporized the mixture in vacuo at 333°K for 8 h. The content of dibutyltin maleate remaining in the PVC homopolymer and the PPTA/PVC composite was 5 wt%.

The PPTA/PVC composites obtained by the above preparation method were molded at 413°K for 2 mins by using hot press and then quenched into ice water to obtain a film. The composite underwent easier thermal degradation, as compared with PVC homopolymer, and the thermal degradation of the composite took place largely at higher mold temperatures than 413°K. In PVC the mold temperature and time were 433°K and 6 mins and then the molded sample was quenched into ice water. The weight loss in thermal degradation was less than 0.3 wt% in both the composite and PVC, under the above mold conditions.

## MEASUREMENTS OF PROPERTIES AND STRUCTURES

**TG and DSC Measurements.** Behavior of weight loss due to thermal degradation was measured at the heating rate of 20°K/min under a nitrogen atmosphere with a Shimazu DT-30 thermal analyzer (Shimazu Seisakusho Co., Ltd.). Glass transition behavior was measured at the heating rate of 10°K/min with a Unix differential scanning calorimeter (Rigaku Denki Co., Ltd.).

**Measurements of Dynamic Viscoelasticity and Stress-Strain Behavior.** Temperature dependence of dynamic viscoelastic properties was measured at 110 Hz under a nitrogen atmosphere with a Rheovibron DDV-IIC dynamic viscoelastometer (Toyo Baldwin Co., Ltd.). Stress-strain curve was obtained at the initial strain rate of 25%/min by using a Tensilon UTM-III tensile tester (Toyo Baldwin Co., Ltd.).

**IR Measurement.** Infrared (IR) spectra were measured with an IR A-2 spectroscopy (Nippon Bunko Co., Ltd.) to clarify intensity change of C=C stretching band due to thermal degradation and the change in the wave number of C=O stretching band with increasing PPTA content in the composite.

**Polarizing Microscopic and Electron-Microscopic Observations.** Optical anisotropy in the film was observed with a POH polarizing microscope (Nippon Kogaku Co., Ltd.) under cross nicols. The PPTA aggregates were observed by using a Hitachi H-500 transmission electron microscope (Hitachi Seisakusho Co., Ltd.). Before the electron-microscopic observation, PPTA aggregates dried on a mesh covered by thin carbon membrane were shadowed by evaporating Pt-Pd.

## RESULTS AND DISCUSSION

### Thermal Stability

Figure 2 shows a change in the weight of residue at the heating rate of 20°K/min in an atmosphere of nitrogen for PVC and PPTA/PVC composites with the weight ratios of 5/95 and 10/90 which are named hereafter 5 wt%

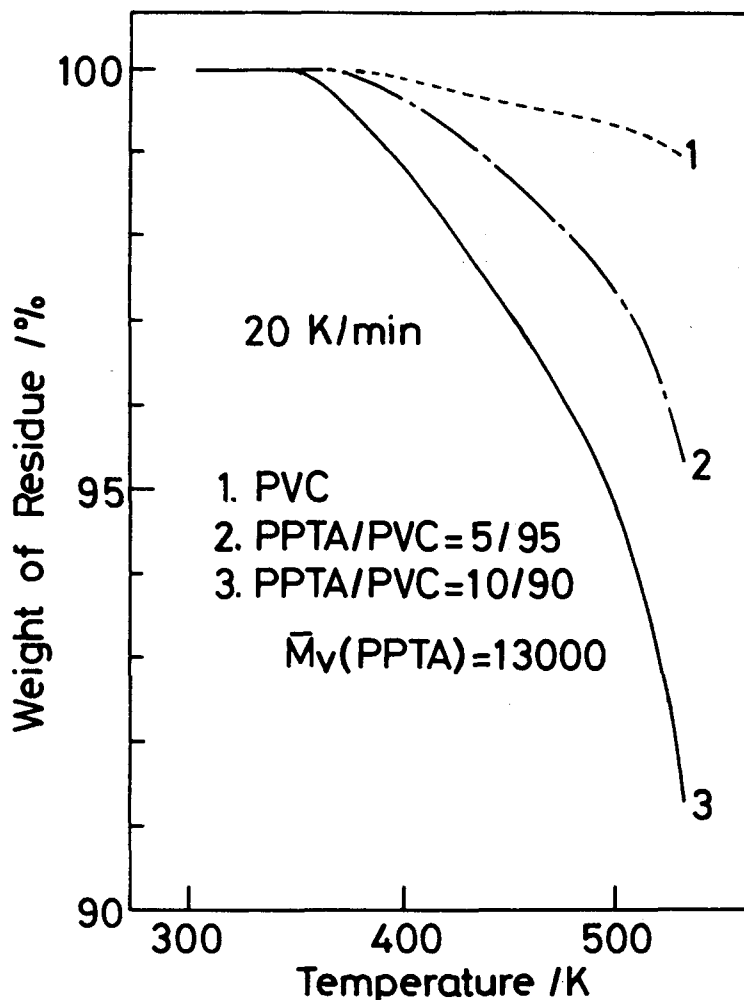


Fig. 2. Weight of residue as a function of temperature at 20°K/min in an atmosphere of nitrogen for PVC, 5 wt% PPTA/PVC and 10 wt% PPTA/PVC.

