

Mechanical α -Dispersion and Interaction in Filled Polystyrene and Polymethylmethacrylate

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Synopsis

Dynamic mechanical properties of polystyrene (PS) and polymethylmethacrylate (PMMA) filled with glass beads and mica flakes have been investigated. The α -dispersion temperature (T_α) increases with filler content in each system. The increase in T_α is larger for PMMA than for PS in the case of the same filler; the increase in T_α is larger for mica than for glass in the case of the same polymer. Polymer-filler interaction energies have been estimated from heats of adsorption of the monomers of the filler surfaces determined by solid gas adsorption chromatography. The increase in T_α can be related to the extent of polymer-filler interaction energy. The thickness of the partially immobilized layer on the filler surface has been estimated to be the orders of 0.1 and 1.0 μm , respectively, for the mica and the glass-filled systems.

INTRODUCTION

Increases in the glass transition temperature T_g as a function of the filler content have been reported for composites involving a wide variety of polymers and fillers.¹⁻⁶ Such increases in T_g have been considered to be due to the consequence of polymer-filler interaction. In general, this interaction seems to include the interfacial forces between the filler and chain, the orientation of the chain in the immediate vicinity of the filler surface, the formation of an interface, nucleation of crystallization, and other physicochemical phenomena.

Yim et al.⁷ reported that for composites of four polymers filled with silicas of different surface properties, the increase in T_g was directly related to the extent of polymer-filler interaction energy. Lipatov and Fabuliak⁶ observed large shifts in the temperature minima of the spin-lattice relaxation time for polystyrene-polymethylmethacrylate copolymers adsorbed on silica and Teflon. On the contrary, they reported no difference in the magnitude of the shifts due to the silica and Teflon. They attributed their results to the configurational factors at the filler surfaces rather than the effects of polymer-filler interaction energy.

It is generally agreed that the thickness of the partially immobilized layer on the filler surface extends from about 20 to 100 \AA . However, a thickness of several hundreds \AA has also been suggested.^{4,5}

From the above citation of the literature, it is obvious that there is much diversity in the opinion of investigators regarding the effects of filler on the glass to rubber transition of polymers. The essential question in the present work revolves the magnitude of the bond strength between the filler and chain and the distance away from the surface at which the force field from the surface may be still in effect.

The purpose of the present work is to describe an investigation undertaken

to study the effect of glass beads and mica flakes on the mechanical α -dispersion temperature in polystyrene and polymethylmethacrylate chosen as representative amorphous polymers.

EXPERIMENTAL

Polymethylmethacrylate (PMMA) and polystyrene (PS) were not characterized for molecular weights, but degassed for 24 hr on a rotary pump before use. Muscovite mica flakes were obtained by crushing mica paper mechanically and sifted out (the 300–400 mesh portion was used). The thickness of the mica flakes was determined 0.36 μm by BET method. The mica flakes were dried over 24 hr at 120°C before use. The glass beads having the particle size range of the 20–60 μm are commercial soda-lime types (supplied by Toshiba Glass Beads Co.). The surface was cleaned by refluxing in ethanol.

The composites were prepared by mixing various amounts of fillers in roughly 10% dichloromethane solution of the polymers. The solvent was removed slowly at room temperature and then dried over 1 to 2 weeks on a rotary pump, until the weight of the mixtures becomes constant. For testing, the specimens were prepared by compressing the dried mixtures in the mold heated from 100°–150°C, depending on the filler contents in the mixtures. The volume fractions of the fillers in the composites were determined from the residue of specimens burned out at 150°C for 3 hr in air. Void contents (%) which were determined from the calculated and observed densities of the composites, did not exceed 3% in the specimens. Table I lists volume fraction of the fillers in each sample.

