Effect of Ultrafine Particles on the Elastic Properties of Oriented Low-Density Polyethylene Composites

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Synopsis

Spherical fine particles with various diameters (70, 160, and 400 Å and 35 μ) were mixed with low-density polyethylene (LDPE). The oriented composites were made by necking drawing. Thus the oriented polymer composites were hexagonal symmetric. Their elastic properties were determined by five compliances or stiffness constants. Four of them, i.e., S_{33}, S_{11}, S_{13}, and S_{44}, were determined for the oriented composites filled with 70-Å and 35-μ fillers. All the compliances of the 70-Å filler composites decrease with filler content, whereas in those of the 35-μ filler composites this relation was reversed. The Young's moduli of the oriented composites filled with relatively small particles (70, 160, and 400 Å) in the restretching directions 0, 45, and 90° against the original draw axis increased with filler content and with decreasing filler size, whereas those of the 35-μ filler composites decreased with filler content. These results show that extremely small particles comparable to the size of the LDPE in the crystalline region exert a considerable reinforcing effect on the oriented polymer matrix.

INTRODUCTION

The effect of dispersed filler on the mechanical properties of polymeric composites has been studied by many authors.[1–3] But most of them deal with filler effect in the composites with unoriented polymer matrix. Polymeric materials are used usually in the form of drawn sheets or fibers to develop the mechanical properties characteristic to the chain-like structure.[4] In this article, we discuss the effect of filler size on the anisotropic elastic properties of oriented low-density polyethylene (LDPE) composites. The filler effect is important for designing oriented polymer composites.

EXPERIMENTAL

Polymer and Filler

LDPE (Sholex M221) from Showa Denko Co. was used as matrix polymer. Soda lime glass particles ($\rho = 2.4$ g/cm^3) from Toshiba Balotini Co. and SiO_2 particles ($\rho = 2.2$ g/cm^3) from Nihon Aerosil Co. were used as fillers. Both the glass and the SiO_2 particles have nearly the same modulus, 7.0×10^5 kg/cm^2. Table I shows the average diameters of these particles.

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TABLE I
Average Primary Diameters of Filler Particles

Particle	Average diameter
SiO_2	
A300	70 Å
A130	160 Å
OX50	400 Å
Glass	
G731	35 μ

Mixing and Molding

Polymer and filler were mixed in a two-roll mill for 15 min at 125°C. A mixing time of 15 min was chosen because the torque of the composites in the molten state became constant in 10 min. The filler contents were 2.5, 5, 10, 15, and 20 wt %. It was difficult to make oriented samples loaded with more than 20 wt %, for the composites could not be drawn. Films about 0.5 mm thick were molded from the mixtures at 140°C under a pressure of 100 kg/cm^2. 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 polymer in the composites was degraded 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 of Toyo Boldwin Co. at room temperature. Draw rate was 200 mm/min. The draw ratio of the necking part decreased with increasing filler content. At a given filler content, the draw ratio of the necking part decreased slightly with increasing filler size. The necking draw ratios for four kinds of fillers are shown against filler content in Table II.

Measurement of Compliances or Stiffness Constants of Oriented Composites

To obtain the compliance of oriented composites specimens, films were cut to the direction of 0, 45, and 90° against the original stretching axis as shown in Figure 1. The Young's moduli in each direction were measured with the Tensilon UTM-III at room temperature at a rate of 50% of the original length per minute. The apparent Poisson's ratio ν_0 was obtained by reading with an optical micrometer the shrinkage in the perpendicular direction of samples under about 3% extension in the original stretching direction. For elastic solids, the component of the strain tensor e_i is linearly related to that of the stress tensor σ_i for

TABLE II
Draw Ratio of Necking Part of LDPE Composites

Particle	0 wt %	5 wt %	10 wt %	15 wt %	20 wt %
SiO_2					
A300		4.5–4.4	4.3	4.2	4.1
A130	4.6	4.5	4.3	4.2	4.0
OX50		4.4	4.2	4.0	3.9
Glass					
G731		4.4–4.3	4.1	4.0	3.9