PPTA/PVC and 10 wt% PPTA/PVC. These samples have dried in vacuo at 353°K for 12 h after coagulation without the stabilizer. The viscosity average molecular weight,  $\bar{M}_v$  of PPTA was 13,000. The initiation temperature of thermal degradation became lower with increasing the content of PPTA. Furthermore, the thermal degradation in higher content of PPTA increased more largely with increasing temperature after the initiation of the thermal degradation.

After annealing in vacuo at 433°K for 30 min the IR stretching band of C=C around 1680  $\text{cm}^{-1}$  appeared clearly in the 10 wt% PPTA/PVC, but not in the PVC. This means that PPTA molecules dispersed in PVC accelerate the thermal dissociation of PVC, in which hydrochloric acid gas is generated from PVC and the double bonds of C=C are formed.

When the stabilizer was included at 5 wt% in PVC and 5 wt% PPTA/PVC, the initiation temperature of the thermal degradation became higher by ca. 40°K in both the samples. After the thermal degradation was initiated, the thermal degradation of the PPTA/PVC composite was also more conspicuous than that of PVC homopolymer, similar to the case where the stabilizer was not used.

### DISPERSION STATE OF PPTA IN PVC MATRIX

According to the polarizing microscopic observation, the PVC film molded by hot press was optically isotropic, whereas the composite film was optically anisotropic and its anisotropic phases were homogeneously dispersed in the film.

Figure 3(a) shows the electronmicrograph of the residue after extracting selectively PVC from the composite film including PPTA of  $\bar{M}_v = 13,000$  and Figure 3(b) shows that of PPTA ( $\bar{M}_v = 34,600$ ) aggregates coagulated from 0.5 wt% sulfuric acid solution by water under ultrasonic irradiation.

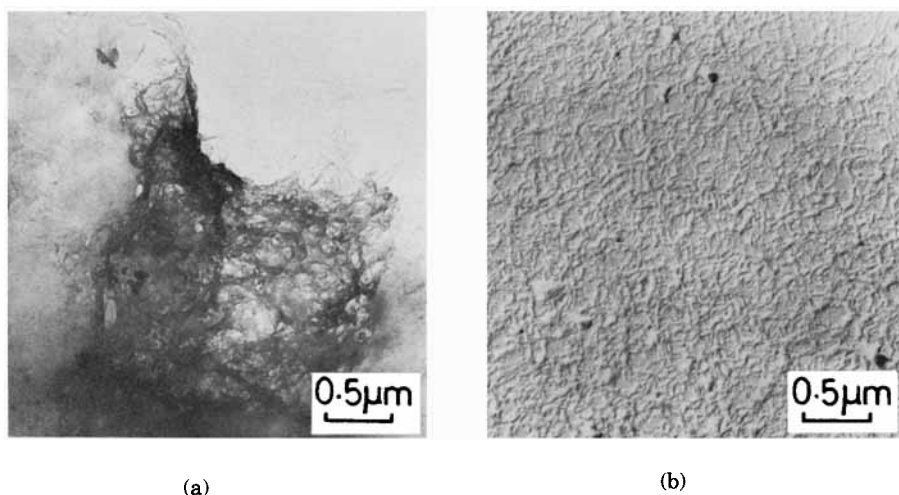


Fig. 3. (a) Electron micrograph of the residue after extracting selectively PVC from the composite film ( $\bar{M}_v$  (PPTA) = 13,000) and (b) Electron micrograph of PPTA ( $\bar{M}_v = 34,600$ ) aggregates coagulated from 0.5 wt% sulfuric acid solution by water under ultrasonic irradiation.

The residue was composed of microfibrils, of which the aggregation form is similar to that shown in Figure 3(b). The diameter of the microfibrils is ca. 20–40 nm. It is inferred from the results of the polarizing microscopic and electron microscopic observations that, in the composite, PPTA molecules are aggregated in the microfibrillar structure and the microfibrils are homogeneously dispersed in PVC matrix.

