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Effect of ultra fine particles on the elastic properties of oriented polypropylene composites

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Fine spherical particles with various diameters (70, 160 and 40 nm, and 35, 65 and 125 μm) were mixed with isotactic polypropylene (PP). For the oriented composites having hexagonal symmetry produced by drawing, the elastic properties were determined by five compliances, S, or stiffness constants, C. Four of these, namely, S_{33}, S_{11}, S_{13} and S_{44} (or C_{33}, C_{11}, C_{13} and C_{44}) were determined for the oriented composites filled with particles whose average diameters were 7 nm and 65 μm. For the composites filled with the smaller particles (7 nm), all the stiffness constants (C_{33}, C_{11}, C_{13} and C_{44}) increased with the filler content, whereas for those with larger particles (65 μm), this relation was reversed. The Young's moduli of the oriented composites filled with relatively small particles (7, 16 and 40 nm) in each re-stretching direction increased with increasing filler content and with decreasing filler size, whereas those of the composites filled with larger filler (35, 65 and 125 μm) decreased with increasing filler content and size. It was concluded that the modulus of the oriented composite is determined by three factors, namely: (1) molecular orientation of matrix polymer; (2) the volume-fraction and size of filler; and (3) the fraction of void introduced by drawing. The moduli observed for the oriented composites are well explained by an equation derived on an assumption of the independence of the three effects. It was also concluded that extremely small fillers with particle sizes comparable to that of the crystalline region in PP matrix have a prominent reinforcing effect in the oriented polymer matrix.

1. Introduction

The effect of dispersed fillers on the mechanical properties of polymeric composites has been studied by many authors [1–3]. Most papers deal with filler effects in the composites with unoriented polymer matrix. Polymeric materials are usually used in the form of drawn sheets or fibres to develop the mechanical properties characteristic of the chain-like structure [4]. In this paper the effect of filler size on the anisotropic elastic properties of oriented polypropylene composites is studied, the understanding of which is essential for designing oriented polymer composites.

2. Experimental procedure

2.1. Polymer and filler

Isotactic polypropylene (PP) (melt index = 7 to 8) from Showa denko Co. was used as the matrix polymer. Soda-lime glass particles ($\rho = 2.4\,\mathrm{g\,cm^{-3}}$) from Toshiba Balotini Co. and SiO_2 particles ($\rho = 2.2\,\mathrm{g\,cm^{-3}}$) from Nihon Aerosil Co. were used as fillers. The glass and SiO_2 particles had almost the same modulus, $7.0 \times 10^5\,\mathrm{kg\,cm^{-2}}$. Average diameters of these particles are shown in Table I.

2.2. Mixing and moulding

Polymer and filler were mixed in a two-roll mill

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TABLE I Average primary diameters of filler particles

Particle	Filler	Average diameter (nm)
SiO_2	A300	7
SiO_2	A130	16
SiO_2	OX50	40
Glass	G731	35 000
Glass	G733	65 000
Glass	AF3	125 000
Glass	D5	220 000

for 15 min at 180° C. The mixing time, 15 min, was chosen because the torque of the composites in the molten state becomes constant after 10 min. The content of fillers were 2.5, 5, 10, 15 and 20 wt%. It was difficult to make oriented samples loaded more than 20 wt%, for the composites could not be drawn. Films about 0.5 mm thick were moulded from the mixtures at 200° C under a pressure of $100\,kg\,cm^{-2}$. Since some thermal degradation of the matrix polymer took place during the mixing and moulding, 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. In order to prepare oriented composites, these films were uniaxially drawn by a Tensilon UTM-III from Toyo Boldwin Co. at room temperature. The draw rate was $200\,mm\,min^{-1}$. The draw ratio of the necked material decreased with increasing filler content. The difference in draw ratios for the different filler types is small, as shown in Table II.

2.3. Measurement of compliances of oriented composites

To obtain the compliances of oriented composite specimens, films were cut out in directions of 0°, 45° and 90° to the original stretching axis as shown in Fig. 1. The Young's modulus of each direction were measured. This measurement was done with the Tensilon UTM-III machine at room temperature at a rate of 50% of the original length per min. The apparent Poisson's ratio, ν_0, was obtained by reading shrinkage in the perpendicular direction of sample under about 3% extension in the original stretching direction, using an optical micrometer. For elastic solids, the components of strain tensor, e_i, are linearly related to the components of stress P_i, for small strain. It was confirmed that the drawn composite sample is isotropic in a plane perpendicular to the direction of drawing. The number of independent elastic constants is reduced to five. Choosing the 3,2,1 direction as the axis of stretching, width and thickness of the sample, respectively, the compliane tensor, S_{ij}^{dc}, is reduced to

