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Effect of Orientation of Two-Dimensional Filler on Dynamic Mechanical Properties of Cured Epoxy Resin

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Synopsis

Dynamic mechanical properties of cured epoxy resin filled with mica flake, as two-dimensional filler, were investigated over the temperature range from room temperature to 200°C. Two series of composite specimens were examined. One is series RM, containing ill-oriented mica flakes, and another is RMB, containing mica flakes oriented in the direction parallel to the specimen surface. Both tensile and shear moduli for RMB series were determined by dynamic mechanical experiments. The tensile modulus for RMB series was always higher than that for RM series over the whole temperature range. The shear modulus for RMB series was low, compared with that of the tensile modulus in the rubbery state. The behavior of the modulus reinforcement, observed both in the glassy and rubbery states, was compared with recently proposed theories of Wu and Padawer and Beecher. In the glassy state, the tensile modulus of RM series follows Wu's theory, while that of the RMB series agrees with Padawer and Beecher's theory. In the rubbery state, the tensile modulus of each series cannot be well explained by either theory. It was proposed that the tensile stress applied to the specimen was converted to shear stress in a thin resinous layer sandwiched by two mica flakes. The modulus behavior of the RMB series can be fully explained by this model.

INTRODUCTION

The addition of fillers to polymers can produce composite materials with a number of desirable properties. In general, fillers increase the modulus of composites. A large number of theories have been developed to explain the effect of fillers on mechanical properties, although almost all the equations have been based on spherical particles.[1] The effect of filler shape on the elastic modulus of a composite is not well understood. Orientation of filler will be an important feature in the case of nonspherical fillers.

Recently, Wu[2] has developed a theory for modulus of composite systems which takes the effect of filler shape into account. The theory predicts that randomly oriented disc-shaped particles should give rise to a higher modulus than needle- or spherical-shaped fillers. Padawer and Beecher[3] have proposed a simple equation predicting its modulus for the composite containing two-dimensional fillers as flakes and ribbons which are uniformly spaced and aligned in plane-parallel.

Nielsen et al.[4] studied the dynamic mechanical properties of polystyrene filled with mica. Hirai and Kline[5] and Jenness and Kline[6] investigated the dynamic mechanical properties of epoxy resin filled with graphite and mica.

Padawer and Beecher[3] reported flexural modulus of glass flake–epoxy composite. Lusis et al.[7] investigated the effect of flake aspect ratio on the flexural properties of mica-reinforced plastics. Up to the present time, however, little experimental data appear to be available to support Wu's and Padawer and Beecher's equations.

The purpose of this study is to investigate the effect of orientation of mica flake on the dynamic mechanical properties of cured epoxy resin.

EXPERIMENTAL

Small muscovite mica flakes about 1 μ in thickness and 470 μ in width were used as the two-dimensional filler. Mica flakes were obtained by mechanically crushing a reconstituted mica paper supplied by the 3M Co. and sifted out (the 28–40 mesh portion was used). The thickness of the mica flake was determined from observation of the sections of mica mats by scanning electron microscopy.

Unfilled batches of epoxy were made with composition ratio of Epikote 828 (Shell Chemical Co.):methyl nadic anhydride:caprylic acid zinc salt = 100: 90:2 and cast into sheet specimens between two glass plates. Preparation of the composites (RM series) containing ill-oriented mica flakes was accomplished by mixing various amounts of fillers and resin with the same composition ratio as unfilled ones in a mortar and casting into sheet specimens between two glass plates. Preparation of the composites (RMB series), in which mica flakes were oriented in the direction parallel to specimen surface, was accomplished as follows. First, mica mats were prepared from mixtures of mica flakes and various small fractions of glass beads (in the 20- to 60-μ particle size range obtained from Toshiba Co.) as shown in Table I by a sheet machine. The mats thus obtained seem to have a different mean spacing distance between two neighboring mica flakes aligned in the thickness direction in each mat, corresponding to the amount of glass beads. Here, disorientation of mica mats by inserting a small amount of glass beads between mica flakes could be small because the size and amount of mica flakes are far larger than those of glass beads. Next, filled specimens were made by impregnating these mica mats with the same resin as unfilled specimens. For comparison,