Figure 4 shows a change in IR wave number associated with C=O stretching band with increasing the content of PPTA blended with PVC. Its wave number in PPTA aggregates was ca.  $1640\text{ cm}^{-1}$ , whereas the wave number in the composites was higher than ca.  $1640\text{ cm}^{-1}$  and increased with decreasing PPTA content. It is inferred from the change in the wave number

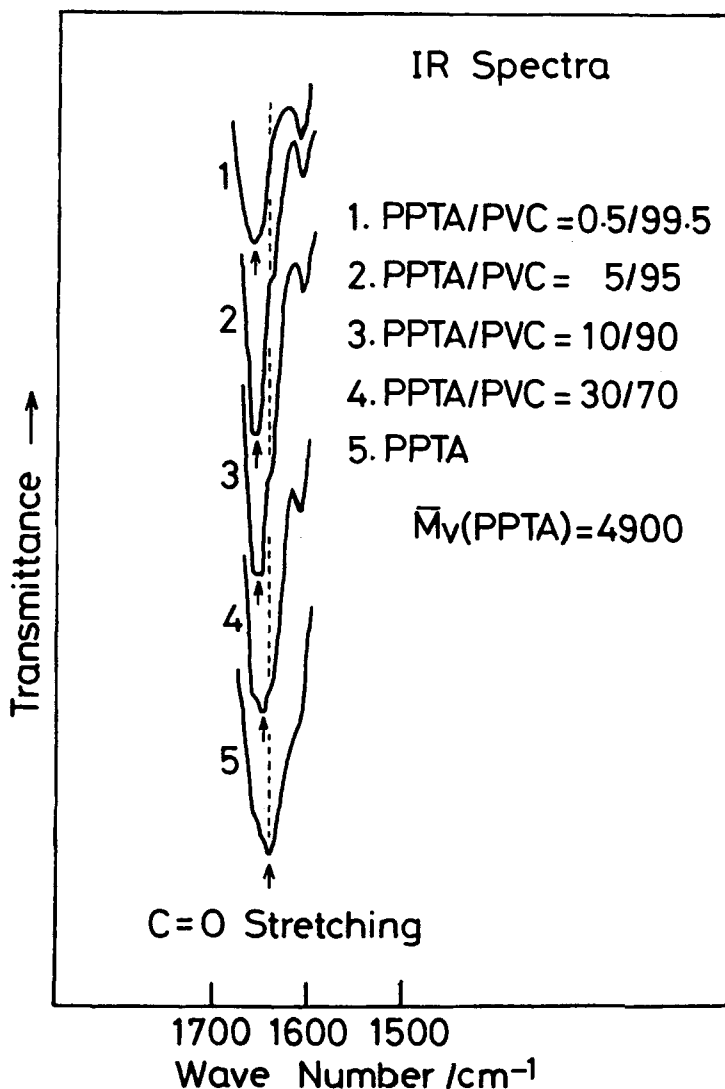


Fig. 4. Change in IR wave number of C=O stretching band as a function of PPTA content in the composites.

that the fraction of the partial dissociation of the intermolecular hydrogen bond between N—H and C=O in PPTA molecules increases with decreasing the PPTA content. This partial dissociation would be originated by the formation of another hydrogen bond between N—H of PPTA and C—Cl of PVC, and takes place in the surface region of PPTA microfibrils formed in the composite. If the diameter of the PPTA microfibrils is smaller, the weight fraction of the surface region of the microfibrils is larger, whereas that of the inner region of the microfibrils is smaller. Therefore, it becomes apparent from the results of Figure 4 that the diameter of the PPTA microfibrils may decrease with decreasing PPTA content. This means that in lower PPTA content PPTA aggregates are more finely and homogeneously dispersed in PVC matrix.

### EFFECT OF PPTA ON GLASS TRANSITION PHENOMENA IN COMPOSITES

Figure 5 shows the temperature dependence of  $\tan \delta$  for PVC and the 5 wt% PPTA/PVC composite films. The absorption around 383°K is associated with micro-Brownian motion of PVC molecules. The  $\tan \delta$  peak temperature in the composites was almost same as that in PVC and was independent of the molecular weight of PPTA. The glass transition temperature,  $T_g$  was also measured by DSC and the  $T_g$ 's of the composite films were almost same as that of PVC films. The  $T_g$ 's of the powder PVC and composites before molding were same as those of the molded films. The C=C band could not be detected in either the unmolded and molded samples. As described previously, the weight losses of the PVC and the composites due to thermal degradation were less than 0.3 wt% after molding, but such slight thermal degradation had no effect on the decrease of  $T_g$  in the molded films. Furthermore, in the mixing solution of PPTA and PVC the metalated PPTA did not accelerate the dissociation of hydrochloric acid from PVC, because the  $T_g$  of the PVC extracted from the powder composites by using tetrahydrofuran was the same as that of PVC before mixing and the C=C band was not detected in the extracted PVC. Thus the elimination of hydrochloric acid from PVC almost does not take place in the preparation process of the composite films. If PPTA molecules are homogeneously dispersed in PVC matrix in molecular level, the  $T_g$  of the composite should be increased, since the  $T_g$  of PPTA is 793°K<sup>5</sup> and is much higher than that of PVC. Therefore, it may be insinuated from phase separation in the composite that the  $T_g$  was not changed by blending PPTA with PVC. This supports the idea that PPTA molecules are aggregated in microfibrillar form in PVC matrix.