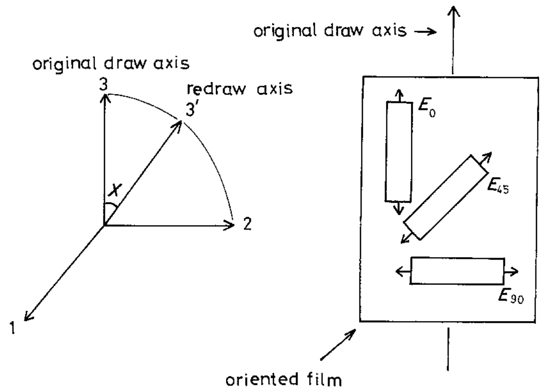

Figure 1 Schematic representation of re-stretching direction of oriented composite film.

$$\begin{vmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{vmatrix} = \begin{vmatrix} S_{11}^{dc} & S_{12}^{dc} & S_{13}^{dc} & 0 & 0 & 0 \\ & S_{11}^{dc} & S_{13}^{dc} & 0 & 0 & 0 \\ & & S_{33}^{dc} & 0 & 0 & 0 \\ & & & S_{44}^{dc} & 0 & 0 \\ & & & & S_{44}^{dc} & 0 \\ & & & & & 2(S_{11}^{dc}-S_{12}^{dc}) \end{vmatrix} \cdot \begin{vmatrix} P_1 \\ P_2 \\ P_3 \\ P_4 \\ P_5 \\ P_6 \end{vmatrix} \quad (1)$$

TABLE II Draw ratio of necking part of polypropylene composites

Particle	Filler	Draw ratio				
		Filler content: 0 wt %	Filler content: 5 wt %	Filler content: 10 wt %	Filler content: 15 wt %	Filler content: 20 wt %
SiO_2	A300		4.6–4.5	4.5	4.4	4.3
SiO_2	A130		4.6–4.5	4.4	4.4–4.3	4.3–4.2
SiO_2	OX50		4.6–4.5	4.6–4.5	4.4	4.3–4.2
Glass	G731	4.6	4.6–4.5	4.5	4.4	4.3–4.2
Glass	G733		4.6–4.5	4.4	4.3	4.2–4.1
Glass	AF3		4.5	4.4	4.3–4.2	4.1–4.0

The relation between Young's modulus, E^{dc}, shear modulus, G^{dc}, Poisson's ratio, ν, of a sample and the compliance values are given by the following equations:

$$S_{33}^{dc} = 1/E_0^{dc}; \quad (2)$$

$$S_{11}^{dc} = 1/E_{90}^{dc}; \quad (3)$$

$$S_{13}^{dc}/S_{33}^{dc} = -\nu_0; \quad (4)$$

$$S_{44}^{dc} = 1/G^{dc}; \quad (5)$$

and

$$S_{12}^{dc}/S_{11}^{dc} = -\nu_{90}. \quad (6)$$

The suffix numbers in E^{dc} and ν of Equations 2 to 6 indicate the re-stretching angle against the original draw axis. The $3'$ axis is the direction of re-stretching of the film. The angle between 3 and $3'$ is denoted by X. The Young's modulus in the $3'$ direction is given by the tensor transformation rule [5],

$$1/E_x^{dc} = S_{11}^{dc}\sin^4 X + (2S_{13}^{dc} + S_{44}^{dc})\sin^2 X\cos^2 X + S_{33}^{dc}\cos^4 X, \quad (7)$$

or

$$E_x^{dc} = C_{11}^{dc}\sin^4 X + 2(C_{13}^{dc} + 2C_{44}^{dc})\sin^2 X\cos^2 X + C_{33}^{dc}\cos^4 X, \quad (8)$$

where S_{ij}^{dc} and C_{ij}^{dc} are the compliance and stiffness tensors of the drawn composites.

2.4. Measurement of molecular orientation

The overall orientation function,

$$f(= 1/2[3\overline{\cos^2\theta} - 1]),$$

of the matrix polymer is given

$$f = f_c X_c + f_a(1 - X_c), \quad (9)$$

where θ is the orientation angle between the stretching direction and the molecular chain of specimens, f_c, and f_a are the crystalline and amorphous orientation factors, respectively, and X_c is the crystallinity of the matrix polymer. The crystalline orientation factors, f_c, of drawn specimens were determined from the (1 1 0) and (0 4 0) X-ray diffractions of PP by the Ni-filtered CuKα radiation in the Rigaku denki Co. XG-type apparatus [6]. The amorphous orientation factor, f_a, of composite specimens was obtained by the following procedure. First, for the non-filled drawn PP samples, the optical densities of a fluorescent dye, Whitex, was measured with a Hitach 139 spectrometer equipped with a polarizer. The absorption dichroism, ϕ_D, was evaluated using the equation

