Effect of Filler Particle Size on Dynamic Mechanical Properties of Poly(methyl Methacrylate)

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Synopsis

Dynamic mechanical properties of poly(methyl methacrylate) (PMMA) filled with mica flakes (M) or glass beads (G) were investigated as functions of particle size and filler concentration. With increasing particle size, dynamic modulus E' slightly decreases for system G, while it increases rapidly at first and then approaches the limiting value for system M. Primary dispersion temperature T_α increases with increasing filler concentration. With increasing particle size, T_α decreases for system G but increases for system M. For the mica-filled system, the effect of particle size on the modulus can be explained in terms of orientation of the filler by comparing the experimental data with Wu's and Padawer and Beecher's predictions of the modulus. In order to explain the dependence of T_α on particle size and concentration, an equation for T_α has been proposed:

$$T_\alpha = K_f \ln S$$

where K_f is a constant and S is the specific surface area of filler per gram of polymer. For system G, T_α can be expressed by the above equation, irrespective of particle size and filler concentration. In the case of system M, it is suggested that T_α is affected also by orientation in addition to the surface area of the filler.

INTRODUCTION

Mechanical properties of filled polymers are affected by size, shape, and orientation of fillers, in addition to the adhesive strength between polymer and filler. In designing composite materials with desirable properties, it is very important to understand the influence of the above factors.

It has been reported that mica, a two-dimensional filler, reinforces the modulus of composite to an extraordinary degree compared to glass beads[1-3] and, when the orientation of the flakes is good, increases the modulus.[4] The dependence of the modulus of composites upon the flake aspect ratio (ratio of average diameter to thickness) was investigated theoretically by Wu[5] and Padawer and Beecher.[6] Lusis et al.[7] reported on the dependence of the flexural properties of mica-reinforced plastics upon the flake aspect ratio. It is interesting to examine the effect of orientation upon the modulus of composites as function of particle size and mica concentration.

Shifts in glass transition temperature T_g to higher temperatures as a function of filler concentration have been reported for composites involving a wide variety of polymers and fillers.[8-13] The glass transition temperature has been shown to be independent of filler size.[14-16] However, since the increase in T_g is due to the segmental immobilization on the filler surface, it will be more directly affected by the surface area than by the volume fraction of the filler. Further, orientation of the filler would be expected to influence the primary dispersion

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temperature corresponding to the glass-to-rubber transition, inasmuch as dynamic mechanical measurement reflects long-range restriction of segmental motion.

The purpose of this paper is to investigate the effect of particle size of the plate-like filler and, for comparison, the spherical filler on the dynamic modulus and the primary dispersion temperature of filled PMMA.

EXPERIMENTAL

Mica flakes and glass beads were used as plate-like and spherical fillers, respectively. Muscovite mica flakes were obtained by crushing mica paper mechanically and sieving it for narrow particle size distributions. The mica flakes were dried over 24 hr at 120°C before use. The thickness of the flake was determined to be 0.36 μm by the BET method. The glass beads, of narrow particle size distributions, were commercial soda lime-type beads (supplied by Toshiba Glass Beads Co.). The surfaces were cleaned by refluxing in ethanol. The polymer used as matrix was poly(methyl methacrylate) (supplied by Mitsubishi Rayon Co.).

The composites were prepared by mixing various amounts of filler in roughly 10% dichloromethane solutions of the polymer. The solvent was removed slowly at room temperature and then dried for one to two weeks on a rotary pump until the weight of the mixtures became constant. For testing, the samples were prepared by compressing the dried mixture in a mold from 100° to 150°C, depending on the filler content in the mixture. The volume fractions of the fillers in the composites were determined from the residue by burning out the specimen at 500°C for 3 hr in air. Voids contents (%) were determined from the calculated and observed densities of the composites. The densities of the mica, glass bead, and PMMA were 2.74, 2.56, and 1.18, respectively. Table I lists the volume fraction of the fillers, particle size of the fillers, and void fraction of each sample.

