

# Dynamic Mechanical Properties of Polypropylene Composites Filled with Ultrafine Particles

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## Synopsis

The dynamic moduli of isotactic polypropylene (PP) filled with ultrafine SiO<sub>2</sub> and micron sized glass particles are measured in the temperature range 30–130°C at frequency 10 Hz. The storage moduli of PP composites,  $E'_c$ , increase with filler content and decreasing filler size in the whole range of temperature. The loss moduli of PP composites,  $E''_c$ , increase with filler content and decreasing filler size above 40°C. The intensity of the broad dispersion which appears at ca. 60°C increases with filler content and decreasing filler size. By assuming that the energy is not dissipated in the effective volume, namely, filler volume plus that of immobilized interfacial region, the effective volume fraction is evaluated from the relative loss modulus,  $E''_c/E'_0$  at 60°C. The effective volume fraction increases with filler content and decreasing filler size. The effect of addition of ultrafine particles on the broad dispersion at ca. 60°C resembles the effect of increasing crystallinity of pure PP. It is concluded that the broad dispersion which appeared at ca. 60°C seemed to be assigned to the grain boundary of PP composites or crystalline boundary of pure PP.

## INTRODUCTION

In a previous paper we have studied the reducible properties of drawing temperature, rate of strain, and filler content with respect to the tensile yield stress of PP composites filled with ultrafine particles. The yield stress is reducible by three factors, i.e., drawing temperature, strain rate, and filler content. The conversion law is relatively simple<sup>1</sup>:

(1) The first shift factor,  $a_T$ , is the Arrhenius type for temperature and for strain rate. The activation energy is not dependent on the filler volume fraction and size.

(2) The logarithm of the second shift factors,  $\log a_c$ , for strain rate and for filler content is proportional to the square root of the filler volume fraction.

The Arrhenius plots of shift factor,  $\log a_T$ , against the reciprocal temperature have two breaks at 60°C and 110°C for filled and nonfilled PP. These breaks are related to some kinds of transition of matrix PP. Many authors have reported about the nature of the broad dispersion which appears at ca. 60°C of isotactic PP. However, the assignment of this transition is not known clearly.<sup>2-6</sup> In the present study, we discuss the effect of filler content and size on this dispersion from the measurement of dynamic modulus of PP filled with ultrafine particles.

## EXPERIMENTAL

**Polymer and Filler.** Isotactic polypropylene (PP) (melt index = 7–8), Shoaromer of Showa Denko Co., was used as matrix polymer. SiO<sub>2</sub> particles

TABLE I  
Average Diameters of Filler Particles

Particles	Average diameters
SiO <sub>2</sub>	
A 300	70 Å
A 130	160 Å
OX 50	400 Å
Glass	
G 733	65 μm
AF 3	125 μm
D 5	200 μm

( $\rho = 2.2 \text{ g/cm}^3$ ) from Nihon Aerosil Co. and Sodalime glass particles ( $\rho = 2.4 \text{ g/cm}^3$ ) from Toshiba Balotini Co. were used as fillers. Both the SiO<sub>2</sub> and glass particles have nearly the same modulus,  $7.0 \times 10^5 \text{ kg/cm}^2$ . Table I shows the average diameters of these particles.

**Mixing and Molding.** Polymer and filler were mixed in a two-roll mill for 15 min at 180°C. The content of the fillers was 5, 10, 15 and 20 wt %. Films about 0.5 mm thick were molded from the mixtures at 200°C under a pressure of 100 kg/cm<sup>2</sup>. Since thermal degradation of matrix polymer took place more or less during the mixing and molding, films without filler were prepared by the same procedures. It was assumed that the degradation of polymer took place in the composites to the same extent as in the pure polymer sample. All the samples were annealed at 130°C for 1 h.

**Measurement of Dynamic Modulus.** Strips 2.0 cm long and 8 mm wide were cut out from the composite film for the measurements of dynamic modulus. The dynamic modulus was measured by Rheograph 651 type apparatus from Toyo Seiki Co. at 10 Hz. The crystallinities of quenched (in dry ice-methanol) and annealed (142°C, 12 h) pure PP samples were measured by wide angle X-ray diffraction XG type apparatus from Rigaku Denki Co.