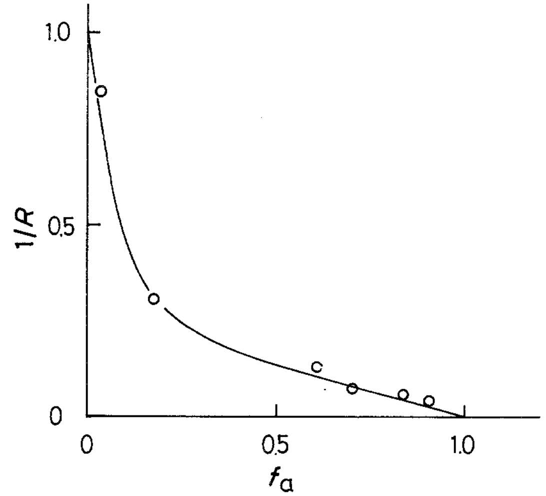

Figure 2 Relation between reciprocal fluorescent dichroic ratio, $1/R$, and amorphous orientation factor, f_a, of polypropylene.

$$\phi_D = (K-1)/(K+2), \quad (10)$$

where $K = D_{\parallel}/D_{\perp}$, $D_{\parallel} = \log(I_0/I_{\parallel})$, $D_{\perp} = \log(I_0/I_{\perp})$, I/I_0 is the transmittance and the symbols $\parallel$ and $\perp$ indicate the direction of the polarizer with respect to the drawing axis of the sample. Our previous study shows that a relation, $f_a \cong \phi_D$, holds for Whitex–PP systems under various draw ratios [7]. We assume that this relation also holds for PP composites. However, as the composites are not transparent, we estimated f_a from the fluorescent dichroism measured by the reflection method [8]. For Whitex-unfilled PP, the relation f_a and the fluorescent dichroic ratio, $R\,[= I'_{\parallel}(0)/I'_{\parallel}(90)]$, as measured by the reflection method [9, 10], was established as shown in Fig. 2. f_a values of Whitex-filled, drawn PP samples were read on this figure from the observed R for the sample. Since our density measurement confirmed that X_c is unchanged upon addition of filler, f can be obtained by Equation 8. The elastic modulus of the matrix polymer is a function of the second and fourth moments of the orientation distribution of the structural units, $\overline{\cos^2\theta}$, $\overline{\cos^4\theta}$, $\overline{\sin^4\theta}$ and $\overline{\sin^2\theta\cos^2\theta}$ [4].

The orientation distribution function, $g(\theta)$, for "pseudo-affine" deformation is assumed [11–14]:

$$g(\theta) = \frac{\lambda^3 \sin\theta}{2}[\lambda^3 - \cos^2\theta(\lambda^3 - 1)]^{-3/2}, \quad (11)$$

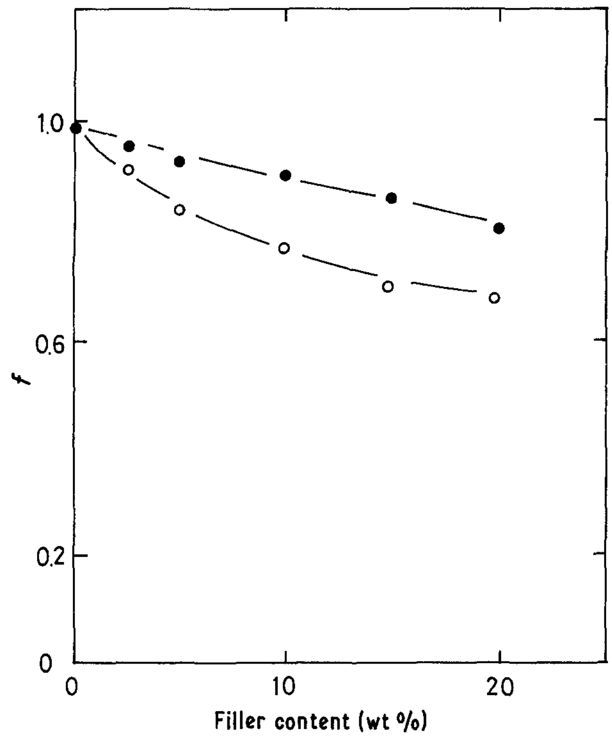

Figure 3 Changes of orientation function, f, of oriented polypropylene composites filled with A300 and G733 fillers against filler content. —•—•— G733; —○—○— A300.

where λ is the draw ratio. Fourth averages for this distribution were calculated from the observed second averages through Equation 11.

