

Dynamic Mechanical Behavior of Poly(2-hydroxyethyl Methacrylate)-Glass Beads Composites

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Synopsis

The dynamic relaxation behavior of a model two-phase system, poly(2-hydroxyethyl methacrylate)-glass beads, was studied by means of a freely oscillating torsional pendulum. The effect of the filler content on the storage and loss moduli of the composites could be described in terms of the modified Kerner equation in complex form. At temperatures below the glass transition temperature of the matrix, the agreement between experimental and theoretical data was satisfactory after correction for thermally induced stress due to different thermal expansion coefficients of matrix and filler. In the presence of filler, the capacity of the matrix to store and dissipate energy increases, but the character of molecular motions underlying the dispersions observed is preserved because the temperature of the dispersions remains unchanged. The effect of water on the dynamic relaxation behavior of composites is primarily reflected in changes in the shape of the temperature dependence of the dissipating capacity of the matrix. The data allow the conclusion to be drawn that the chain mobility at the interphase boundary does not decrease and that no additional frictional mechanisms appear.

INTRODUCTION

Polymethacrylates rank as model polymers which are frequently used in the study of molecular mobility in the glassy state. Generally, it can be said¹ that besides the main (α) dispersion corresponding to the glass transition, polymethacrylates exhibit a secondary (β_1) dispersion at a temperature of about 20°C (1 Hz) and a low-temperature (γ) dispersion at temperatures lower than -120°C. The latter two dispersions are assigned^{1,2} to the hindered rotation of the —COOR or —R side groups (where R is alkyl, hydroxyalkyl, halogenalkyl, etc.). The interaction of low molecular weight compounds with polar groups of the side chains gives rise³⁻⁶ to the "diluent" (β_{sw}) dispersion in the temperature range between the γ and β_1 dispersions.

In a number of earlier papers,^{3,5-11} we investigated in detail the dynamic relaxation behavior of poly(2-hydroxyethyl methacrylate) (PHEMA), which exhibits the above dispersions (related to a frequency of 1 Hz) at temperatures $T_\alpha = 104^\circ\text{C}$, $T_{\beta_1} = 28^\circ\text{C}$, $T_\gamma = -133^\circ\text{C}$, and $T_{\beta_{sw}} = -70$ to -120°C (according to the type and concentration of diluent). If at cooling of swollen PHEMA, a certain amount of the diluent contained is separated in the form of a second phase, the heterogeneous system exhibits, moreover, dispersions characteristic of the phase of the glassy or crystalline diluent.⁵ We attempt-

ed to use the knowledge gathered so far and briefly outlined above for studying the molecular mobility of heterogeneous systems which recently have been increasingly gaining in importance.

Composites consisting of the polymer matrix and a particulate filler can be regarded as ordinary multiphase polymer systems. A number of equations based on theoretical models¹²⁻¹⁶ were derived in order to calculate their properties, such as the modulus of elasticity, mechanical damping, electrical and thermal conductivity, etc., from the respective properties of the components. However, verification of the models and their further refinement requires extensive and reliable experimental data. So far, only few data have been collected on particular composites where the matrix and filler are in the glassy state. It can be assumed that the parameters of the relaxation motion of side chains or short segments of main chains will be sensitive toward a possible interaction between the filler and matrix. It has been the objective of this work to find out what effect the volume fraction of filler (glass beads) has on the temperature and intensity of the PHEMA dispersions. We assumed that the data obtained will allow us to complete the earlier information^{17,18} on the PHEMA-glass bead interaction and at the same time to estimate the character of the new mechanisms that may arise and lead to energy losses in heterogeneous systems. From this viewpoint, we also investigated the dynamic relaxation behavior of the three-component, two-phase system (PHEMA + water)-glass beads.

EXPERIMENTAL

The preparation of PHEMA filled with glass beads, an essential fraction of which had a diameter about 30 μm , has been described earlier.^{17,18} Samples approximately $1.5 \times 7 \times 60 \text{ mm}^3$ in size were dried to constant weight over P_2O_5 at a temperature ca. 90°C. Before measurement, the samples were annealed at 130-140°C and slowly cooled to room temperature. The samples swollen with water were sealed into ampoules and stored at room temperature for at least one month. The dynamic mechanical properties were measured with a torsional pendulum having digital recording of free damped oscillations¹⁹; an average increase in temperature with time was 1°C/2 min.