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

The heats of adsorption of the monomers on the filler surfaces were determined by solid-gas chromatography (Gaschromatograph Model G-8, Yanagimoto Seisakusho Co. Ltd., Kyoto). The retention time t_m of the monomer on the filler packed in a column was measured as a function of the temperature over 100°–200°C. Helium gas was used as the carrier gas of the constant flow rate. The heat of adsorption ΔQ was estimated from the temperature dependence of the retention time by the following equation⁸:

$$\log_{10} t_m = C - (\Delta Q/2.303R) \cdot (1/T) \quad (1)$$

where C is a constant.

TABLE I
Volume Fraction of Filler (%)

Sample	Filler (%)		Sample	Filler (%)	
	Glass	Mica		Glass	Mica
PMMA	0	0	PS	0	0
PMMA-G1	17.5	0	PS-G1	10.7	0
PMMA-G2	34.9	0	PS-G2	28.0	0
PMMA-G3	67.3	0	PS-G3	38.8	0
PMMA-M1	0	6.7	PS-M1	0	9.5
PMMA-M2	0	25.0	PS-M2	0	23.6
PMMA-M3	0	47.5	PS-M3	0	44.0
PMMA-M4	0	63.8	PS-M4	0	60.0

The fracture surface of the specimen was observed by a scanning electron microscope (SEM, JSM-2 Nihon Denshi Co. Ltd., Tokyo) in order to examine the adhesive state between polymer and filler.

RESULTS AND DISCUSSION

Figures 1 and 2 show the temperature dependence of storage modulus E' and loss modulus E'' observed at 10 Hz for the PS and PMMA composites, respec-

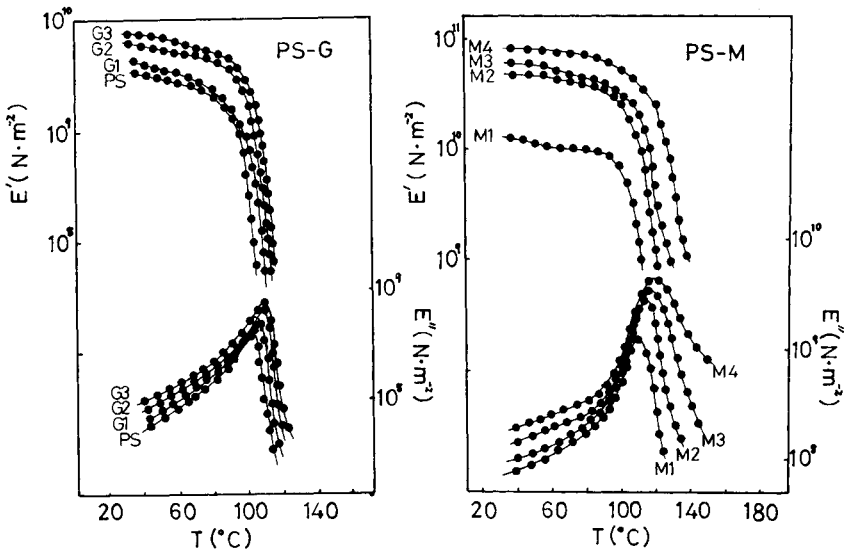


Fig. 1. Temperature dependence of storage modulus E' and loss modulus E'' for the PS composite.