TABLE I
Composition (vol-%)

Sample	Resin	Mica	Bead
RM1	93.8	6.2	0
RM2	83.6	16.4	0
RM3	71.4	28.6	0
RM4	51.1	48.9	0
RMB1	90.4	7.7	1.9
RMB2	86.0	12.6	1.4
RMB3	71.7	17.6	0.7
RMB4	64.0	36.0	0
RB1	61.4	0	38.6
RB2	50.4	0	47.6
R	100	0	0

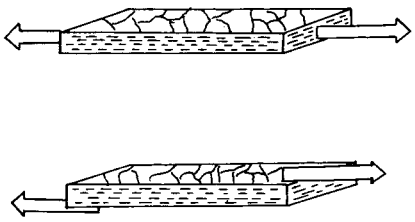

Fig. 1. Two kinds of deformation modes in viscoelastic experiment. (a) Tensile deformation. (b) Shear deformation.

the composites (RB series) containing the same glass beads were prepared as described above. These samples were cured at 150°C for 16 hr followed by 200°C for 3 hr. Table I lists volume fractions of filler in each composite determined from the residue by burning out the specimen at 500°C for 3 hr in air.

Measurements of dynamic mechanical properties were carried out over the temperature range from room temperature to 200°C at 1 Hz by a viscoelastic spectrometer (Iwamoto Seisakusho Co. Ltd., Kyoto, Japan). In each specimen, both tensile and shear moduli were determined by two kinds of deformation modes as shown in Figure 1.

RESULTS

Figure 2 shows the temperature dependence of tensile storage modulus E' for the RM series. Figure 3 shows the temperature dependence of tensile E' and shear storage modulus G' for the RMB series. For mica flake-filled sam-

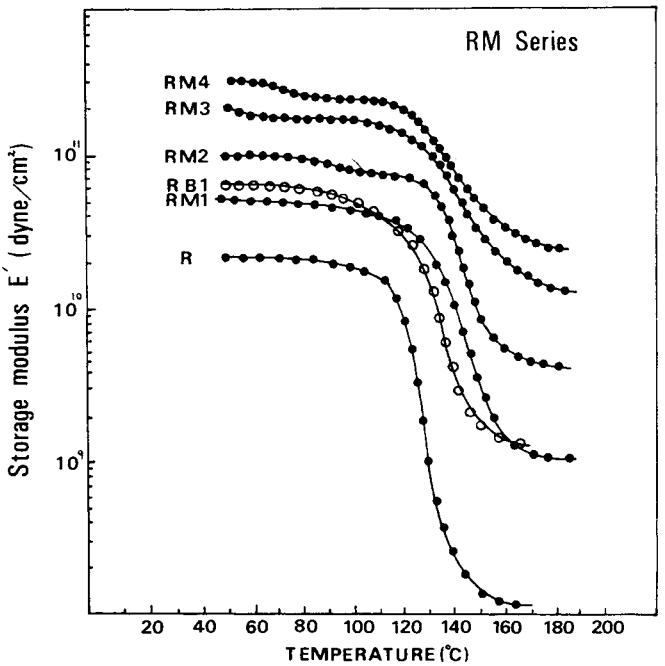

Fig. 2. Temperature dependence of tensile storage modulus on RM series.