A change in heat capacity during glass transition,  $\Delta C_p$  can be evaluated from DSC thermogram. The ratio of the heat capacity change during the glass transition,  $\Delta C_{p2}/\Delta C_{p1}$ , where  $\Delta C_{p1}$  is the heat capacity change for PVC film and  $\Delta C_{p2}$  is that of PVC molecules in the composite film, was evaluated for the composites. In all the composites used in this work the value of  $\Delta C_{p2}/\Delta C_{p1}$  was 0.81 to 0.85. The ratio  $\Delta C_{p2}/\Delta C_{p1}$  may correspond to the weight fraction of PVC molecules which form the pure PVC phases in the composite. The value of  $(1 - \Delta C_{p2}/\Delta C_{p1})$  may correspond to the weight fraction of PVC molecules present in the surface region of PPTA microfibrils. In the surface

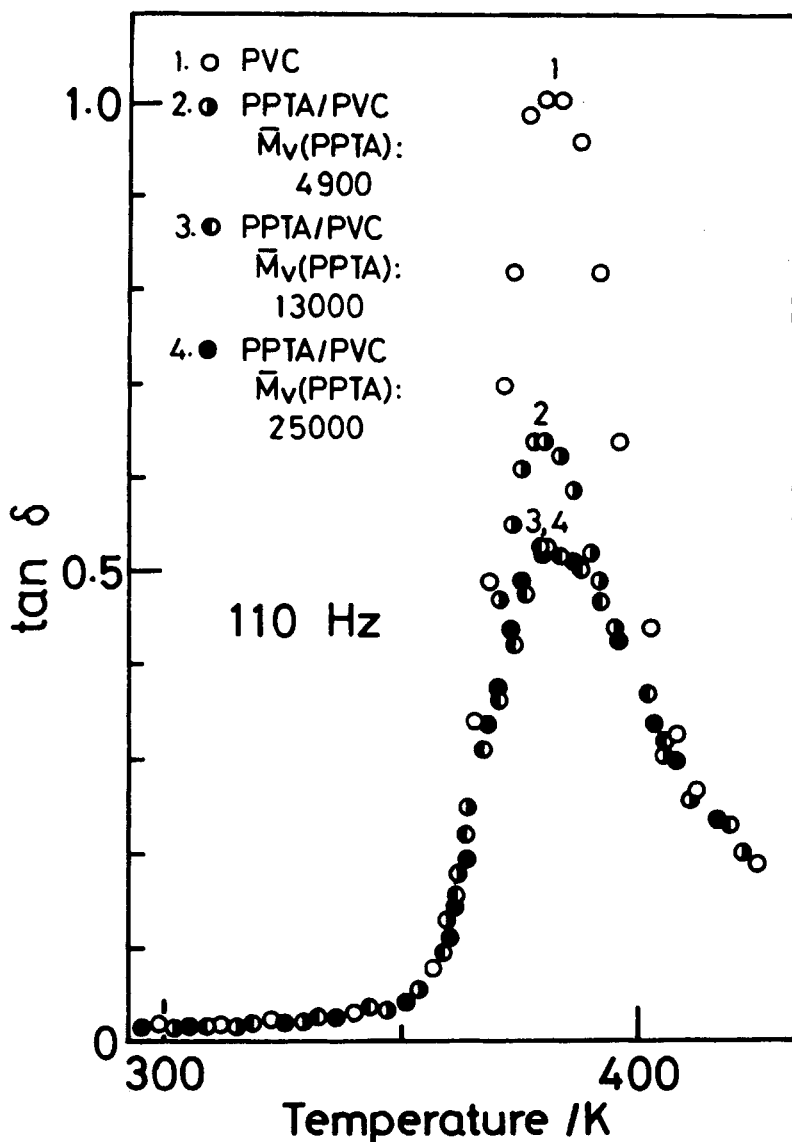


Fig. 5. Temperature dependence of  $\tan \delta$  at 110 Hz for PVC and the composites of 5 wt% PPTA/PVC.

region of the PPTA microfibrils the hydrogen bond between N—H and C—Cl would be formed, as mentioned above. Therefore, the PVC molecules in the surface region may not initiate micro-Brownian motion at the  $T_g$  of the PVC homopolymer and its initiation temperature will be higher. Actually the initiation temperature could not be detected to bring about conspicuous thermal degradation of PVC molecules above ca. 430°K. It should be noted that such thermal degradation may preferentially take place in the surface region of PPTA microfibrils, considering the result of Figure 2.