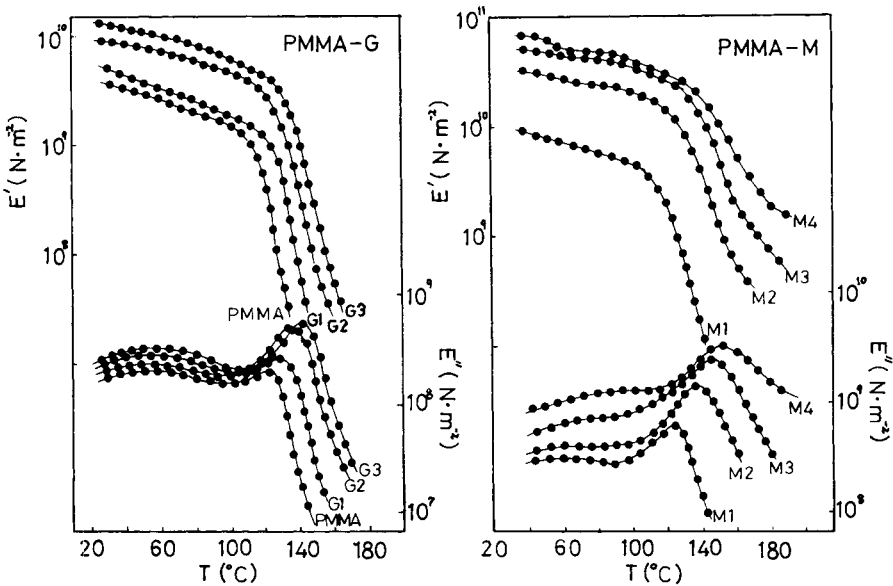


Fig. 2. Temperature dependence of storage modulus E' and loss modulus E'' for the PMMA composite.

tively. For the mica filled polymers, the increase in E' with loading is outstanding over the whole temperature range compared to the glass filled ones, as reported in the previous study.⁹ The primary α -dispersion temperatures T_α , corresponding to glass to rubber transition, were observed at 104 and 119°C for the unfilled PS and PMMA, respectively. The T_α shifts to higher temperature with filler content. Figure 3 shows the dependence of T_α on the volume fraction of the fillers for each system. The T_α increases rapidly at a lower loading region and gradually at a higher loading region with the volume fraction of the filler ϕ_f . The increase in T_α is larger, for PMMA than for PS in the case of the same filler and for mica than for glass in the case of the same polymer.

We have suggested¹⁰ that it is possible to examine the primary dispersion temperatures of the filled polymers in the same way as the treatments^{11,12} on network polymers. That is, if one junction point is assumed to correspond to one site of adsorption on filler surface in a polymer, crosslinking density ρ can be substituted by the amount of adsorption per unit volume of the chain segments. The dependence of T_α on filler content has been analyzed by the following equation, proposed in the previous report¹⁰:

$$T_\alpha = K_f l_n K_0 S \quad (2)$$

where K_f and K_0 are constants and S is a specific surface area of filler per gram of polymer. Figure 4 shows T_α vs logarithm of S plots for each system. A linear relation can be obtained for all systems. The results suggest that the increase in T_α is due to the segmental immobilization by the adsorption of the chain segments on the filler surface.

Lipatov and Fabulyak⁶ have considered the restriction of chain mobility in surface layers to be associated with the entropy factor. Moreover, they have suggested that the change of the entropy depends on the chain stiffness and in the case of a stiff chain polymer, e.g., cellulose acetate, any effects of the filler surface on the molecular motion cannot be observed.

In the present study, PS and PMMA can be considered to have nearly the same

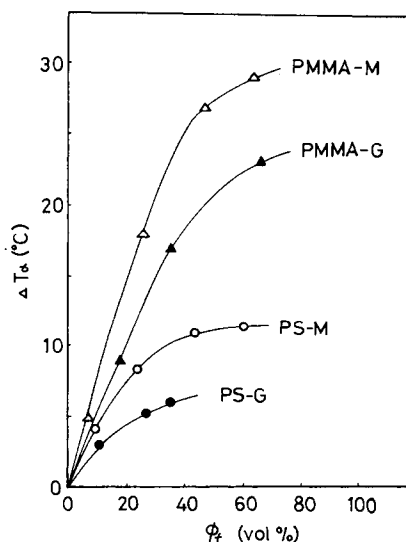


Fig. 3. Dependence of the primary α -dispersion T_α on the volume fraction of the fillers for each system.