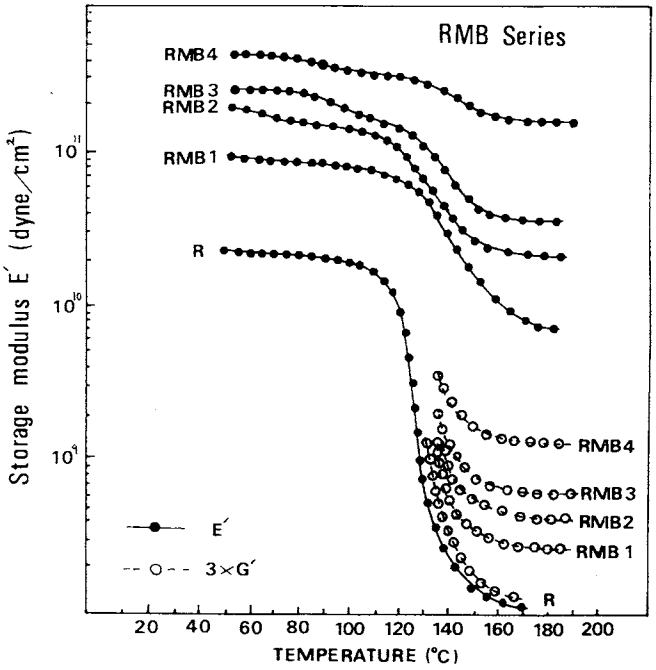

Fig. 3. Temperature dependence of tensile and shear storage modulus on RMB series.

ples, the increase in tensile storage modulus by loading is outstanding over the whole temperature range. Especially, values of E' in the rubbery state for mica flake-filled samples are extraordinarily high compared to values for glass bead-filled samples. But the increase in shear storage modulus G' is minor compared to that in tensile storage modulus E' by loading, as shown in

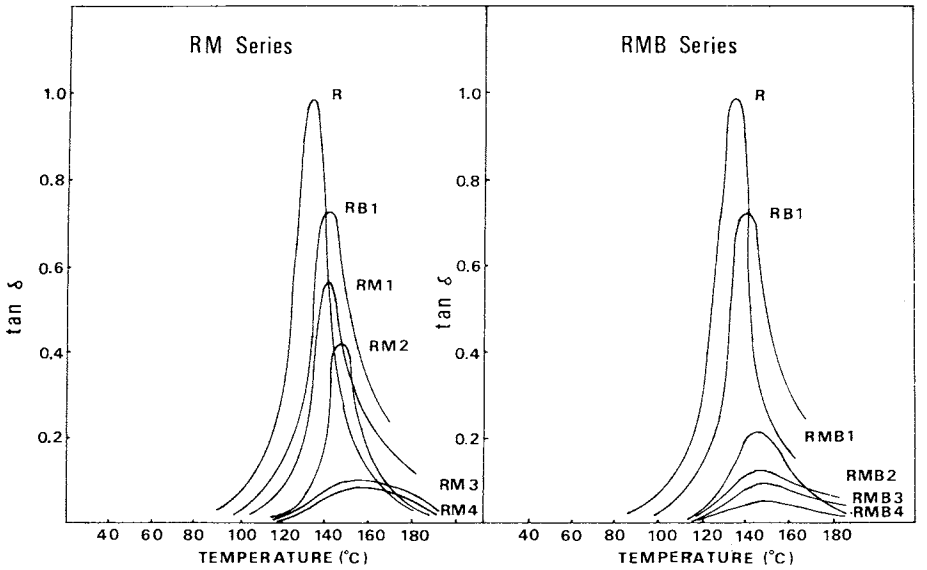

Fig. 4. Temperature dependence of tan δ on RM and RMB series.

Figure 3. Values of E' for the RMB series are always higher than for the RM series over the whole loading range.

Temperature dependence of mechanical loss tan δ is shown in Figure 4. Mechanical loss peaks were observed over the temperature range from about 130° to 150°C for unfilled and filled samples on tan δ curves. These peaks shift to higher temperature with increase in filler concentration. They can be ascribed to the onset of micro-Brownian motion of matrix chain segments, corresponding to glass-to-rubber transition.

DISCUSSION

Relative modulus Ec'/Er' (Ec' and Er' are modulus of filled and unfilled samples, respectively) is plotted against temperature for each sample in Figures 5 and 6. The relative modulus in the glassy and rubbery states remains nearly constant, except for the transition region. Change in relative modulus with temperature is primarily due to induced tensile stresses by the difference in thermal expansion coefficients of the phases.[8] The experimental result shows that the induced tensile stress is not present for the present filled systems.