Dynamic mechanical properties were measured over the temperature range from room temperature to about 200°C at a frequency of 10 Hz by a viscoelastic spectrometer (Iwamoto Seisakusho Co. Ltd. Kyoto).

RESULTS

Figure 1 shows the temperature dependence of storage modulus E' and loss modulus E'' for series M1 and G1. For the mica flake-filled samples, the increase in E' by loading is outstanding over the whole temperature range compared to the glass bead-filled samples. The primary dispersion temperature T_α, which can be ascribed to the onset of micro-Brownian motion of the chain segments, corresponding to the glass-to-rubber transition, was observed at 119°C for the unfilled PMMA. The T_α shifts to a higher temperature with increasing filler concentration. The increase in T_α by loading is larger for the M1 than for the G1 series. Figure 2 shows the dependence of the increment in T_α on filler volume fraction for both series.

Figure 3 shows the temperature dependence of the storage modulus E' and loss modulus E'' for the samples loaded by roughly the same volume fraction of filler having various particle size. With increasing particle size, E' slightly de-

TABLE I
Sample Characterization

Sample no.	Volume fraction of filler, %	Volume fraction of void, %	Particle size, μ
M1-1	7.9	0.23	
M1-2	16.0	0.49	41
M1-3	24.8	0.26	(300–400 mesh)
M1-4	39.3	1.69	
M1-5	63.8	2.05	
M2-1	6.7	3.47	
M2-2	14.2	2.47	163
M2-3	21.2	0.80	(80–100 mesh)
M2-4	25.8	3.90	
M3-1	19.0	3.04	324 (42–48 mesh)
M4-1	8.7	4.10	715
M4-2	15.1	3.75	(20–28 mesh)
M4-3	26.0	4.83	
M5-1	18.8	4.08	1785 (8–14 mesh)
G1-1	18.4	1.21	
G1-2	35.8	1.59	40
G1-3	67.3	2.67	
G2-1	16.8	2.43	100
G3-1	18.0	3.87	200
G4-1	15.8	4.09	400

creases for the glass bead-filled system, but increases greatly for the mica-filled system, over the whole temperature range. Dependence of T_α on particle size of mica flakes was different from that of the glass bead-filled system, namely, T_α decreases with increasing particle size for the glass bead-filled system while T_α increases with increasing particle size for the mica-filled system. Figure 4 shows the temperature dependence of the relative modulus $E'_{rel} = E'_c/E'_r$, where E'_c and E'_r are the modulus of composite and resin, respectively. E'_{rel} slightly changes with temperature in the glassy state, owing to the small internal stress in the samples.

DISCUSSION

Effect of Filler Size on Dynamic Modulus E'

Figure 5 shows the dependence of E'_{rel} upon particle size for both systems G and M with nearly the same filler volume fraction. The data in Figure 5 were obtained by extrapolation of relative modulus–temperature data to T_α in order to eliminate the effect of induced stresses on the modulus. In Figure 4, the relative modulus increases with temperature in the transition region. In general, relative modulus is larger for the rubbery region than for the glassy region, since the difference between moduli of matrix and filler is larger in the rubbery state. For system G, E'_{rel} slightly decreases from about 1.20 to 1.05 when particle di-
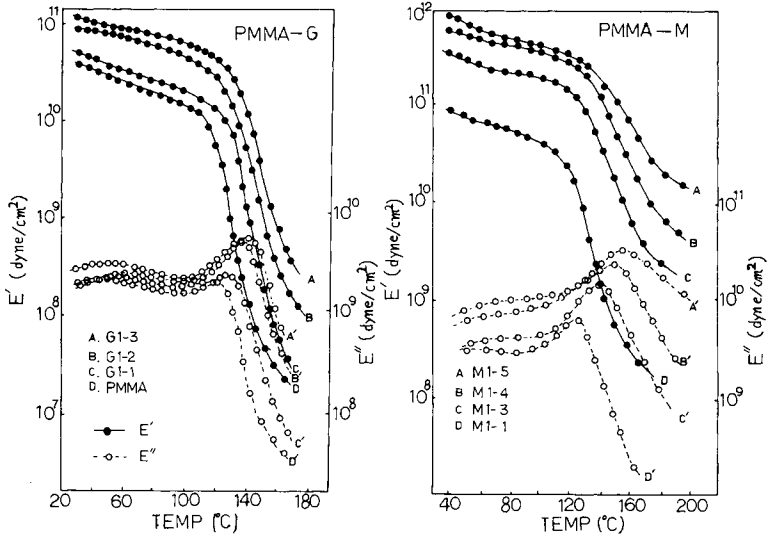
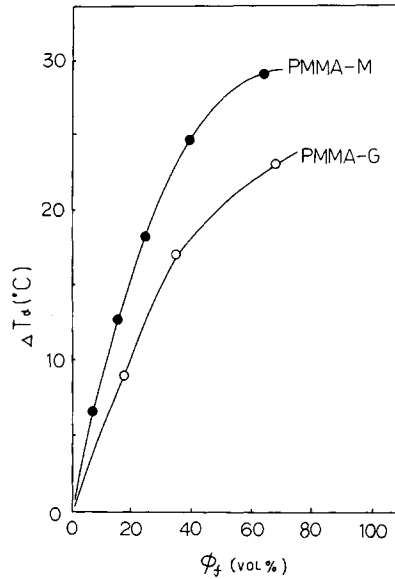Fig. 1. Temperature dependence of storage and loss moduli for series G1 and M1.