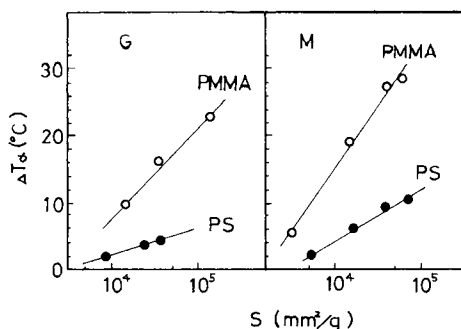


Fig. 4. ΔT_α vs logarithm of S plots for each system. S is a specific surface area of filler per gram of polymer.

chain stiffness since the steric factors σ , as a measure of the chain stiffness, are 2.2 and 2.4, for PS and PMMA, respectively ($\sigma^2 = \langle h^2 \rangle_0 / \langle h^2 \rangle_f$, where $\langle h^2 \rangle_0$ and $\langle h^2 \rangle_f$ are mean-square end-to-end distances for an unperturbed chain and for a model freely rotating chain, respectively). Hence, the difference between the increases in T_α observed in PS and PMMA systems will be predicted to be due to that of the effects of polymer-filler interaction energy.

The extent of the polymer-filler interaction energy has been measured by the heat of adsorption of the model compound of the polymer on the filler surface. Here, though the monomer of the polymer has been used as a model compound, this may be expected to give a measure of the magnitude of the interaction energy. Figure 5 shows plots of the logarithm of the retention time against the reciprocal of the absolute temperature $1/T$. The heat of adsorption ΔQ can be estimated from the slope of a straight line derived by each plot. The values of ΔQ in each system are shown in Table II. The heat of adsorption of methylmethacrylate on the filler is always larger than in the case of styrene, irrespective of the kind of filler. In the case of the same monomer, the heat of adsorption is slightly larger for mica than for glass. The values of ΔT_α at $\phi_f = 60$ vol % are plotted against ΔQ in Figure 6. The increase in T_α is related to the heat of adsorption, irrespective of the kind of polymer-filler system. The mechanism for immobilization might involve hydrogen bond formation and dipole interaction at the interface. It is reasonable that the polymer-filler interaction is larger for PMMA than for

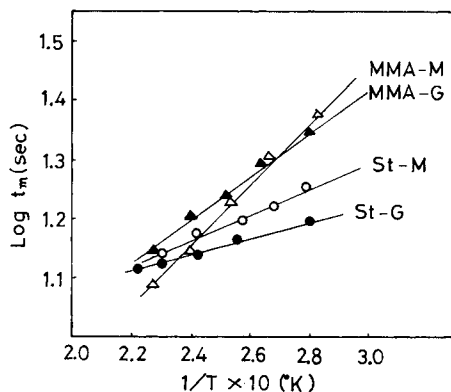


Fig. 5. Logarithm of the retention time t_m vs the reciprocal of the absolute temperature $1/T$ plots.

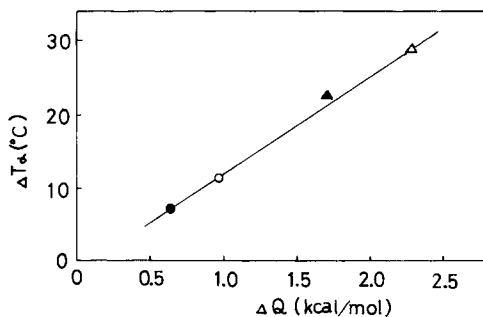


Fig. 6. Values of ΔT_{α} at $\phi_f = 60$ vol % vs the heat of adsorption ΔQ plots.

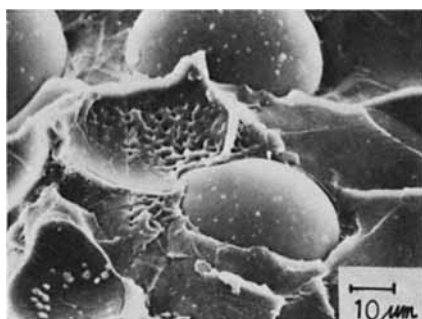
PS since the dipole moment of PMMA ($\mu = 1.30D$) is larger than that of PS ($\mu = 0.26D$).