Relative modulus is plotted against volume fraction of filler in the glassy and the rubbery states in Figures 7 and 8, respectively. In these figures, calculated results using Kerner's, Wu's, and Padawer and Beecher's equations are also shown. Here, 2.2×10^{10} and 1.1×10^{8} dynes/cm^2 were used as the

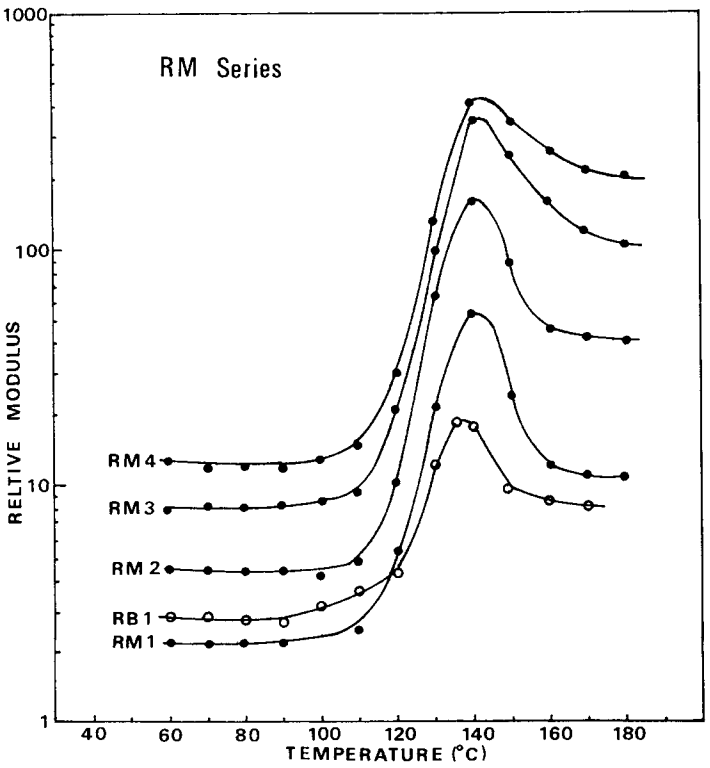

Fig. 5. Temperature dependence of relative modulus on RM series.

30° and 180°C values of the matrix dynamic moduli, respectively. Young's modulus of the mica flake was determined as 7.1×10^{11} dynes/cm^2 from the tensile deformation experiment. The calculated results using Kerner's equation are considerably lower than the experimental values for each sample, although Kerner's equation can not be expected to hold for nonspherical fillers. In general, Kerner's predictions have been found to be too low.[9]