**Effective Volume Fraction of Dispersed Phase.** The effective volume fraction of dispersed phase,  $\phi_e$ , are composed of the volume of a high modulus filler plus that of a region of the "immobilized" matrix associated with the interface which does not contribute to energy loss. Ziegel reported energy loss aspects of polyurethane composites with emphasis on the importance of interfacial regions adjacent to the filler particles.<sup>7</sup> The energy dissipated per cycle of vibration in a unit volume of homogeneous material related to the loss modulus and extensional strain  $\epsilon$  as shown below:

$$W = \pi E'' \epsilon^2 \quad (1)$$

If a polymer composite is considered to consist of a "lossy" matrix phase plus a nondissipative dispersed phase whose effective volume fraction is  $\phi_e$ , then the energy dissipation per cycle for a unit volume of composites is

$$W_c = \pi E_m'' \epsilon_c^2 (1 - \phi_e) \quad (2)$$

where the subscript  $m$  refers to the viscoelastic matrix. From eq. (2) the ratio of energy dissipation for the filled ( $W_c$ ) to the unfilled ( $W_0$ ) system is approximately

$$W_c/W_0 = (\epsilon_c/\epsilon_0)^2 (1 - \phi_e) \quad (3)$$

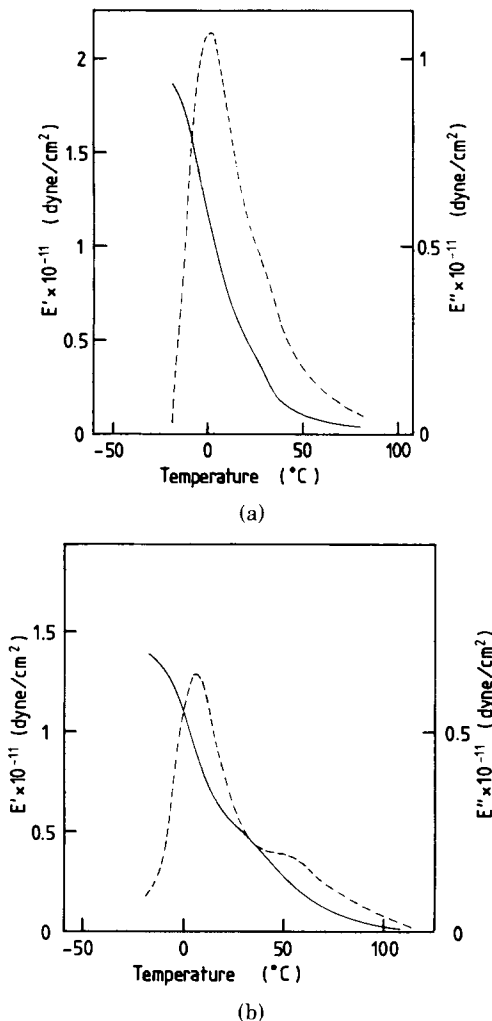


Fig. 1. Dynamic modulus of PP vs. temperature: (a)  $X_c = 0.15$ ; (b)  $X_c = 0.56$ .

where  $\epsilon_c/\epsilon_0$  is the ratio of the relative extension of the matrix phase in the filled material to that of the unfilled matrix of identical dimension. It is apparent that if two polymer samples of equal dimension—one of which contains an extensible dispersed phase and the other, pure matrix—are each subjected to the same elongation,  $\Delta L$ , the actual strain in the extensible matrix phase of the composites sample will be greater than that in the unfilled matrix. The relative elongation of the matrix phase in the filled system compared to that in the unfilled polymer is

$$\epsilon_c/\epsilon_0 = (\Delta L/L'_0)/(\Delta L/L_0) = L_0/L'_0 \tag{4}$$

where  $L_0$  is the initial sample length (equal in both cases) and  $L'_0$  is an effective dimension in the direction of the extensible phase in the composites. Assuming the restriction of elongation in the other two directions (series model),

$$\epsilon_c/\epsilon_0 = 1/(1 - \phi_e) \tag{5}$$

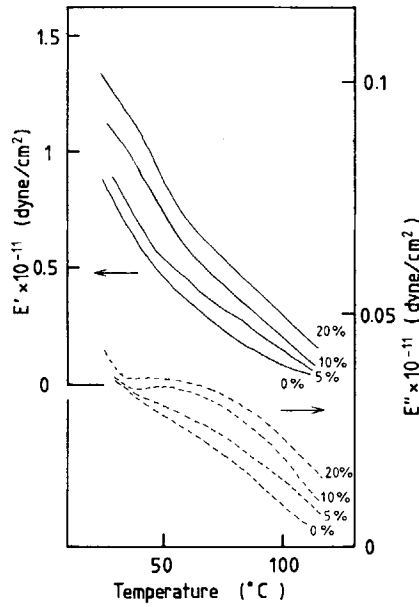


Fig. 2. Dynamic moduli of 70-Å SiO<sub>2</sub>-filled PP composites vs. temperature as a function of filler content.