## MECHANICAL PROPERTIES

Figure 6(a) and 6(b) show the stress-strain curves at room temperature (a) and at 353°K (b) for the PVC homopolymer and the composites. Young's modulus, yield stress, and breaking stress at room temperature were higher in the composite than those in the PVC and increased with increasing the molecular weight of PPTA. It becomes apparent that the dispersion of PPTA microfibrils in PVC matrix increases modulus, yield stress, and breaking stress. As shown in Figure 4, in the surface region of PPTA microfibrils the hydrogen bond between N—H and C—Cl would be formed. Therefore, the large friction is originated between PPTA microfibrils and PVC during stretching and the high strength of PPTA becomes effective in the composites. The reasons for which the modulus and the breaking stress are higher in higher molecular weight PPTA, will be considered later by using an approximate mechanical model of the composites.

At the testing temperature of 353°K the elastic moduli of the composites were much higher than that of PVC and increased with increasing molecular weight. The same situation was encountered with breaking stress but to a lower extent. The large plastic deformation took place in PVC and therefore the breaking stress was higher because of the orientation of PVC molecules along the drawing direction, whereas the composites became more brittle. It is inferred from the stress-strain behavior at 353°K that the hydrogen bond formed in the surface region of PPTA microfibrils is still effective with respect to the appearance of the brittle-like properties of the composites.

Figure 7 shows the temperature dependence of the absolute value of complex modulus  $|E^*|$  for PVC and the composites. The  $|E^*|$  curve for the composite including higher molecular weight PPTA had a tendency to locate on the side of higher  $|E^*|$  value, especially at higher temperatures than  $T_g$ .

Figure 8(a) shows the quasi-three-dimensional microfibrillar model,<sup>6</sup> which could be applied as the approximate structure model of the composites, since the composites have the optically anisotropic phases dispersed homogeneously in PVC matrix and the residue after extracting PVC from the composite was composed of PPTA microfibrils as shown in Figure 3(a). In the model, the homogeneous dispersion of PPTA microfibrils in PVC matrix is approximated to the three-dimensional lattice composed of the microfibrils.

Figure 8(b) shows the mechanical model equivalent to the quasi-three-dimensional microfibrillar model. The temperature dependence of  $|E^*|$  in the composites can be calculated by using the mechanical model. In calculating  $|E^*|$  the following is assumed: (1) the diameter of all the microfibrils is 30 nm from Figure 3(a); (2) the continuity of the microfibrils was disturbed by the PVC polymers and therefore the length of the microfibrils is shortened by this disturbance. In this case it can be considered that each microfibril has defects filled by PVC. The volume fraction of the defects in a microfibril is much smaller than 1; (3) the modulus in the direction parallel or perpendicular to the microfibrillar axis does not change in the measurement temperature region of 300 to 430°K and the parallel modulus is 100 times the perpendicular modulus.

The modulus of the composite,  $E_{cal}$  is calculated by using the mechanical model as follows:

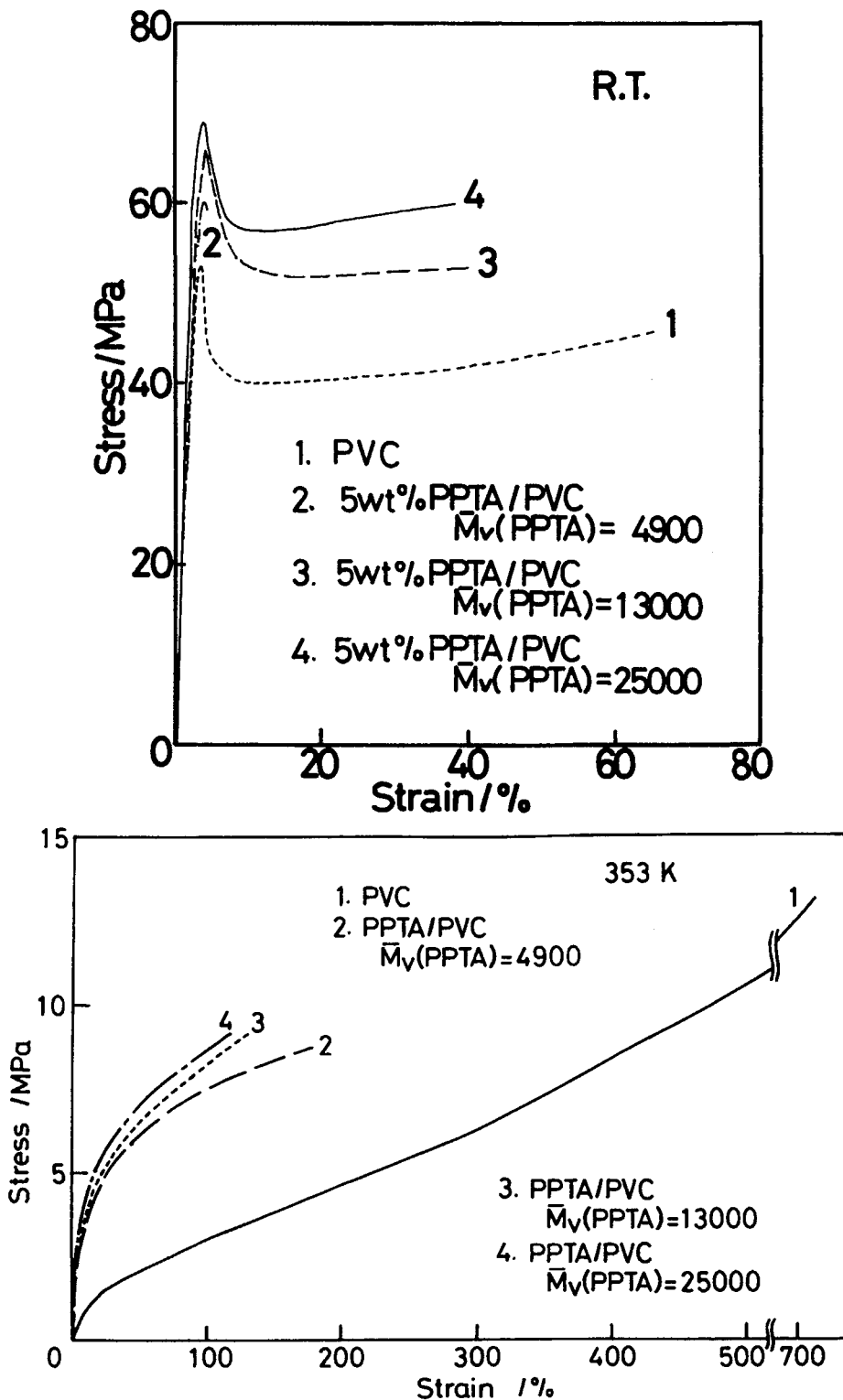


Fig. 6. Stress-strain curves (a) at room temperature and (b) at 353 K for PVC and the composites of 5 wt% PPTA/PVC.

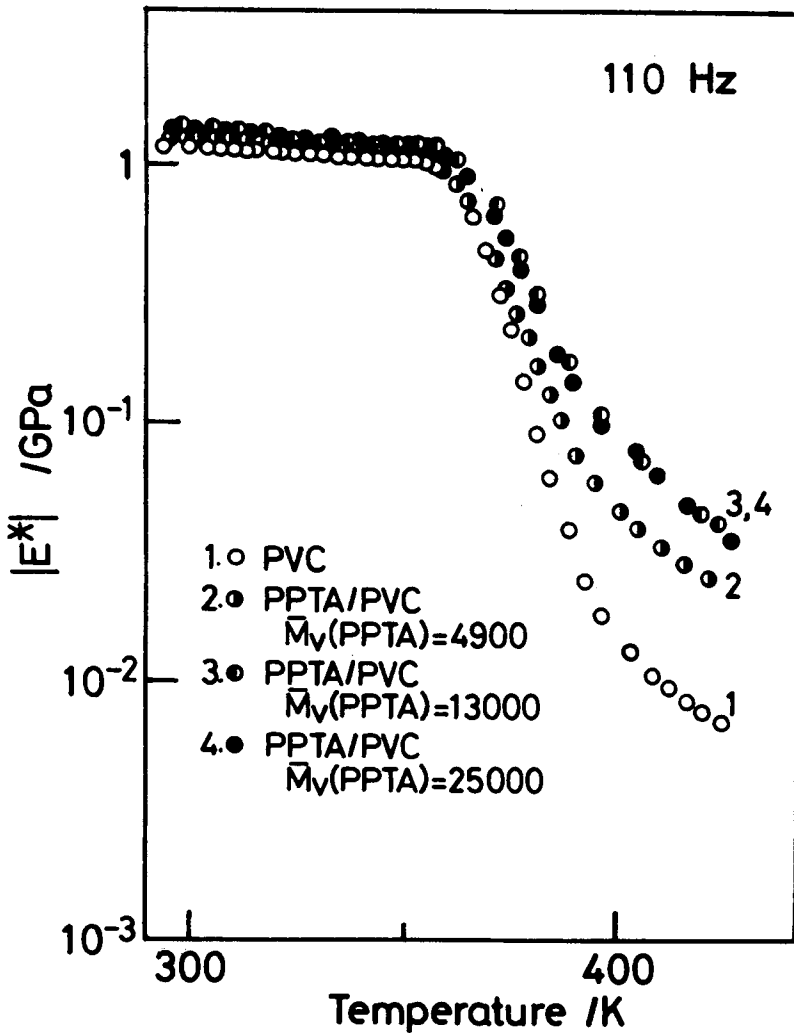


Fig. 7. Temperature dependence of the absolute value of complex modulus,  $|E^*|$  at 110 Hz for PVC and the composites of 5 wt% PPTA/PVC.