RESULTS AND DISCUSSION

Effect of Thermally Induced Stress

The level of the storage modulus of composites increases with the content of glass beads within the whole temperature range of the glassy state investigated (Fig. 1). At the same time, the filler modifies the shape of the temperature dependence of the storage modulus, so that the relative modulus $G'_{rs} = G'_{cs}/G'_m$ (index m denotes the unfilled matrix) decreases with decreasing temperature (Fig. 2). The cause of this frequent phenomenon is seen²⁰⁻²² as a thermally induced stress arising in the composite during cooling because of the different thermal expansion coefficients of components (hence the index s). Since the modulus of the polymer matrix decreases with stress, the polymer layer surrounding the filler particle has a lower modulus of elasticity

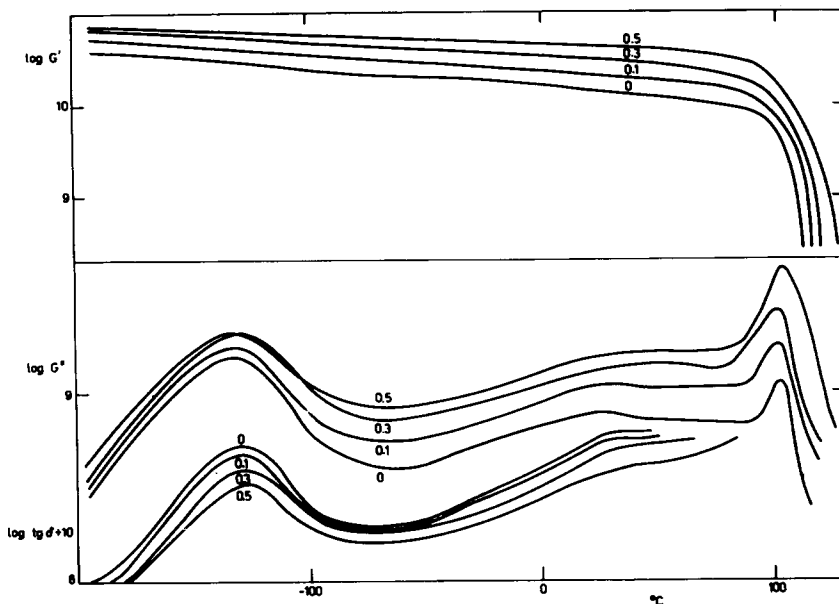


Fig. 1. Temperature dependence of moduli G' and G'' (dyn/cm²) and $\text{tg } \delta$ of poly(2-hydroxyethyl methacrylate)-glass beads composites. Number at curve gives volume fraction of filler.

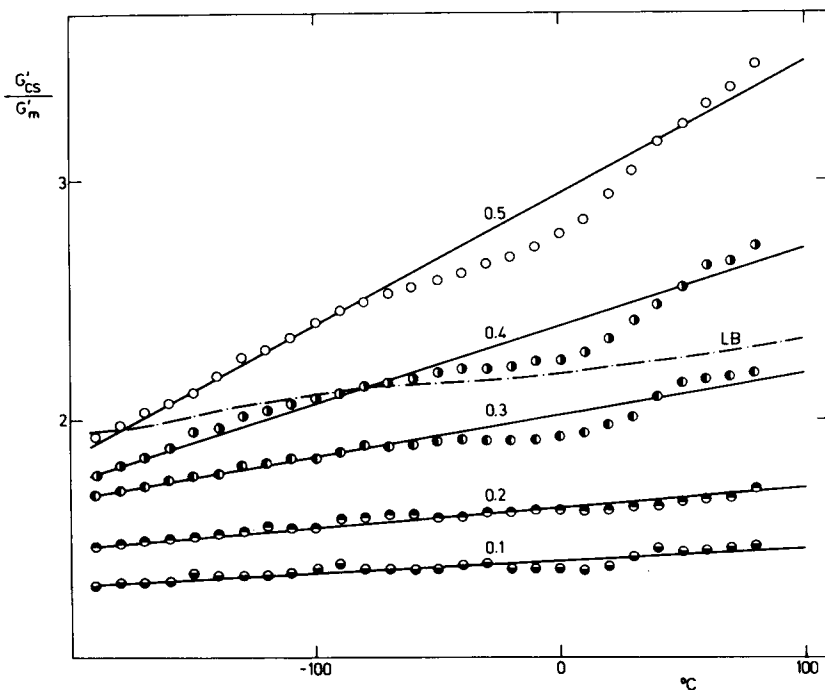


Fig. 2. Temperature dependence of relative modulus of poly(2-hydroxyethyl methacrylate)-glass beads composites. Straight lines indicate average slope of temperature dependence of relative modulus, respective numbers give volume fraction of filler; LB is lower boundary of temperature dependence of relative modulus for $v_b = 0.4$ calculated using eq. (6).

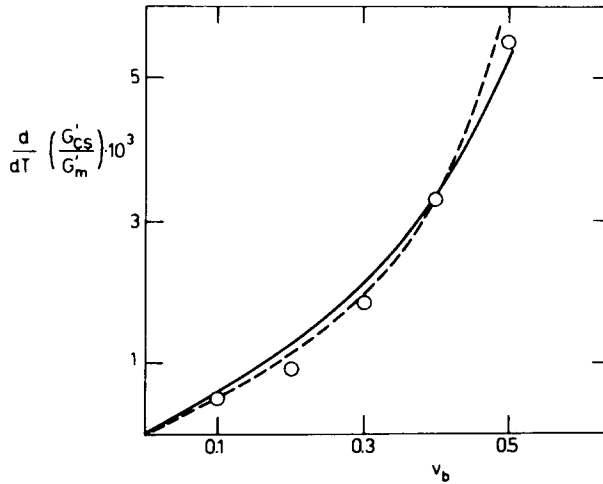


Fig. 3. Effect of filler content on slope of temperature dependence of relative modulus of composites: (O) experimental data read from Fig. 2; full or broken lines respectively calculated from eq. (1) by using extrapolated G'_{re} or relative modulus values from eq. (3).