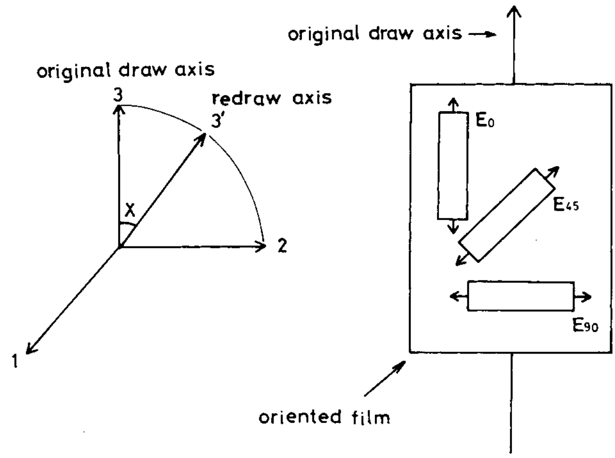


Fig. 1. Schematic representation of restretching direction of oriented composites film.

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 then reduced to five. Choosing the 3,2,1 direction as the axis of the stretching, the width and the thickness of the sample, respectively, the compliance tensor S_{ij} reduces to eq. (1):

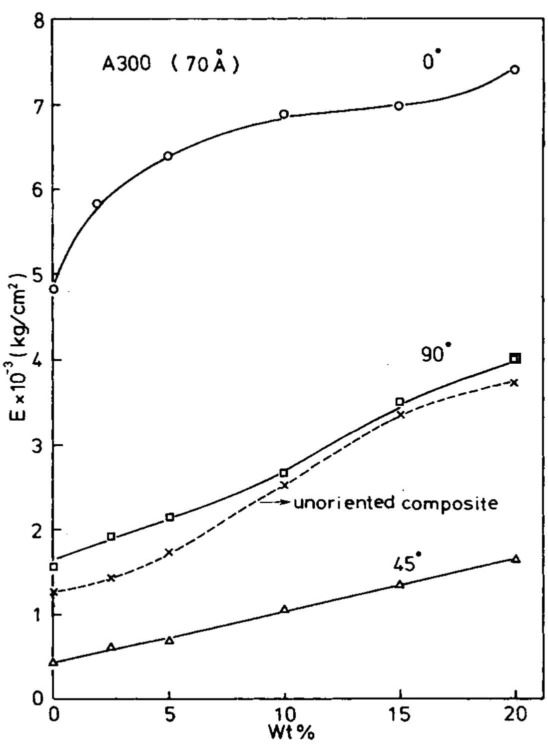
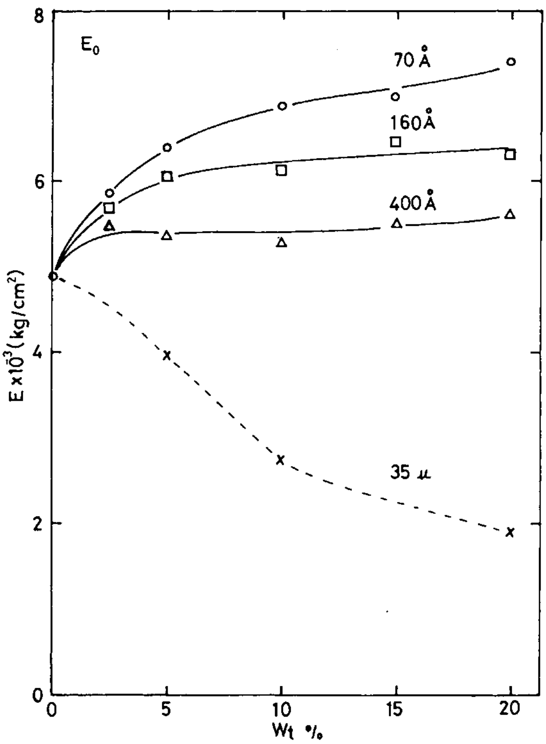
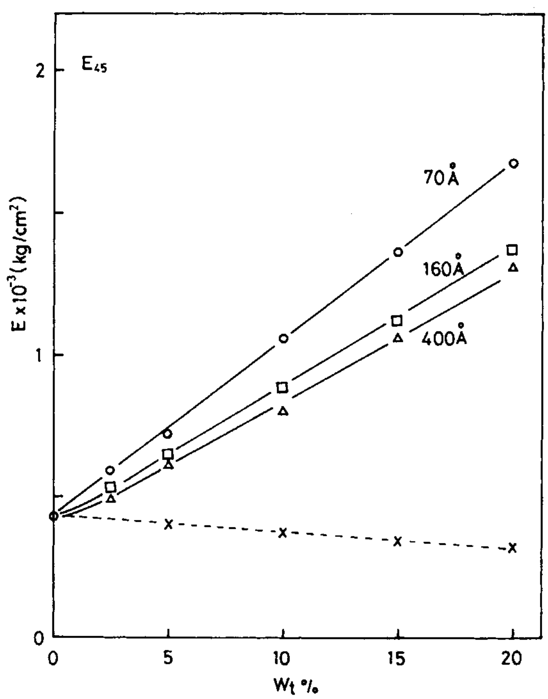