2.5. Density measurements

The densities of specimens were measured by a Toyo Seiki automatic densitometer M-I-II-type at 25° C.

3. Theory

The elastic properties of oriented polymer composites are known to depend on such factors as

(1) the molecular orientation of matrix polymer,

(2) the volume-fraction and size of filler, and

(3) the fraction of void introduced by the drawing in the preparation of oriented composites [15].

These three factors, having correlations with each other, determine the modulus of oriented polymer composites. Since the correlations are too complicated to analyse, we simply assume here that these three factors affect the modulus independently:

$$E_x^{dc} = F_1 \cdot F_2 \cdot F_3, \tag{12}$$

where E_x^{dc} is the modulus of oriented polymer composites. F_1 is a function depending only on the molecular orientation of matrix polymer; F_2 is that depending only on filler; and F_3 is that depending only on the void formed by the drawing. Now, we approximate F_1 by the modulus E_x^{do} of oriented unfilled polymer with certain orientation:

$$F_1 = E_x^{do}. \tag{13}$$

In the cases of these oriented samples, the elastic properties are anisotropic and, therefore, the suffix x in E_x^{dc} and E_x^{do} shows the direction in which the values are measured, while the superscripts dc and do denote drawn composites or drawn neat polymers, respectively. E_x^{do} is assumed to be equal to the modulus of neat polymer with same extent of orientation. The orientation effect of matrix polymer is calculated by assuming that samples consist of an aggregate of structural units with hexagonal symmetry. Moduli are given by following equations in the directions parallel and perpendicular to the original stretching direction [5]:

$$\begin{aligned} E_0^{do} = C_{33}^{do} = {} & [C'_{11}\,\overline{\sin^4\theta} \\ & + 2(C'_{13} + 2C'_{44})\,\overline{\sin^2\theta\,\cos^2\theta} \\ & + C'_{33}\,\overline{\cos^4\theta}\,], \end{aligned} \tag{14}$$

$$\begin{aligned} E_{90}^{do} = C_{11}^{do} = {} & [(1/8)(3\,\overline{\cos^4\theta} + 2\,\overline{\cos^2\theta} \\ & + 3)C'_{11} + (1/4)(3\,\overline{\sin^2\theta\,\cos^2\theta} \end{aligned}$$

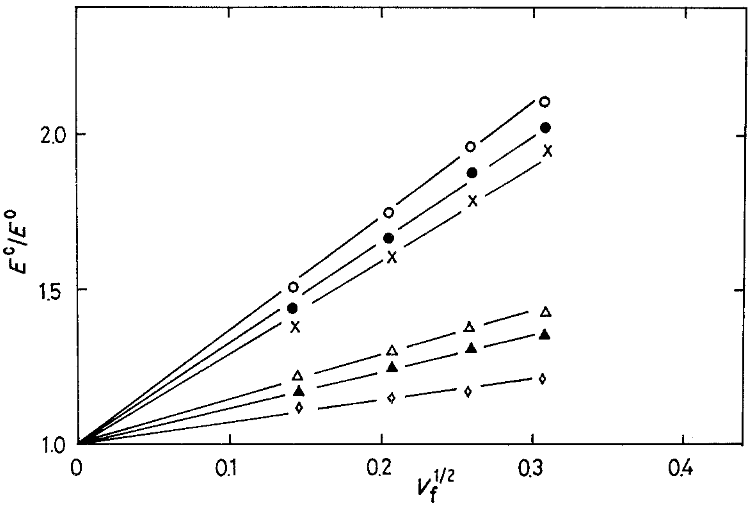

Figure 4 Relative modulus, E^c/E^o, of unoriented polypropylene composites filled with several kinds of particles, plotted against the square-root of filler volume-fraction, $V_f^{1/2}$. E^c and E^o are the modulus of unoriented polypropylene composites and unfilled, undrawn polypropylene matrix, respectively. —○—○— A300; —△—△— G733; —●—●— A130; —▲—▲— AF3; —X—X— OX50; —◇—◇— D5.

$$+ \overline{\sin^2\theta})C'_{13} + (3/8)\,\overline{\sin^4\theta}\,C'_{33} + (1/2)(3\,\overline{\sin^2\theta\cos^2\theta} + \overline{\sin^2\theta})C'_{44}], \quad (15)$$

where C'_{11}, C'_{13}, C'_{33} and C'_{44} are the stiffness constants of structural units. These values are assumed to be equal to those of unfilled polymer. These values are then determined from the Young's moduli in the directions 0°, 45° and 90° to the original draw axis and the Poisson's ratio of unfilled, drawn PP which has almost complete orientation (see Fig. 3). The reason for assuming stiffness averaging rather than compliance is that from the present phenomenological viewpoint, it is more straightforward to list the numerical values which are directly linked to the elastic properties of the material.