Fig. 2. Shift in T_α as a function of filler concentration.

ameter varies from 40 μm to 400 μm. On the other hand, for system M, E'_{rel} rapidly increases and approaches a limiting value with increasing particle size.

For the spherical particle-filled system, the dependence of the relative modulus on particle size has been explained in terms of the stress field produced within the specimen during experiment[14] or the packing density of the filler in the composite.[15] It is not the purpose of this study to make clear the small effect of particle size.

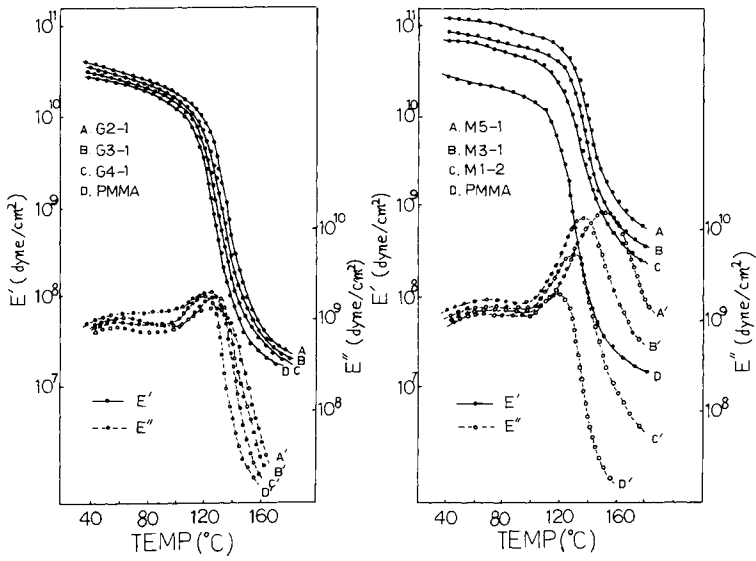The behavior observed in Figure 5(b) is similar to the flexural modulus de-

Fig. 3. Temperature dependence of storage and loss moduli for the samples loaded by roughly the same volume fraction of the fillers with various particle sizes.
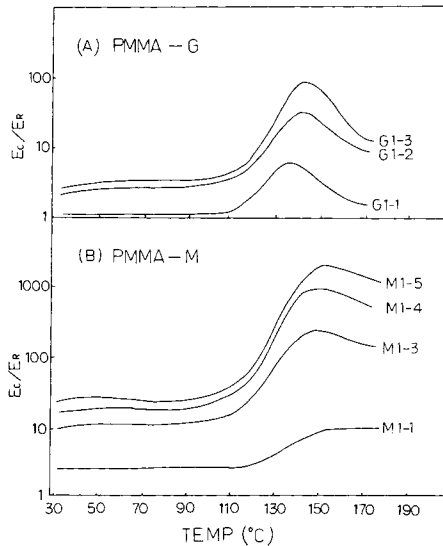