Fig. 2. Young's moduli in each restretching direction of oriented LDPE composites filled with A300 filler. Dotted line shows Young's moduli of the unoriented composites.

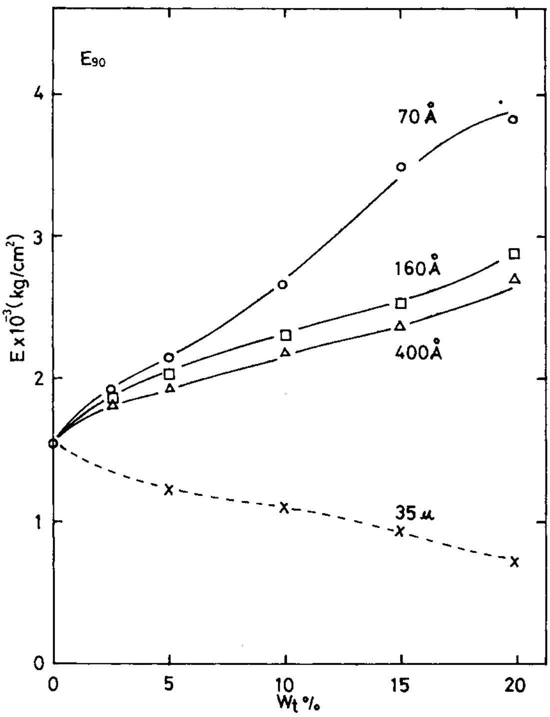


(a)



(b)

Fig. 3. Young's moduli of oriented LDPE composites filled with four kinds of fillers in the direction (a) 0°, (b) 45°, and (c) 90° to the original draw axis, plotted against filler content.



(c)

Fig. 3. (*Continued from previous page.*)

$$\begin{vmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{vmatrix} = \begin{vmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ & S_{11} & S_{13} & 0 & 0 & 0 \\ & & S_{33} & 0 & 0 & 0 \\ & & & S_{44} & 0 & 0 \\ & & & & S_{44} & 0 \\ & & & & & 2(S_{11} - S_{12}) \end{vmatrix} \begin{vmatrix} \sigma^1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{vmatrix} \quad (1)$$

The relations between Young's modulus E, shear modulus G, Poisson's ratio ν of a sample, and the compliance values are given by eqs. (2)–(6):

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

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

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

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

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

The suffix numbers for E and ν of eqs. (2)–(6) indicate the restretching angle to the original draw axis. The 3′ axis in Figure 1 is the direction of restretching 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]

$$S_x = S_{11} \sin^4 X + (2S_{13} + S_{44}) \sin^2 X \cos^2 X + S_{33} \cos^4 X$$

or

$$E_x = C_{11} \sin^4 X + 2(C_{13} + 2C_{44}) \sin^2 X \cos^2 X + C_{33} \cos^4 X \quad (7)$$