From eq. (3)

$$W_c/W_0 = 1/(1 - \phi_e) \tag{6}$$

$W_c/W_0$  is approximately equal to  $E''_c/E''_0$ , the relative loss modulus:

$$W_c/W_0 = E''_c/E''_0 = 1/(1 - \phi_e) \tag{7}$$

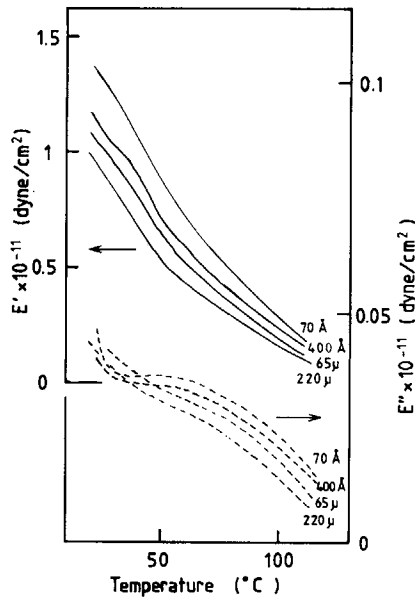


Fig. 3. Dynamic moduli of PP composites filled with 20 wt % fillers of which diameters are 70 Å, 400 Å, 125 μm, and 220 μm.

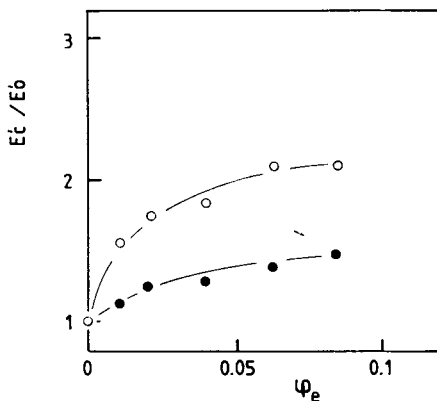


Fig. 4. Relative storage moduli  $E'_c/E'_0$  of composites filled with 160-Å  $\text{SiO}_2$  at 30°C (●) and 80°C (○).

If the volume of a particle is enlarged in all dimensions by  $\Delta r$ , then it follows that

$$E''_c/E''_0 = (1 - \phi_f \cdot B)^{-1} \quad (8)$$

$$B = (1 + \Delta r/R_0)^3 \quad (9)$$

where  $R_0$  is the radius of a particle.

## RESULTS AND DISCUSSION

Figure 1(a) shows the dynamic modulus of PP quenched at  $-45^\circ\text{C}$  in a dry ice-methanol bath from melts and Figure 1(b) shows that of the sample annealed at  $142^\circ\text{C}$  for 12 h in  $\text{N}_2$  atmosphere. The crystallinity of the samples in Figures 1(a) and 1(b) are 0.15 and 0.56, respectively, from X-ray diffraction. The relative peak height of dynamic loss modulus in main dispersion which appears at ca.  $0^\circ\text{C}$  is nearly equal to that of the amorphous fraction,

$$E''_a(0^\circ\text{C})/E''_b(0^\circ\text{C}) = [1 - X_c(a)]/[1 - X_c(b)]$$

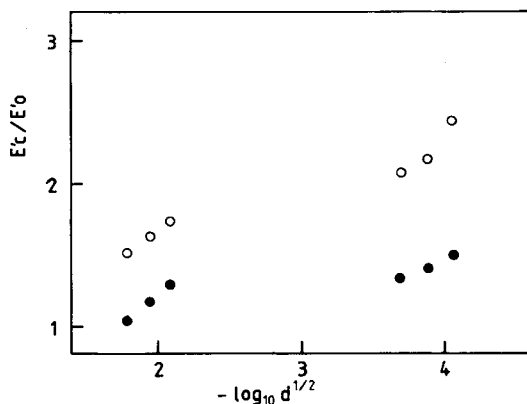


Fig. 5. Relative storage moduli  $E'_c/E'_0$  of PP composites filled with 15 wt % fillers of several kinds of particles of which diameters are 70 Å, 160 Å, 400 Å, 65  $\mu\text{m}$ , 125  $\mu\text{m}$  and 220  $\mu\text{m}$  as a function of the reciprocal log of the square root of the filler size ( $\mu\text{m}$ ). (○) 80°C; (●) 30°C.