$$E_{\text{cal}} = (1 - \lambda) \left[ \frac{1 - 2\lambda}{E_m} + \frac{2\lambda}{(1 - \phi)E_{f\perp} + \phi E_m} \right]^{-1} \quad (1)$$

$$+ \lambda \left[ \frac{1 - \phi}{E_{f\parallel}} + \frac{\phi}{E_m} \right]^{-1} \quad (2)$$

$$\lambda = \frac{\pi b^2}{4a^2}$$

where  $a$  is the distance between microfibrils,  $b$  is the diameter of the microfibril, 30 nm,  $E_m$  is the modulus of PVC matrix,  $E_{f\parallel}$  is the modulus of the microfibril parallel to its axis,  $E_{f\perp}$  is the modulus of microfibril perpendicular to its axis, and  $\phi$  is the volume fraction of the defects. The volume fraction of PPTA microfibrils,  $V_f$  can be represented by  $a$  and  $b$  as follows

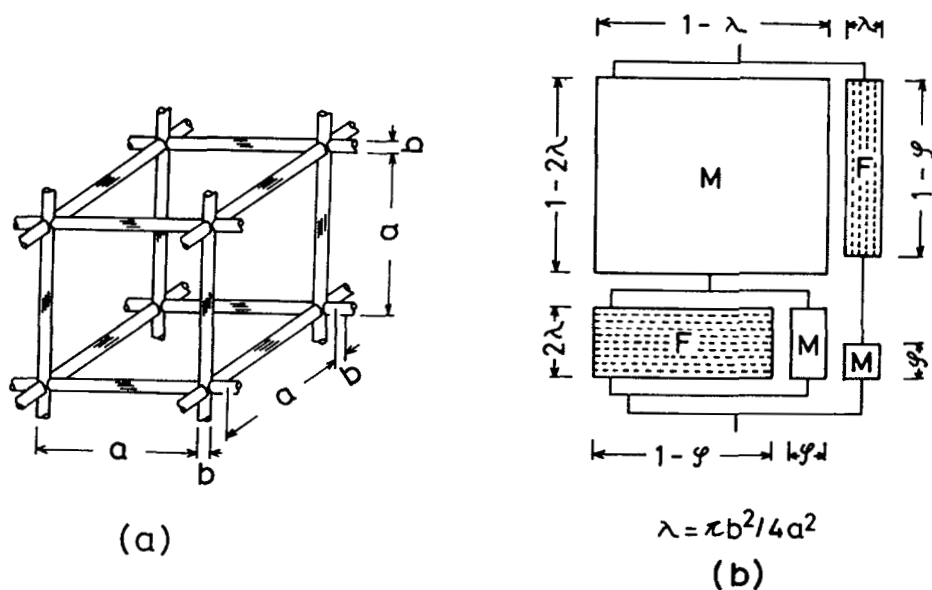


Fig. 8. (a) Quasi-three-dimensional microfibrillar model of the composites and (b) its equivalent mechanical model.

and was evaluated by using the density of PPTA microfibril, 1.5 g/cm<sup>3</sup> and that of PVC, 1.4 g/cm<sup>3</sup>:

$$V_f = \left[ \frac{3}{4} \pi b^2 a - 4 \left( 1 - \frac{1}{\sqrt{2}} \right) b^3 \right] / a^3 \quad (3)$$

Figure 9 shows, for example, both the measured and calculated  $|E^*|$  curves for the composite, in which the  $\bar{M}_v$  of PPTA is 13,000. The calculated curve is best fitted for the measured curve. The  $|E^*|$  value of PVC shown in Figure 7 is used as the value of  $E_m$  in Eq. (1). The calculated curve is obtained from the values of  $E_{f//}$  and  $\phi$  shown in Table I, in which the best fitting values of  $E_{f//}$  and  $\phi$  in the other composites are also shown. The modulus of PPTA fiber, Kevlar<sup>®</sup> which is prepared by omitting the process of annealing at high temperature, is 55 to 65 GPa.<sup>7</sup> The evaluated modulus of PPTA microfibril is much lower than 55 to 65 GPa. The origins of the difference would be as follows: (1) the orientation of crystal *c* axis in the microfibrils is worse than that in Kevlar fiber; (2) the packing of PPTA molecules in Kevlar is more regular and compact than that in microfibrils; (3) the modulus of PPTA microfibrils in the composite becomes apparently lower than the true modulus of the microfibrils because of negative effect of the ends of the microfibril, if Cox's theory<sup>8</sup> and Outwater's theory<sup>9</sup> in the fiber-reinforced composite can be applied to the composite.