Figure 7 shows the SEM photographs of the fracture surface for the PMMA composites. Some fragments of the resin adhered on the filler surface have been observed. The similar photographs have been observed also for the PS composites. These observations support the presence of the adhesion between the polymer and filler.

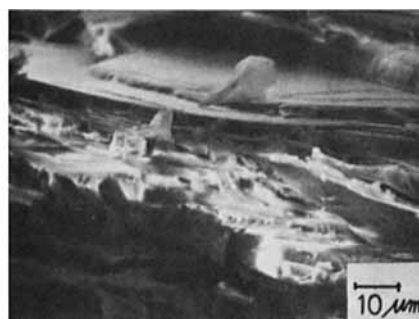
A parameter B which represents the extent of polymer-filler interaction, can be estimated from comparison of the loss moduli E'' of filled and unfilled specimens, using the equation¹³

$$E_c''/E_0'' = [1 - (\phi_f B)^n]^{-1} \quad (3)$$

where E_0'' and E_c'' are loss moduli of unfilled and filled specimens, respectively. A plot of the logarithm of $1 - E_0''/E_c''$ vs. the logarithm of ϕ_f yields the exponent n as slope, and B can be evaluated from the intercept. The experimental data (calculated by using the E'' values at 80°C) yield nearly linear plots for each system, as shown in Figure 8.



PMMA-G



PMMA-M

Fig. 7. SEM photographs of the fracture surface for the PMMA composites.

TABLE II
Heats of Adsorption of the Monomers on the Filler Surface

Sample	ΔQ (kcal/mol)
St-Glass	0.64
St-Mica	0.98
MMA-Glass	1.7
MMA-Mica	2.3

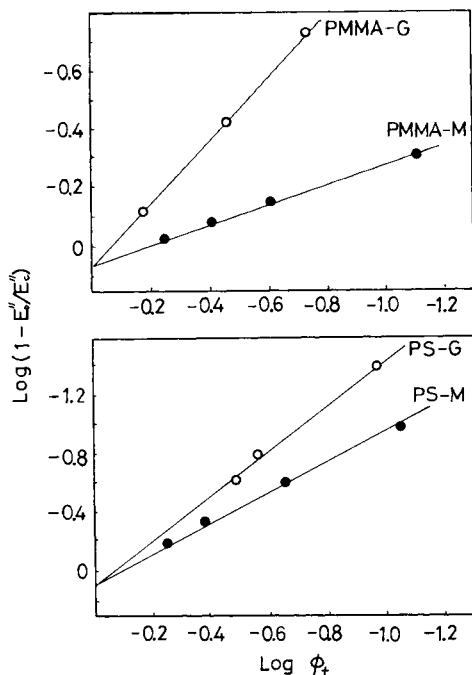


Fig. 8. Logarithm of $(1 - E''/E_c')$ vs the logarithm of ϕ_f plots.

The parameter B is related with the geometry of the filler particle and the effective thickness ΔR of the interfacial region, as follows¹⁴:

for sphere:

$$B = (1 + \Delta R/R_0)^3 \quad (4)$$

for plate:

$$B = (1 + 2\Delta R/D)^2(1 + 2\Delta R/X) \quad (5)$$

where R_0 is the radius of the sphere, D is the diameter of a plate, and X is the thickness of a plate. The ΔR values can be computed from the experimental B values by eqs. (4) and (5). The values of B and ΔR for each system are shown in Table III. The B values are larger for PMMA than for PS and for mica than for glass, respectively. The ΔR values are larger for PMMA than for PS, but

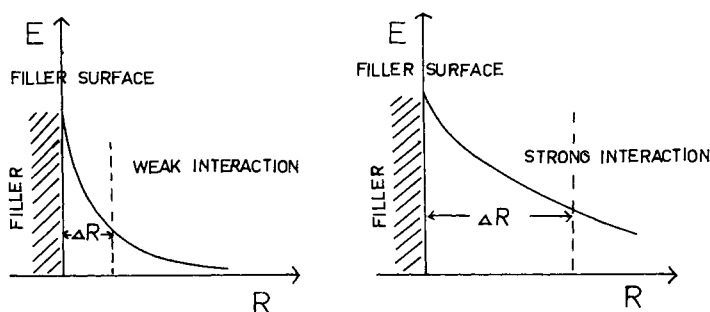


Fig. 9. Postulated matrix immobilization at the interface of a filler particle. The extent of polymer-filler interaction E is shown as a function of R , the distance from the filler. R is the effective thickness of the interfacial region.