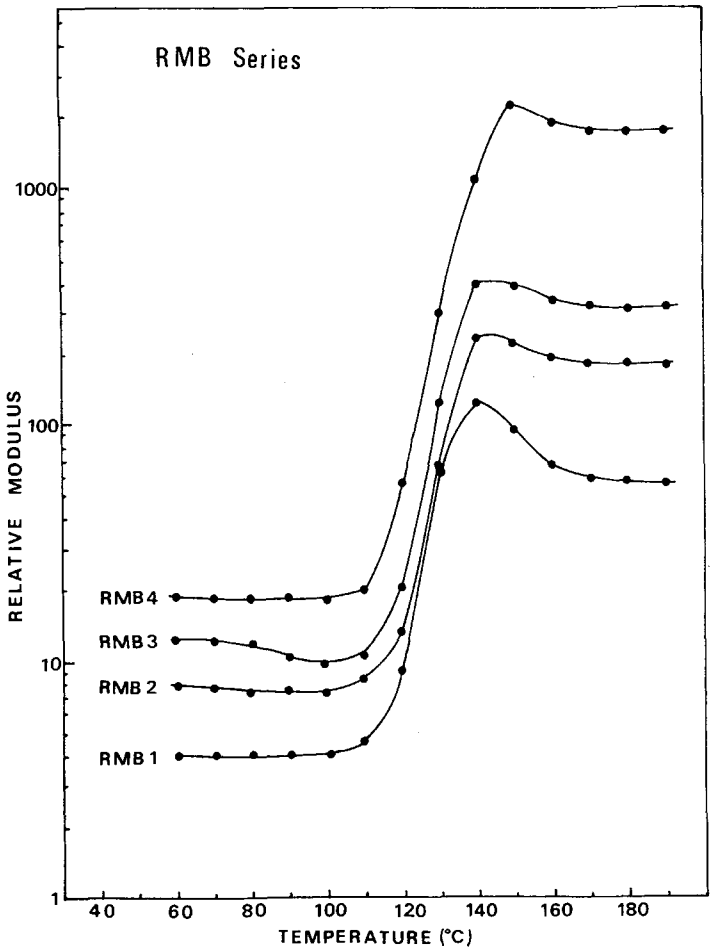

Fig. 6. Temperature dependence of relative modulus on RMB series.

The effect of inclusion shapes on elastic moduli has been recently investigated by Wu.[2] Wu's theory predicts that disc-shaped inclusion has the greatest effect in changing the elastic moduli of the matrix. For a composite with randomly oriented disc-shaped fillers, Wu proposed the following relationship:

$$\frac{1}{Gc} = \frac{1}{Gr}\left\{1 + \frac{\phi f}{5}\left[\frac{2}{1+A} + 1 + \frac{2 + (2 - 4R/3)A + 2(3 - 4R)B}{1 + A + (3 - 4R)B}\right]\frac{Gr - Gf}{Gc}\right\} \tag{1}$$

where

$$A = \frac{Gf}{Gc} - 1$$

$$B = \frac{1}{3}\left(\frac{Kf}{Kc} - \frac{Gf}{Gc}\right)$$

$$R = \frac{3Gc}{3Kc + 4Gc}$$

and ϕf = volume fraction of the filler, G = shear modulus, and K = bulk modulus.

In these equations, the composite, the filler, and the matrix resin are specified by the subscripts of c, f, and r, respectively. Equation (1) expresses the limiting case of the prolate spheroids, $a = b \gg c$ (the radii of the ellipsoid are denoted by a, b, and c). In order to simplify the calculation, the Poisson's ratio $\nu = 0.25$ was assigned for the matrix, filler, and composite in eq. (1), since ν does not exert a strong influence on the calculated value of the modulus of the composite. As the aspect ratio of mica flake, $c/a = 0.002$ was used.

Padawer and Beecher[3] have proposed the theory to predict the planar type of reinforcement. The composite modulus Ec can be stated simply as

$$Ec = (Ef)\,\phi f\,(\mathrm{MRF}) + Er\,(1 - \phi f) \tag{2}$$

$$(\mathrm{MRF}) = 1 - \frac{\tan h(u)}{u} \tag{3}$$

$$u = \alpha \frac{Gr \cdot \phi f}{Ef(1 - \phi f)} \tag{4}$$

where α is aspect ratio of filler defined by α = w/t (w and t are width and thickness, respectively). For $0.1 \leq \phi f \leq 0.7$, the factor (MRF) varies from about 0.96 to 0.99 at 30°C and from about 0.58 to 0.91 at 180°C. Here, α = 470 and Ef/Gr = 101 at 30°C and $Ef/Gr = 1.92 \times 10^4$ at 180°C were used to carry out the computation.