Next the effect of filler is considered. From the assumption of independence orientation and filler effects, filler effects in the oriented and unoriented polymer matrices are the same. Then the following equation is given at same filler volume-fraction and size:

$$F_2 = E^c/E^o = E_x^{dc}/E_x^{do}, \quad (16)$$

where E^c, E^o are the moduli of unoriented composite and unoriented unfilled polymer, respectively and E^c is a function of filler volume-fraction and size. This function was determined experimentally. In Fig. 4, the relative modulus E^c/E^o of unoriented PP composites was plotted against the square-root of filler volume-fraction ($V_f^{1/2}$), which shows an approximately linear relation for fillers having different size, expressed by

$$E^c/E^o = K(d)\{V_f^{1/2} + 1\}. \quad (17)$$

The slopes of these lines, $K(d)$, increase with decreasing filler size.

The third is the effect of cavitation caused by the drawing of unoriented composites. The unoriented composites have practically no voids (see Fig. 5). For the two-phase system of matrix and void, Young's modulus has been given by Hirai *et al.* [16], on the basis of the theory of Cohen and Ishai [17] and Wu [18],

$$E^{ov} = E^o(1 - 2C_v), \quad (18)$$

where E^{ov} is the modulus of matrix–void system and C_v is the volume-fraction of void. Therefore, F_3 is represented as:

$$F_3 = E^{ov}/E^o = E_x^{dov}/E_x^{do}, \quad (19)$$

where E_x^{dov} is the modulus of oriented matrix–void system. Thus we obtain

$$F_3 = (1 - 2C_v). \quad (20)$$

To summarize all the effects, the modulus of oriented PP composites is given by

$$E_x^{dc} = F_1F_2F_3 = E_x^{do}[K(d)V_f^{1/2} + 1](1 - 2C_v). \quad (21)$$

For the directions parallel and perpendicular to the original draw axis,

$$E_0^{dc} = [C'_{11}\,\overline{\sin^4\theta} + 2(C'_{13} + 2C'_{44})\,\overline{\sin^2\theta\cos^2\theta} + C'_{33}\,\overline{\cos^4\theta}]\{K(d)V_f^{1/2} + 1](1 - 2C_v)$$

and (22)

$$E_{90}^{dc} = [(1/8)(3\,\overline{\cos^4\theta} + 2\,\overline{\cos^2\theta} + 3)C'_{11} + (1/4)(3\,\overline{\sin^2\theta\cos^2\theta} + \overline{\sin^2\theta})C'_{13} + (3/8)\,\overline{\sin^4\theta} + (1/2)(3\,\overline{\sin^2\theta\cos^2\theta} + \overline{\sin^2\theta})C'_{44}]\{K(d)V_f^{1/2} + 1\}(1 - 2C_v). \quad (23)$$

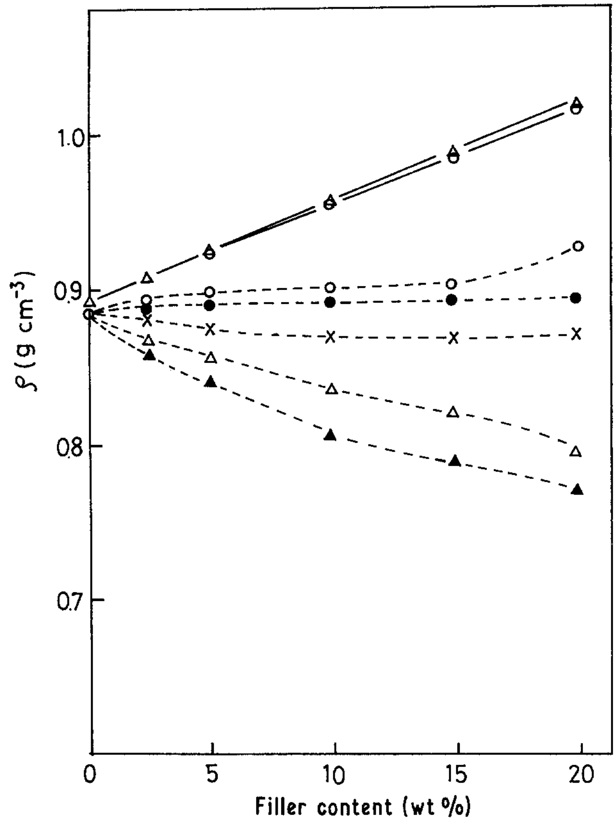

Figure 5 Changes of densities of unoriented and oriented polypropylene composites against filler content and size. —○—○— SiO_2 and —△—△— glass, both unoriented compositions. ------ oriented composition. --○--○-- A300; --△--△-- G733; --●--●-- A130; --▲--▲-- AF3; --X--X-- OX50.