RESULTS AND DISCUSSION

Figure 2 shows Young's moduli E_0, E_{45}, and E_{90} of oriented LDPE composites filled with A300 filler against filler content in wt %. For each direction, the Young's modulus increases with filler content. The dotted line shows the modulus of unoriented LDPE composites. As shown by Raumann and Sanders for a highly oriented LDPE sheet,[6] the unusual feature is observed that the oriented composites sheets show the lowest stiffness in a direction making an angle of 45° to the initial draw direction. This experimental result implies that $(2S_{13} + S_{44})$ is much larger than either S_{11} or S_{33}, since when $X = 45°$, these terms in eq. (7) will be equally weighted. Figures 3(a), 3(b), and 3(c) show E_0, E_{45}, and E_{90} of oriented LDPE composites filled with four kind of fillers as functions of filler content and size, respectively. For oriented composites filled with relatively small filler—A300, A130, and OX50—Young's moduli for the three directions increase with filler content and with decreasing filler size. But for a relatively larger filler—G731—these relations are reversed. Figure 4 shows Poisson's ratio ν_0 against filler content for oriented LDPE composites filled with A300 and G731 fillers. Both ν_0 values decrease with filler content. At a given filler content, the smaller filler—A300—gives a larger ν_0 value.

Figure 5 shows the relative value S/S^0 against filler content for oriented A300- and G731-filled composites, where S and S^0 are the compliances of oriented composites and oriented pure LDPE, respectively. For the G731-filled sample, all the compliances increase with filler content; S_{33} increases most among the four compliances. On the other hand, for A300-filled samples, all the compliances decrease with filler content; S_{44} decreases most among the compliances. The reason why the A300 particles have a more prominent reinforcing effect than

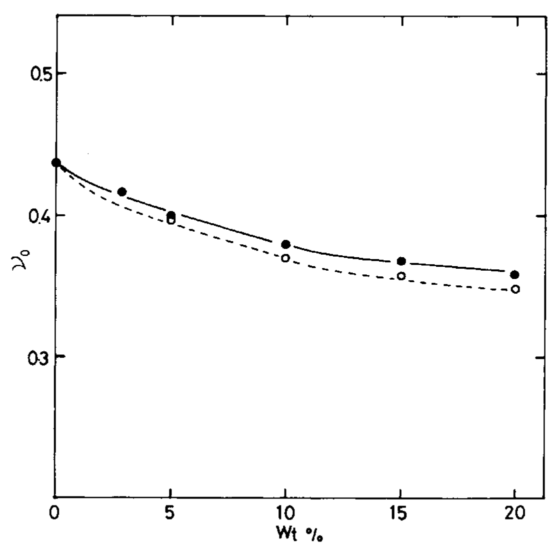


Fig. 4. Poisson's ratio ν_0 of oriented LDPE composites filled with A300 and G731 fillers plotted against filler content: (●) 70 Å; (○) 35 μ.

the G731 particles despite an essentially equal draw ratio is that the elastic properties of oriented polymer composites are known to depend on (1) the molecular orientation of matrix polymer, (2) the volume fraction and size of the filler, and (3) the fraction of void introduced by drawing.[7] The theoretical treatment of these procedures has been submitted elsewhere.[8] It is considered that oriented LDPE composites filled with fine A300 particles have a larger reinforcing effect than G731 particles in unoriented composites and that they have a smaller fraction of voids than G731-filled composites in the oriented state.

Figure 6 shows the relative value E_0/E^0 plotted against the logarithm of filler size in micron units for oriented LDPE composites in the direction of the original draw axis, where E_0 is the Young's modulus of the composite and E^0 is that of the oriented pure LDPE, respectively. Points P_b^* are Funada's data for oriented LDPE composites filled with lead glass with an average diameter of 6 μ.[9] In this figure, the filler size for $E_0/E^0 = 1$ is about 90 mμ. This value corresponds to the size of the crystalline region of the matrix polymer.[10] With a size smaller than this, the filler effect becomes positive in the oriented LDPE matrix.