Fig. 4. Temperature dependence of relative modulus for series G1 and M1.

pendence on the aspect ratio of the mica flake reported by Lusis et al.[7] The flexural modulus at volume fraction of filler $\phi_f = 0.5$ reported in that study showed only a slight increase with increasing aspect ratio above $\alpha = 100$, and the experimental data were explained by Padawer and Beecher's theory. Our experimental results show a further increase with increasing particle size above the smallest particle size (M1), which corresponds to $\alpha = 114$. This seems to result from the difference between the orientation degrees of the mica flakes in both composites.
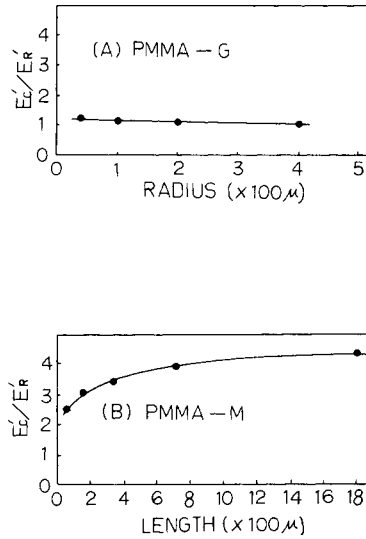
Fig. 5. Relative modulus vs particle size: (a) ϕ_f = ca. 17 vol-%; (b) ϕ_f = ca. 19 vol-%.

In order to examine the influence of the particle size on the modulus for the mica-filled system, the dependence of the modulus upon the filler concentration was determined for each particle size in Figure 6.   The experimental data points show the void-corrected relative moduli.[2]   The experimental data were compared with the results calculated according to Wu's theory, which predicts the modulus of a composite with randomly oriented disc-shaped fillers, and according to Padawer and Beecher's theory, which predicts the planar type of reinforcement. The calculation according to Wu's theory was carried out by assuming a Poisson's ratio ν = 0.25 for the matrix, filler, and composite for simplicity.   A value of 7.1
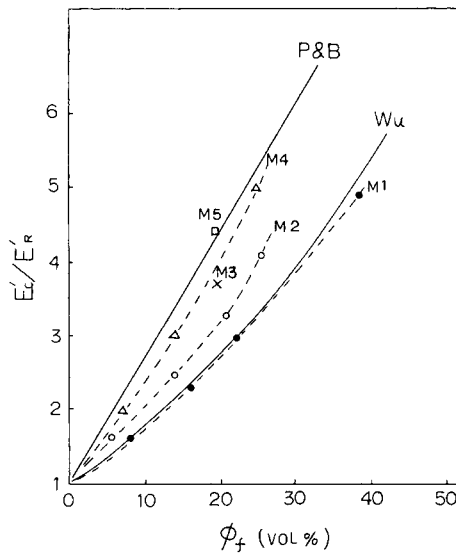

Fig. 6. Relative modulus vs filler volume fraction of mica-filled samples.

$\times 10^{11}$ dynes/cm^2 was used as Young's modulus of the mica flake. The calculation according to Padawer and Beecher's theory was carried out with aspect ratio $\alpha = 1000$. The M1 series lies near Wu's prediction over the whole loading range studied here. With increase in particle size, both series deviate from Wu's prediction in the higher loading region and approach Padawer and Beecher's line; and, finally, the M5 series, with the largest particle size, lies on Padawer and Beecher's line.