To estimate E_x^{do}, we assume the orientation distribution function for "pseudo-affine" deformation given by Equation 12, from which the average orientation function can be calculated: $\overline{\sin^4\theta}$, $\overline{\cos^4\theta}$ and $\overline{\sin^2\theta\cos^2\theta}$ in Equations 22 and 23 corresponding to the change in the observed $\overline{\cos^2\theta}$ value obtained in Fig. 3.

4. Results and discussion

Fig. 6 shows relative values, E_x^{dc}/E^o, in the directions of 0°, 45° and 90° to the original draw axis, as a function of filler content for oriented PP composites filled with several kinds of particles. E^o, with a value of 5.08×10^3 kg cm^{-2}, is Young's modulus of non-filled and unoriented PP. For composites filled with relatively small filler, volume-fractions A300, A130, OX50, their Young's moduli of each direction increase with the filler content and decreasing filler size. But for G733, AF3 fillers, the composites moduli decrease with increasing filler content and size. Fig. 7 shows Poisson's ratio, ν_0, against filler content for oriented composites filled with A300, G731, G733 and AF3 fillers. ν_0 values of composites decrease with filler content. At a given filler content, the smaller filler size gives a larger ν_0

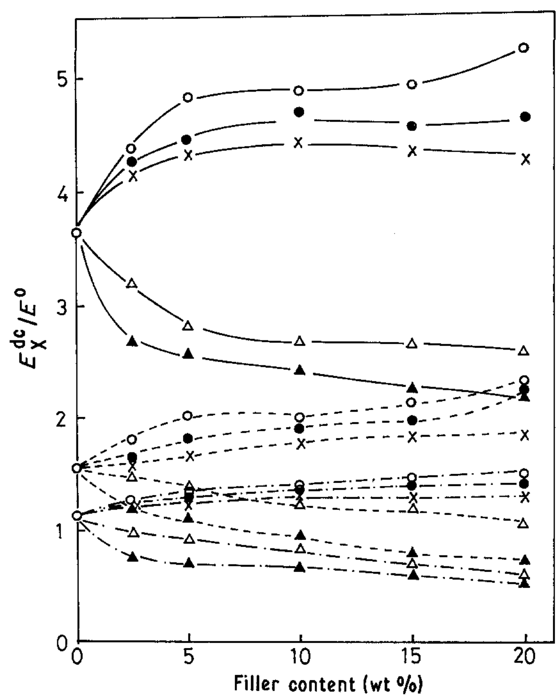

Figure 6 Relative values, E^{dc}/E^o, of oriented polypropylene composites in each re-stretching direction as functions of filler content and size. E^{dc} and E^o are the modulus of oriented composites and undrawn polypropylene matrix, respectively. —— 0°; ------ 45°, —·—·— 90°; ○ A300; ● A130; X OX50; △ G733; ▲ AF3.

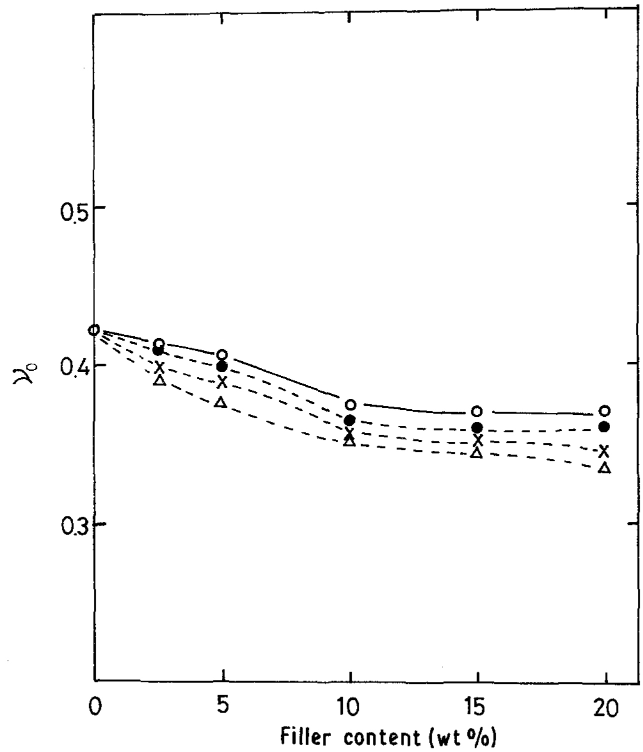

Figure 7 Poisson's ratio of oriented polypropylene composites filled with A300, G731, G733 and AF3 fillers against filler content. —o—o— A300; --o--o-- G731; --x--x-- G733; --△--△-- AF3.