TABLE III
 Values of B and ΔR

Sample	B	ΔR (μm)
PMMA-G	1.23	1.4
PMMA-M	1.51	0.11
PS-G	1.16	1.0
PS-M	1.31	0.06

smaller for mica than for glass. The ΔR values which represent the thickness of an immobilized layer of the chain segment in the region adjacent to the interface, are wholly large compared with those previously reported.^{4,7,15} The ΔR value seems to be a function of the strength or magnitude of surface interaction. It is consistent with the ΔQ value for each polymer system in the case of the same filler, but inconsistent with that for each filler in the case of the same polymer. In general, the platelike fillers have larger B values than the spherical fillers, since the formers are more effective than the latters in magnifying the strain. However, it must be taken into consideration that the equations used here are based on the oversimplified model. That is, the square of the average value of the strain is used in place of the precise strain function, though the distribution of the strain in matrix would be broader for the nonspherical particle than for the spherical particle.

The formation of an interfacial region by polymer-filler interaction is illustrated schematically for the case of interacting system, in Figure 9. The thickness of the interfacial region ΔR which is effective, depends on the technique used. The α -dispersion, corresponding to the glass to rubber transition, occurs when $\omega\tau_c \simeq 1$. Here, ω is the frequency of a measurement and τ_c is the correlation time of motion. In the case of the techniques which measure the physical quantities associated with shorter correlation times, e.g., nuclear magnetic relaxation, the two regions between the strongly immobilized portion and the portion far from a filler surface would be possibly distinguished. However, in the case of the techniques where, associated with longer correlation times, e.g., volume expansion, dynamic mechanical measurements, an average of the physical quantity in the two regions would be possibly observed. In such case, the effective thickness of an immobilized layer seems to be detected as the larger values like observed here.

References

1. R. F. Randel, *Trans. Soc. Rheol.*, **2**, 53 (1958).
2. R. F. Randel and T. L. Smith, *Rubber Chem. Technol.*, **35**, 291 (1962).
3. L. Galperin, *J. Appl. Polym. Sci.*, **11**, 1475 (1967).
4. A. Yim and L. E. St. Pierre, *Polym. Lett.*, **37**, 237 (1967).
5. D. H. Droste and A. T. DiBenedetto, *J. Appl. Polym. Sci.*, **13**, 2149 (1969).
6. Y. S. Lipatov and F. Y. Fabulyak, *J. Appl. Polym. Sci.*, **10**, 2131 (1972).
7. A. Yim, R. S. Chahal, and L. E. St. Pierre, *J. Colloid Interface Sci.*, **43**, 583 (1973).
8. P. E. Eberly, Jr., *J. Phys. Chem.*, **65**, 68 (1961).
9. K. Iisaka and K. Shibayama, *J. Appl. Polym. Sci.*, **20**, 813 (1976).
10. K. Iisaka and K. Shibayama, *J. Appl. Polym. Sci.*, to appear.
11. T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

12. K. Shibayama and Y. Suzuki, *J. Polym. Sci., Part A*, **3**, 2637 (1965).
13. K. D. Ziegel and A. Romanov, *J. Appl. Polym. Sci.*, **17**, 119 (1973).
14. K. D. Ziegel, *J. Colloid Interface Sci.*, **29**, 72 (1969).
15. G. Kraus, J. T. Gruver, *J. Polym. Sci., A-2*, **8**, 571 (1970).

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