Figure 7 shows the dependence of E'_{rel} on the aspect ratio at different values of ϕ_f determined from the experimental curves in Figure 6. The results calculated by Padawer and Beecher's theory are also shown as dotted lines in the figure. The predicted lines indicate that the relative moduli are independent of aspect ratio above $\alpha = $ ca. 200 at any volume fraction of the filler. On the other hand, the observed relative moduli still continue to increase with increasing aspect ratio over $\alpha = 200$ and approach the theoretical lines at the higher aspect ratios. The increase in relative moduli with aspect ratio becomes more considerable as ϕ_f increases. The critical values of the aspect ratios when the observed relative moduli amount to 95% of the theoretical values are shown by the vertical arrows in the figure. The critical values of $\alpha = $ ca. 1800, 1200, and 800, correspond to $\phi_f = 10$, 19, and 25, respectively, indicating that the critical values are approximately inversely proportional to ϕ_f.

In conclusion, in the case of the plate-like filler, the orientation of the flakes depends on the product of ϕ_f and α, and the modulus of the composite can be expressed by Padawer and Beecher's equation when the product is over a characteristic value dependent on the specimen thickness.

Effect of Filler on Primary Dispersion Temperature T_α

T_α increases with volume fraction of the filler ϕ_f, reaching a nearly constant value, as shown in Figure 2. This shape of the curve suggests that all the segments are restricted under the influence of the filler above a specific filler concentration. The thickness of the matrix under the influence of the filler surfaces can be estimated from the dependence of T_α on the filler concentration. The portion of the polymer matrix V_R under the influence of the filler surfaces can be expressed by

$$V_R = V_T \phi_f \bar{a} \delta \tag{1}$$

where V_T is the total volume of the composite, $\bar{a}$ is the specific surface area of the filler, and δ is the thickness of influence range around each filler particle. When eq. (2) or (3) is satisfied, the entire polymer phase is exposed to the in-
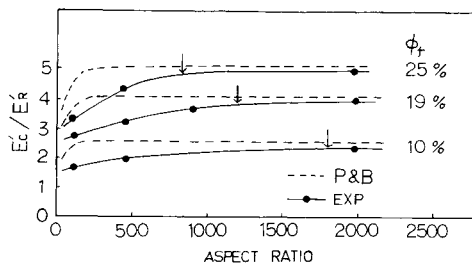

Fig. 7. Dependence of relative modulus on aspect ratio at different values of ϕ_f.

fluence of the filler:

$$V_R = (1 - \phi_f)V_T \qquad (2)$$

$$\phi_f = \frac{1}{(1 + \bar{a}\delta)} \qquad (3)$$

A rough estimation of δ, from the volume fraction of the filler where T_α reaches the upper limiting value, leads to values of about 0.5 μm and 1 μm for the glass bead-filled and the mica-filled system, respectively.

The influence of particle size on T_α for the glass bead-filled system differs from that of the mica-filled system. Figure 8 shows the dependence of T_α on particle size for both G and M systems with nearly the same filler volume fraction. At constant concentration, the total surface area of the glass beads contained in the composite is inversely proportional to the radius of the beads. On the other hand, the total surface area of the mica flakes contained in the composite is nearly independent of particle size, since the thickness of the flakes is extremely small compared with their width. Particle size, as well as filler concentration, determines the interfacial area which plays a large part in determining the magnitude of the ineraction between filler and matrix. In the case of the glass bead-filled system, the increase in T_α seems to be affected mainly by the surface area of the filler, while in the case of the mica-filled system, the increase in T_α seems to be also affected by another factor in addition to the surface area. It is necessary to examine what factors exert a substantial influence on T_α.

In general, bulk polymers are usually considered to exist in the form of three-dimensional network structures because their molecular chains are aggregated by various junctions, e.g., chemical crosslinking, chain entanglement, and other intermolecular couplings. The addition of fillers to polymers produces another junction point which results from the segmental adsorption on the filler surface.
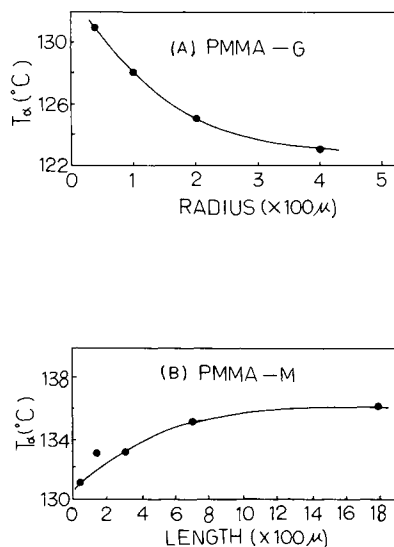

Fig. 8. T_α vs particle size: (a) ϕ_f = ca. 17 vol-%; (b) ϕ_f = ca. 19 vol-%.