CONCLUDING REMARKS

The elastic properties of the oriented composites were considered to depend on such factors as (1) the molecular orientation of matrix polymer, (2) the volume fraction and size of the filler, and (3) the fraction of voids produced by drawing.

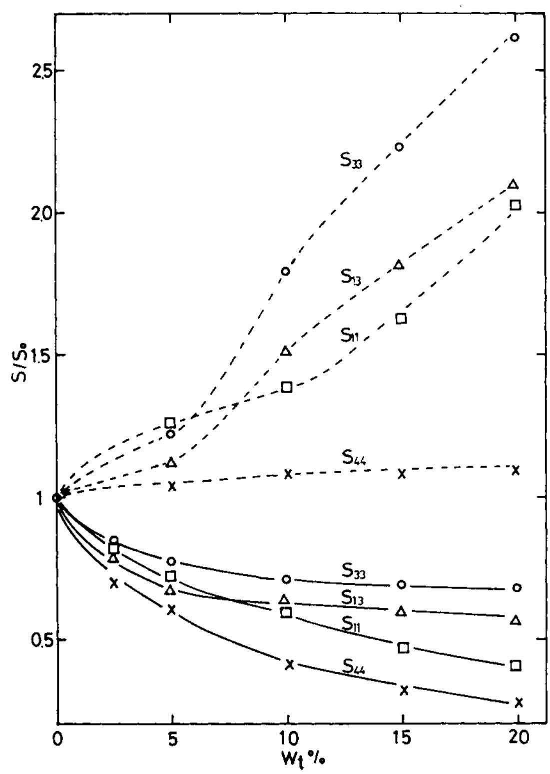


Fig. 5. Relative compliances S/S^0 of the oriented LDPE composites filled with A300 or G731 fillers plotted against filler content. S and S^0 are the compliances of oriented composites and oriented pure LDPE, respectively: (—) 70 Å; (- - -) 35 μ.

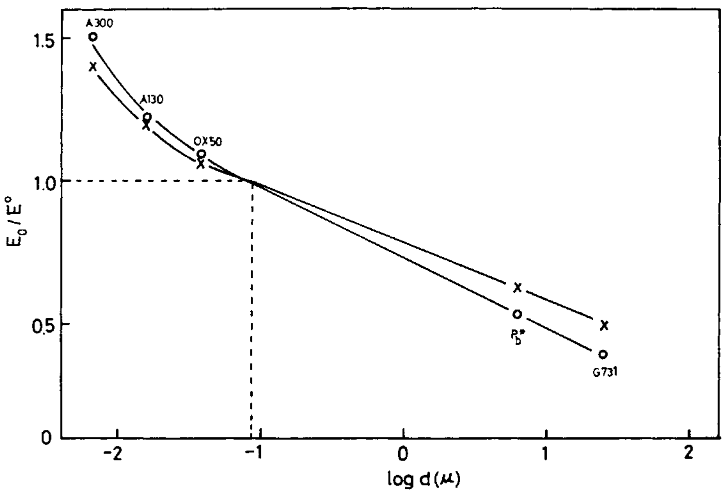


Fig. 6. Relative modulus E_0/E^0 plotted against logarithm of filler size in micron units for oriented LDPE composites. E_0 and E^0 are Young's moduli of the oriented LDPE composites in the direction of the initial draw axis and of oriented pure LDPE. Points P_b^* are Funada's data for oriented LDPE composites filled with lead glass with an average diameter of 6 μ[9]: (O) 20 wt %; (X) 10 wt %.

Extremely small (70 Å) filler particles probably have a stronger reinforcing effect than 35-μ particles in unoriented composites and 70-Å filled composites have smaller fraction of voids than 35-μ filled ones in the oriented state. These results show that extremely small particles comparable to the size of the LDPE crystalline region have a prominent reinforcing effect in the oriented polymer matrix. This filler size effect may be applied to other composites of any crystalline polymers.

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