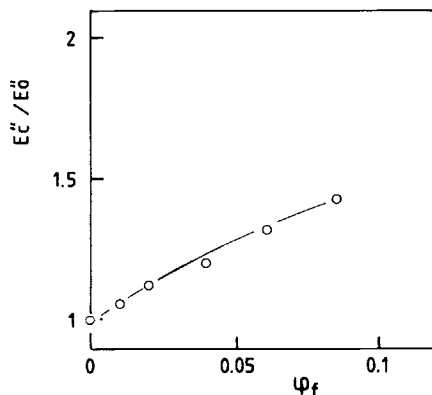


Fig. 6. Relative loss moduli of PP composites,  $E''/E''_0$ , filled with 160-Å  $\text{SiO}_2$  particles as a function of filler volume fraction.

where  $X_c$  is the crystallinity. In the highly crystalline sample [Fig. 1(b)], the  $E''$  curve has a broad dispersion which appears to ca. 60°C, while that of the quenched sample [Fig. 1(a)] does not have a clear shoulder at this region. The transition at ca. 60°C is too high to the glass transition. We and many others have already shown that some kind of transition of the crystalline region or crystalline boundary play an important roll in the drawing property of polymers.<sup>8,9</sup> Miller<sup>2</sup> and Flocke<sup>3</sup> found the existence of very broad dispersion at 60°C. Muus and McGrew identified this dispersion to be a disorder transition of crystals.<sup>4</sup> On the other hand, Wyckoff<sup>5</sup> and Zannetti et al.<sup>6</sup> found that smectic crystals transform to the normal monoclinic ones at about 70°C. These studies suggest that the transition observed here at ca. 60°C is very likely to be related to the crystalline region.

Figure 2 shows dynamic storage moduli  $E'$  and loss moduli  $E''$  of 70-Å  $\text{SiO}_2$  filled PP as functions of temperature and filler content. The storage modulus  $E'$  of the PP composites increases with filler content in the whole range of temperature. The loss moduli  $E''$  increase with filler content at above 40°C. Figure 3 shows dynamic moduli of PP composites filled with 20 wt % fillers of which

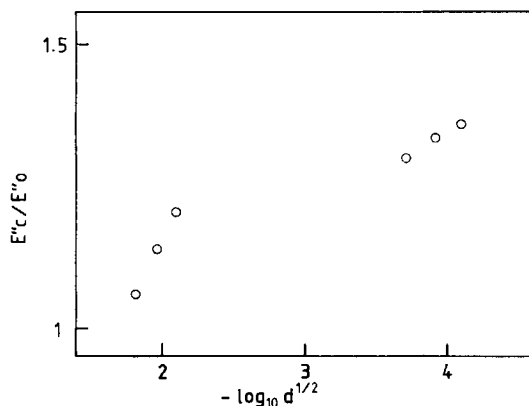


Fig. 7. Relative loss moduli,  $E''/E''_0$  of PP composites at 60°C filled with 15 wt % fillers of several kinds of particles as a function of the reciprocal log of the square root of the filler size ( $\mu\text{m}$ ).

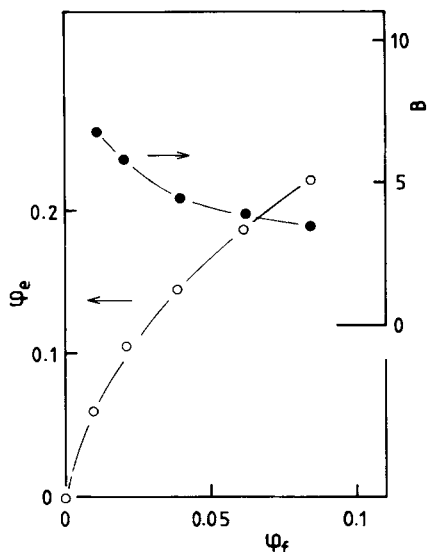


Fig. 8.  $\phi_e$  and  $B$  of PP composites filled with 160-Å  $\text{SiO}_2$  vs. filler volume fraction.