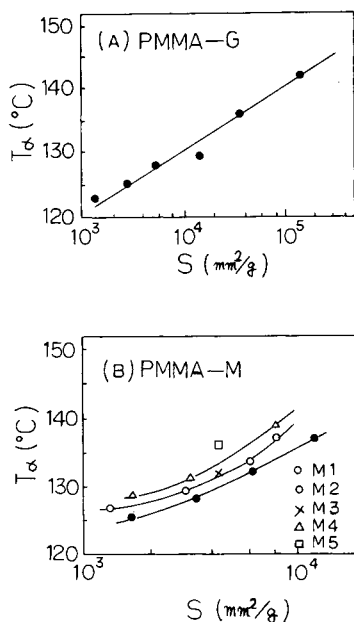Fig. 9. T_α vs filler surface area per gram of polymer matrix.

It is well known that introducing crosslinkages into a polymer raises the glass temperature.[17] In addition, there is a decrease in the specific volume, since introducing crosslinkages involves the exchange of van der Waals bonds for shorter, more compact primary bonds. Thus, the process of crosslinking should affect the segmental mobility. It should be possible to examine the filled polymers in the same way as the previous treatments[17,18] on network polymers.

Fox and Loshaek[17] have derived an equation which relates T_g to the degree of crosslinking in a polymer. However, the equation fails at higher degrees of crosslinking because of the simple assumptions used in the development. It has been found for several types of polymers that the dependence of T_g on crosslinking density can be predicted by eq. (4) even at higher degrees of crosslinking ρ[18]:

$$T_g = K_1 \ln K_2 \rho \qquad (4)$$

where K_1 and K_2 are characteristic constants for a homogeneous series of polymers. If one junction point is assumed to correspond to one site of absorption on the filler surface in a polymer, ρ in eq. (4) could be replaced by S, which is the specific surface area of filler per gram of polymer matrix; S is related to polymer weight fraction x by eq. (5):

$$S = \text{(specific surface area of filler)} \times x/1 - x \qquad (5)$$

Figure 9 shows T_α versus logarithm of S plots for both systems G and M. In the glass bead-filled system, a linear relation can always be obtained irrespective of particle size and filler concentration. In the composite system with isotropic particles, the increase in T_α by filling can be described by eq. (4) in the same way as the treatments on network polymers. On the other hand, for the mica-filled system, a group of curves classified by particle size is obtained. The curves are

shifted upward and are more curved with increasing particle size, although those of the M1 series are approximately linear. All curves do not approach the same value of T_α even in the lowest S value studied here. They would extrapolate to $T_\alpha = 119°C$ for the unfilled polymer in a very low S value. As an explanation for the increase in T_α for the mica-filled system, orientation effect can be assumed besides the surface area of the filler, in view of the similar dependences of E'_{rel} and T_α upon particle size, as shown in Figures 5(b) and 8(b).

Prediction of the temperature shift in T_α by filling has been offered by Zorll[19] who has calculated it by means of the theory based on a simple model in which the filler particles are assumed to be of uniform size, of cubic shape, and dispersed in such a manner as to occupy the point of a cubic-shaped lattice. In view of the simplification of the model, better fitting of the experimental results to the theory cannot be expected. However, the theory shows that the temperature shift appears as a consequence of the slight deformability of the filler. The modulus of a composite with fibers randomly oriented in one plane is approximately one third that for one with fibers uniaxially oriented.[20] The load-carrying capacity of fibers increases rapidly with increasing the degree of orientation with line of stress, becoming considerable for orientation less than about 15°.[21] As mentioned above, the deformation of the mica flakes becomes larger with increasing orientation of the flakes, and an increase in T_α seems to appear as a result.

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