For the relative moduli of the composites in the glassy state, the experimental data points for the RM series lie near Wu's curve. On the one hand, the experimental results for the RMB series lie near Padawer and Beecher's prediction, as shown in Figure 7. Here, the experimental data points have smaller slopes at the higher concentrations than those at the lower ones. The decrease of modulus at the higher concentrations seems to be due to voids, because the correction of modulus due to deformation of the apparatus was done for all experimental data. Hirai and Klein[5] derived a void correction factor based on Wu's formula for spherical filler particles by assuming a composite with voids to be a homogeneous material containing spherical particles of zero modulus. They assumed a composite poisson ratio $\nu = 0.2$, which leads to

$$\frac{Ecv}{Ec} = 1 - 2Vv \tag{5}$$

where Ecv is the modulus of a composite with a volume fraction of voids Vv. The samples RMB4 and RM4 with the highest values of ϕf had voids con-

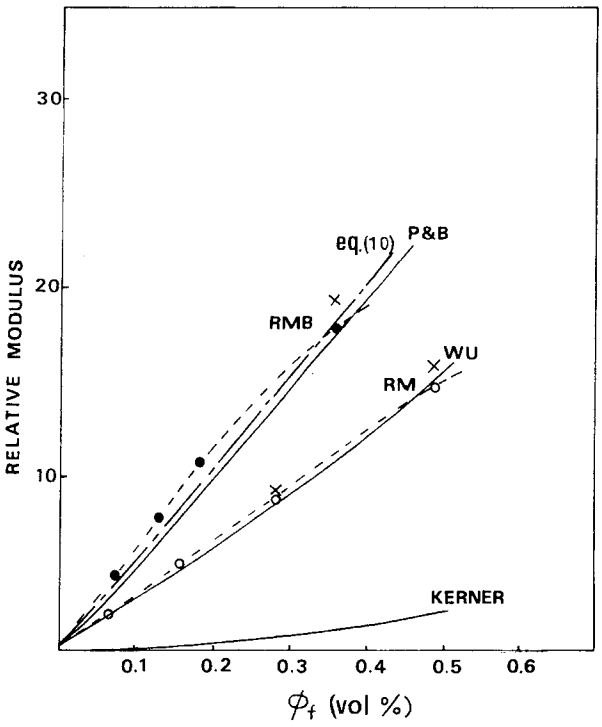

Fig. 7. Relative modulus vs. volume fraction of filler relations on each sample at 30°C.

tents Vv = 0.035 and 0.055, and the void correction factors computed by eq. (5) are 0.93 and 0.89, respectively. The void-corrected relative modulus was calculated and is shown by X in Figure 7. For the RM series, the flakes must be partly oriented at the higher concentrations. However, the increase in relative modulus due to the partial orientation was relatively minor within the loading range studied here. These results show that the RM series consists of nearly random orientation, while the RMB series consists of planar orientation of the flakes in the composite.

In the case of the rubbery state, the relative tensile moduli of the RM and RMB series do not fit to any previous theoretical predictions. That is, the RM series falls below Wu's and Padawer and Beecher's, but above Kerner's equations. The RMB series increases steeply with filler loading and rises above Wu's and Padawer and Beecher's predictions in the higher loading regions. Though the induced tensile stresses which exert an influence upon the modulus of the composite vary with temperature, their variations are minor, as shown in Figures 5 and 6.

On the contrary, the relative moduli of the RMB series measured by shear deformation mode are found to be very small compared with the tensile ones. They fall in a range which is similar to one usually met with particulate-filled systems.[9] They follow Kerner's prediction, as shown by the lowest curve in Figure 8.

None of the previous theories can explain the tensile modulus behavior of the composite sample in both the glassy and the rubbery states. For the ex-