value. The difference among filler types for SiO_2 particles was small. Fig. 8 shows the relative compliance values, S_{ij}^{dc}/S_{ij}^{do}, against filler content for oriented A300, G733 filled PP composites. For the G733 filled samples, all the compliances increase with filler content. Of the compliances, S_{11}^{dc} increases the most, but for A300 filler, this relation is reversed. These results show that oriented PP composites filled with extremely small particles exhibit a prominent positive reinforcement effect, whereas those with relatively larger particles exhibit a negative one. The modulus of oriented polymer composites is considered to be related to the changes of molecular orientation and void fraction accompanied by drawing of unoriented composites. For the oriented PP composites filled with A300 and G733 fillers, Fig. 3 shows the relationship between orientation function, f, and filler content. For both specimens, f decreases with filler content. At a given filler content, the f value of smaller particles is lower than those of larger ones. This fact indicates that the size dependence of elastic properties of oriented PP composites cannot be explained by the changes of orientation of the matrix polymer alone. Fig. 8 shows density changes of oriented and unoriented PP composites with filler content. For all the unoriented composites, observed densities agree with the calculated ones obtained by

$$1/\rho_s = V_f/\rho_f + (1 - V_f)/\rho_p, \qquad (24)$$

where ρ_s, ρ_f and ρ_p are densities of sample, filler and matrix polymer, respectively. For the oriented composites, observed densities are lower than those of calculated values. The difference becomes larger with increasing filler content and size. These results show that unoriented composites have practically no void fraction, whereas oriented composites have a void fraction that increases with filler content and size. In summarizing the discussion given so far, it is concluded that the modulus of the oriented PP composites is determined by three factors, namely, those of (a) matrix orientation, (b) filler and (c) void. An attempt is made to correlate quantitatively the composites modulus with these three factors. If the independence of the three effects is assumed, the moduli of oriented PP composites in the directions parallel and perpendicular to the original draw axis are given by Equations 22 and 23. Fig. 9 shows Young's moduli, E_0^{dc} and E_{90}^{dc}, for oriented PP composites filled with A300 and G733 fillers against filler content. Dotted lines represent the values calculated by Equations 22 and 23, which

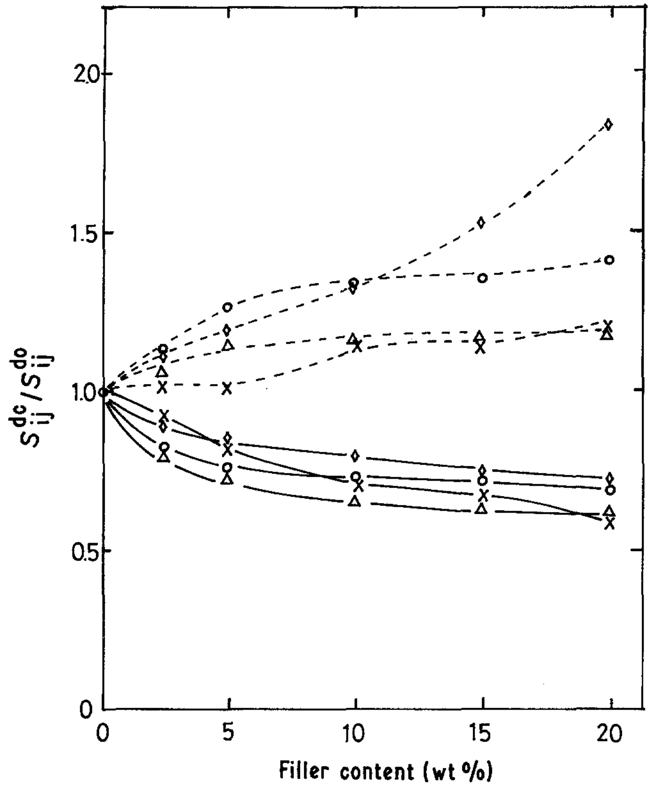

Figure 8 Relative compliances, S_{ij}^{dc}/S_{ij}^{do}, of oriented polypropylene composites filled with A300 and G733 fillers against filler content. ------ G733; —— A300; ◇ S_{11}^{dc}; ○ S_{33}^{dc}; X S_{44}^{dc}; △ S_{13}^{dc}.

agree essentially with the observed values in both directions. In the direction perpendicular to the original draw axis, the magnitude of the positive deviation from the observed values is larger than that in the other direction. This may be due to fibrillation of the matrix, implying that Young's modulus depends not only on the void fraction, but also on the shape and size of the void [19]. Fig. 10 shows relative values, E_0^{dc}/E_0^{do}, plotted against the logarithm of filler size in micrometres for oriented PP composites filled with contents of 10 and 20 wt% of A300, A130, OX50, G731, G733, AF3 fillers. In Fig. 10, the values marked with an asterisk, are data obtained by Im [20],