diameters are 70 Å, 400 Å, 125  $\mu\text{m}$ , and 220  $\mu\text{m}$ . The storage moduli  $E'$  of PP composites increase with decreasing filler size in the whole range of temperature. The loss moduli  $E''$  also increase with decreasing filler size at above 40°C. Figure 4 shows relative storage moduli,  $E'_c/E'_0$ , of PP composites filled with 160-Å  $\text{SiO}_2$  at 30°C and 80°C. In both temperatures, the relative storage moduli increase with the filler content. At a given filler content, the relative storage modulus at 80°C is higher than that at 30°C. This is because the bonding ability between fillers and matrix becomes larger in a higher temperature than in a lower one, for the extent of thermal expansion of the matrix becomes large as the temperature rises. Figure 5 shows relative storage moduli,  $E'_c/E'_0$ , of PP composites filled with 15 wt % fillers of several kinds of particles of which the diameters are 70 Å, 160 Å, 400 Å, 65  $\mu\text{m}$ , 125  $\mu\text{m}$ , and 220  $\mu\text{m}$  as a function of the reciprocal log of the square root of the filler size ( $\mu\text{m}$ ). The relative values of  $E'_c/E'_0$  of PP composites increase with decreasing filler size. Figure 6 shows the relative loss moduli,  $E''_c/E''_0$  at 60°C of PP composites filled with 160-Å  $\text{SiO}_2$  particles as a function of filler volume fraction. The relative loss moduli of this composite increase with filler content. Figure 7 shows the relative loss moduli,  $E''_c/E''_0$ , at 60°C of 15 wt % filler filled PP as a function of the reciprocal log of the square root of filler size ( $\mu\text{m}$ ). The relative values of  $E''_c/E''_0$  at 60°C increase with decreasing filler size. According to the procedure mentioned in the previous section, the effective volume fraction is  $\phi_e$  and  $B$  is the relative value of the effective volume per single particle. By substituting the measured values of  $E''_c/E''_0$  in Figure 6 to eqs. (7), (8), and (9),  $\phi_e$  and  $B$  are obtained for the PP composites filled with 160-Å  $\text{SiO}_2$  particles. Figure 8 shows  $\phi_e$  and  $B$  of the PP composites filled with 160-Å  $\text{SiO}_2$  filler as a function of filler volume fraction. The effective volume  $\phi_e$  increases with the filler volume fraction.  $B$ , the relative value of the effective volume per single particle, decreases with filler volume fraction. This means the extent of aggregation of particles increases with filler content.

Figure 9 shows changes of  $\phi_e$  and  $B$  of the 15 wt % filled composites with the reciprocal log of the square root of the filler size ( $\mu\text{m}$ ).  $\phi_e$  and  $B$  increase with

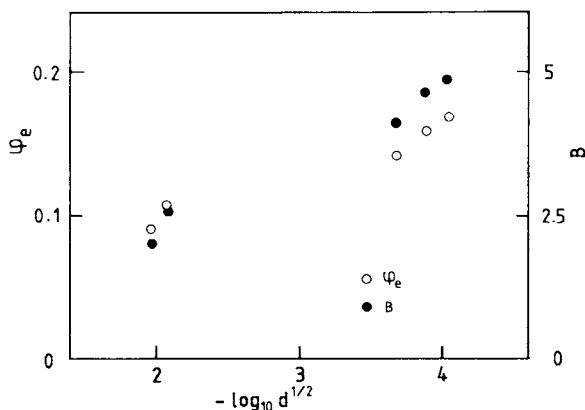


Fig. 9.  $\phi_e$  and  $B$  of PP composites filled with 15 wt % fillers against the reciprocal log of the square root of the filler size ( $\mu\text{m}$ ).

decreasing filler size. The extent of increasing of these values seems to be larger in a larger filler than in a smaller one. This suggests that the extent of aggregation becomes large in a smaller filler series ( $\text{SiO}_2$  series).

### CONCLUDING REMARKS

The dynamic moduli of particulate PP composites were measured as functions of temperature and filler content. The following results were obtained:

(1) The relative storage moduli  $E'_c/E'_0$  increase with filler content and decreasing filler size in the whole range of temperature examined.

(2) The relative loss moduli  $E''_c/E''_0$  at  $60^\circ\text{C}$ , in which temperature the broad dispersion is observed, depend upon the content of effective volume fraction, i.e., the fraction of filler volume plus that of the interfacial region. The effective volume fraction increases with filler content and decreasing filler size. The effect of additions of ultrafine particles resembles the effect of increasing crystallinity of pure PP. From these results, it is concluded the broad dispersion which appears ca.  $60^\circ\text{C}$  in PP composites or pure PP seems to be assigned to the region of grain boundary of composites or crystalline boundary in pure PP.

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