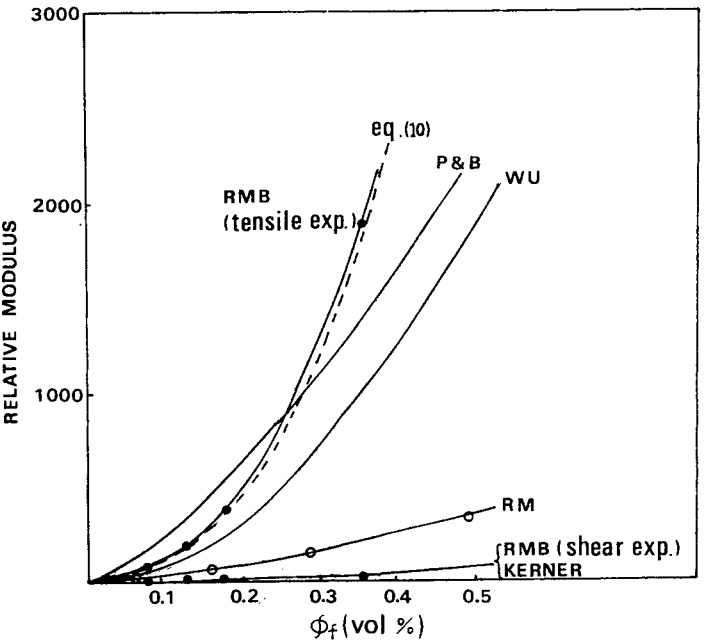

Fig. 8. Relative modulus vs. volume fraction of filler relations on each sample at 180°C.

planation of this fact as well as the modulus behavior by shear deformation mode, a new idea is needed.

It will be plausible to consider that for the RMB series, a major part of the tension applied to bulk specimen is converted to shear stress in thin polymeric layer sandwiched between two mica flakes. An equivalent mechanical model can be constructed to explain the validity of the above scheme more quantatively, as shown in Figure 9.

Mechanically, the model is composed of two kinds of elastic elements; one corresponds to shear stress between two mica flakes adjoining each other in the direction perpendicular to mica flake surface, and the other corresponds to tensile stress between two mica flakes adjoining each other in one plane. Response of the model under an applied tensile force F in the direction parallel to the mica flake surface can be expressed as in eqs. (6)–(9):

$$\frac{F}{n \cdot w} = Gr \cdot \frac{\Delta lr}{dr} \cdot l^2 + Er \cdot \frac{\Delta lr}{\beta \cdot l} \cdot dm \cdot Ed \tag{6}$$

$$\frac{F}{n \cdot w} = Em \cdot dm \cdot Ed \cdot \frac{\Delta lm}{l} \tag{7}$$

$$\Delta l = \Delta lr + \Delta lm = \frac{F}{n \cdot w} \Big/ \left(Gr \cdot \frac{l^2}{dr} + Er \cdot \frac{dm \cdot l}{\beta \cdot l} \right) + \frac{F}{n \cdot w} \Big/ Em \cdot dm \tag{8}$$

$$\frac{F}{n \cdot w} = \Delta l \left\{ \frac{1}{Gr \cdot \dfrac{l^2}{dr} + Er \cdot \dfrac{dm \cdot l}{\beta \cdot l}} + \frac{1}{Em \cdot dm} \right\}^{-1} \tag{9}$$

where Gr and Er are shear and tensile moduli of resin, respectively; Em is tensile modulus of mica flake; n and w are number of mica flakes aligned in

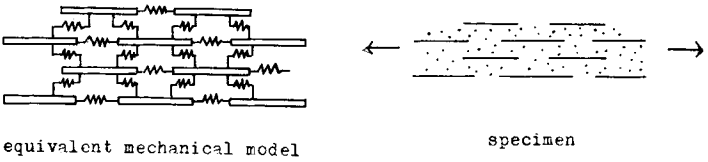

Fig. 9. Model explanation for (high rubbery) modulus of RMB series.

thickness and length directions of specimen, respectively; Δlr and Δlm are deformation of resin per mica flake and of one mica flake, respectively; $\Delta l = \Delta L/N$ (ΔL and N are macroscopic deformation of specimen and the number of mica flakes in a plane parallel to specimen length, respectively); l^2 is surface area of mica flake, assuming its square shape; dr and dm are thickness of one resin layer and mica flake, respectively; β is a factor which takes spacing and geometry of tensile stress field between neighboring mica flakes in an oriented plane. Here, eq. (7) takes the tensile deformation of mica flakes into account.