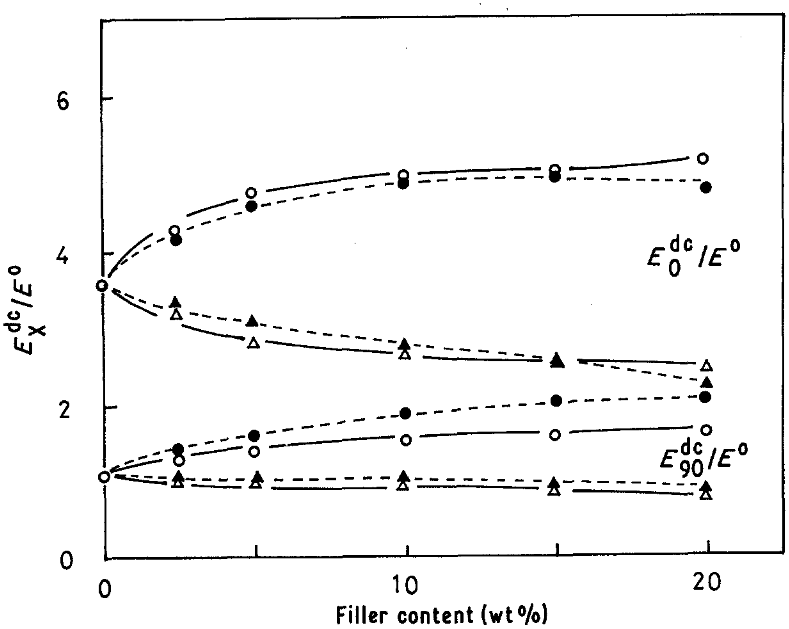

Figure 9 Relative modulus, E_x^{dc}/E_x^{do}, of oriented polypropylene composites both in the direction of and perpendicular to the original draw direction plotted against filler content. Dotted lines are value calculated using Equations 22 and 23. —○—○— A300; —△—△— G733; ------ calculated value.

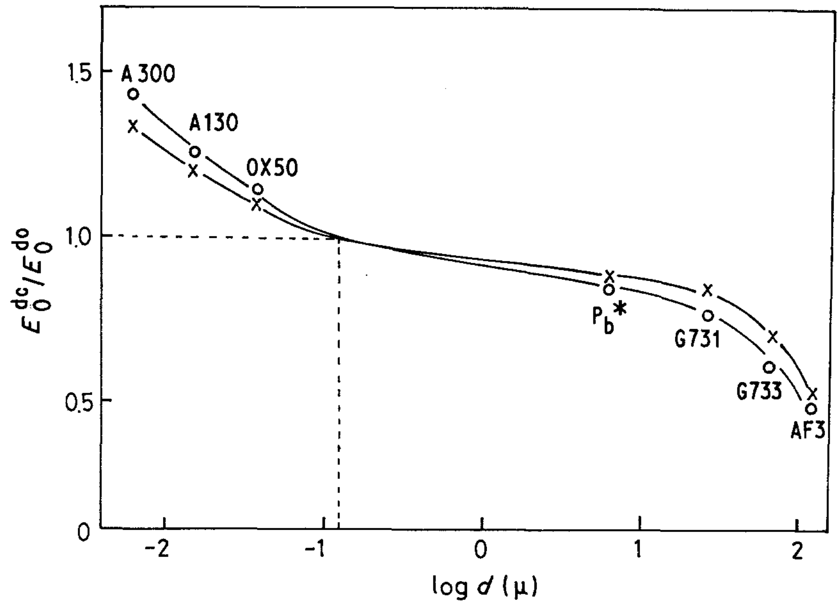

Figure 10 Relative values, E_0^{dc}/E_0^{do}, of oriented polypropylene composites against the logarithm of filler size in micrometres. E_0^{dc} and E_0^{do} are the modulus of oriented composites and drawn polypropylene matrix in the direction of the original draw axis, respectively. Values symbolized Pb* are from the data obtained by Im [20] for oriented polypropylene composites filled with lead glass of which the average diameter is 6 μm. —o—o— 20 wt%; —x—x— 10 wt%.

for oriented PP composites filled with lead glass whose average diameter is 6 μm. In Fig. 10, the filler size when $E_0^{dc}/E_0^{do} = 1$, is about 110 nm. This value corresponds to the size of the crystalline region of the matrix polymer. With a smaller size than this value, filler effects become positive in the oriented PP matrix.

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