The evaluated values of  $E_{f//}$  for  $\bar{M}_v = 13,000$  and  $\bar{M}_v = 25,000$  are higher than that for  $\bar{M}_v = 4,900$ , whereas the evaluated values of  $\phi$  for  $\bar{M}_v = 13,000$  and  $\bar{M}_v = 25,000$  are lower than that for  $\bar{M}_v = 4,900$ . This may mean the following: in the microfibrils of higher molecular weight PPTA, (1) the con-

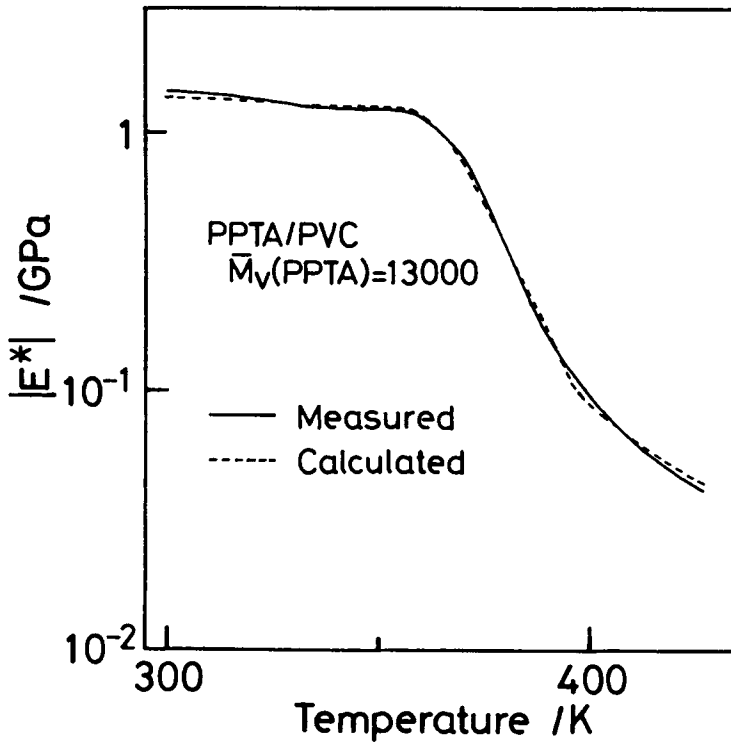


Fig. 9. Temperature dependence of measured and calculated moduli for the composite of 5 wt% PPTA/PVC ( $M_v(\text{PPTA}) = 13,000$ ).

TABLE I  
The Evaluated Values of  $E_{f1}$  and  $\phi$  in the Composites

$\bar{M}_v$ of PPTA	$E_{f1}$	$\phi$
4,900	16 GPa	0.0070
13,000	20	0.0025
25,000	20	0.0030

tinuity of the microfibrils is higher; (2) the orientation of PPTA molecules in the microfibril is higher; and (3) its packing is more regular and compact. The lower value of  $\phi$  in the higher molecular weight PPTA may be correlated to the higher breaking stress, as shows in Figure 6(a).

### CONCLUSION

In the PPTA/PVC composites PPTA molecules are aggregated in microfibrillar structure. The diameter of the microfibrils may decrease with decreasing the PPTA content. The PPTA microfibrils accelerate the thermal degradation of PVC molecules located on their surface region. The PVC molecules in the surface region of PPTA microfibrils may not initiate micro-Brownian motion at the  $T_g$  of PVC homopolymer to form the hydrogen

bond between the two polymers. The modulus, yield stress, and breaking stress were higher at room temperature in the composites than those in PVC homopolymer. Such an improvement of the mechanical properties becomes conspicuous when using higher molecular weight PPTA. The modulus and continuity of the PPTA microfibril are higher in the higher molecular weight PPTA.

### References

1. K. Tashiro, M. Kobayashi, and H. Tadokoro, *Macromolecules*, **10**, 413 (1977).
2. M. Takayanagi, T. Ogata, M. Morikawa, and T. Kai, *J. Macromol. Sci. Phys.*, **B17**, 591 (1980).
3. W. -F. Hwang, D. R. Wiff, C. L. Benner, and T. E. Helminiak, *J. Macromol. Sci. Phys.*, **B22**, 231 (1983).
4. M. Takayanagi and T. Katayose, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 1133 (1981).
5. G. A. Kuznetsov, V. M. Savinov, L. B. Sokolov, V. K. Belyakov, A. I. Maklakov, and G. G. Pimenov, *Vysokomol. Soyed.*, **A11**, 1491 (1969).
6. M. Takayanagi, *Pure Appl. Chem.*, **55**, 819 (1983).
7. J. Preston and W. B. Black, Witco Award Symp. Honoring P. W. Morgan, Am. Chem. Soc. Meet., New York (1976).
8. H. L. Cox, *Br. J. Appl. Phys.*, **3**, 72 (1956).
9. J. O. Outwater Jr., *Mod. Plast.*, **33**, 156 (1956).

Received July 9, 1985

Accepted January 13, 1986