Equation (9) is rewritten as eq. (10), assuming $Er = 3Gr$ with regard to modulus of resin:

$$\frac{F}{n \cdot w} = Gr \cdot \frac{\Delta l}{dr} \cdot l^2 \left(\frac{1}{1 + \dfrac{3 \cdot dm \cdot dr}{\beta \cdot l}} + \frac{Gr}{Em} \cdot \frac{l^2}{dm \cdot dr} \right)^{-1}. \tag{10}$$

In the rubbery region, the second term in parenthesis in the right-hand side of eq. (9) is neglected because of $Gr(= 10^8$ dynes/cm$^2) \ll Em$ $(= 10^{12}$ dynes/cm$^2)$.

Accordingly, eq. (9) is simply rewritten as eq. (11):

$$\frac{F}{n \cdot w} = Gr \cdot \frac{\Delta l}{dr} \cdot l^2 \left(1 + \frac{3dm \cdot dr}{\beta \cdot l} \right) \tag{11}$$

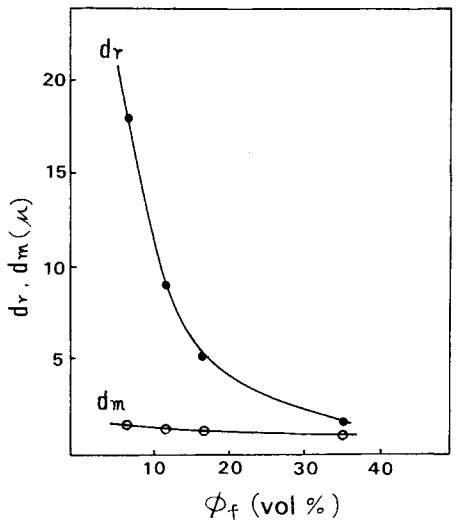

Fig. 10. Plot of dr and dm vs. volume fraction of filler relations on RMB series.

The second term in the right-hand side of eq. (11) can be neglected because it hardly exceeds 10^{-1} when dr is less than 100 μ. Modulus behavior for the whole temperature region including the glassy state can be analyzed by eq. (10). In the rubbery region, the calculated results analyzed by eqs. (10) and (11) are nearly the same.

Calculated values of relative modulus from eq. (10) assuming $dm = 1$ μ are plotted as the dotted lines in Figures 7 and 8. The experimental data are expressed satisfactorily by the calculated curve.

The thickness of resin layer dr may be computed by the equation from observed stress and strain of the RMB series. It is necessary to determine the number of layers n in order to carry out the computation. Thickness of specimen D is given by $n(dr + dm)$, and it can be assumed that the ratio dr/dm is proportional to the ratio of volume fraction of resin to mica, $\phi r/\phi f$, hence

$$n = D/dr(1 + \phi f/\phi r). \tag{12}$$

Calculated results by equation (10) are shown in Figure 10. Resin thickness dr decreases with ϕf, and its magnitude is comparable to direct microscopic data. Thickness of mica flake dm thus computed shows almost constant values. These results suggest that inserting a small amount of glass beads between mica flakes varies effectively the mean spacing distance between two neighboring mica flakes aligned in the thickness direction, without disturbing the orientation degree of the mica flakes.

The increase in α-peak temperature (T_α) by loading suggests the partial immobilization of portions of the polymer chains by their strong interaction with filler surface.

This pinning of the chains reduces the average segmental mobility just as crosslinking does and as a result, tends to increase the rubbery modulus. In the RB series, the increase in T_α is quite small and compares to the results reported by Lewis et al.[9] However, the greater increase in modulus for the RM series than that for the RB series is not considered to be substantially due to the segmental immobilization. It is shown on amine-cured epoxy resin systems[10] that the increase of 10°C in the α-peak position by crosslinking gives only an increase of several times in the rubbery modulus. The contribution of the segmental immobilization to the rubbery modulus of mica-filled system seems to be minor.

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