than the unfilled matrix (at the same temperature), even though the overall modulus of the composite increases. The magnitude of the induced stress near the filler particle increases with decreasing temperature, so that the reduced modulus G'_{rs} decreases accordingly. Under these assumptions, the following equation has been derived²⁰ for the temperature dependence of the relative modulus (the equation is given here in the notation for the storage shear modulus, because in isochronous measurements one can with good accuracy assume that $G_{cs}/G_m = G'_{cs}/G'_m$):

$$\frac{d(G'_{cs}/G'_m)}{dT} = K(G'_c/G'_m) \frac{(\alpha_m - \alpha_b)f(\nu_b)}{\epsilon_{ym}} \quad (1)$$

where G'_{cs} and G'_c , respectively, denote the shear modulus of the composite in the presence and absence of the thermally induced stress; α_m and α_b are the linear thermal expansion coefficients of matrix and filler; ϵ_{ym} is the matrix elongation at yield; and K is a factor dependent on the shape of the filler particles. Calculating the factor K according to²⁰

$$K = (1/2)[(1 + \nu_m)/2 + (1 - 2\nu_b)/(E_b/E_m)]^{-1}$$

we used $\nu_m = 0.35$ and $\nu_b = 0.22$ for Poisson's ratio of matrix and filler²⁰ and $E_b/E_m = 20$ for the filler-to-matrix ratio of Young's moduli; hence $K = 0.71$. Owing to the marked temperature dependence²³ of α_m , the difference $(\alpha_m - \alpha_b)$ is a function of temperature; the average value $4 \times 10^{-5} \text{ deg}^{-1}$ was used in the calculations. If the stress-strain curve is described by means of the first two terms of a power series, the resulting expression for the decrease in the modulus with deformation is²⁰ $E_{ms} = E_m[1 - (\epsilon/\epsilon_{ym})]$. Since at temperatures deeply below the glass transition temperature T_g the samples are destructed before reaching the yield point, ϵ_{ym} should be regarded only as a parameter of eq. (1) expressing the decrease in the matrix modulus with increasing deformation. Such ϵ_{ym} is not connected with the real ultimate properties of PHEMA and their dependence on temperature. With respect to

TABLE I
Parameters of Dispersions of Poly(2-hydroxyethyl Methacrylate)-Glass Beads Composites
Low-Temperature Dispersion

v_b^a	T_{γ}^b , °C	$G''_{\gamma} \times 10^{-8},^c$ dyn/cm ²	$\bar{G}''_{\gamma} \times 10^{-8},^d$ dyn/cm ²	$(\bar{G}''_{\gamma})_{cor} \times 10^{-8},^e$ dyn/cm ²	$tg_{\gamma} \delta \times 10^{2f}$	$tg_{\gamma} \delta \times 10^{2c}$	Q_{γ}^i	$G''(-60^{\circ}C) \times 10^{-8},^c$ dyn/cm ²	$G''(-60^{\circ}C) \times G''(-60^{\circ}C)_{cor} \times 10^{-8},^e$ dyn/cm ²
0	-132	15.7	15.7	15.7	5.2	5.2	0.180	4.0	4.0
0.1	-132	17.2	17.9	16.7	4.8	4.9	0.175	5.6	4.5
0.2	-130	20.0	20.9	18.5	4.7	4.7	0.180	6.0	5.1
0.3	-131	20.3	24.6	20.1	3.9	4.4	0.170	7.0	6.0
0.4	-130	19.5	29.1	21.0	3.6	3.9	0.175	7.5	6.6
0.5	-130	21.0	33.5	21.0	3.2	3.2	0.185	8.5	8.2

Main Dispersion						
v_b^a	T_{α}^b , °C	$G'_{re}{}^g$	$\bar{G}'_r{}^h$	$G_{\alpha}''(T_{\alpha}) \times 10^{-8},^c$ dyn/cm ²	$G''_r(T_{\alpha})^c$	$\bar{G}_{\alpha}''(T_{\alpha}) \times 10^{-8},^d$ dyn/cm ²
0	103	1.00	1.00	11	1.00	11.0
0.1	102	1.45	1.22	18	1.6	13.4
0.2	102	1.70	1.53	19	1.7	16.6
0.3	101	2.20	1.99	27	2.5	21.4
0.4	102	2.70	2.76	30	2.7	29.2
0.5	104	3.50	4.31	45	4.1	45.0

^a Volume fraction of glass beads in composite.

^b Temperature of dispersion read off for the loss peak.

^c Experimentally determined height of loss maximum or minimum.

^d Value calculated using eq. (4).

^e Corrected value (explanation in text).

^f Value calculated using eq. (5).

^g Value obtained by extrapolation in Fig. 2.

^h Value calculated using eq. (3).

ⁱ Parameter of the distribution of relaxation times (explanation in text).

data published for polymethacrylates,²⁴ we chose $\epsilon_{ym} = 0.03$. The quantity $G'_{re} = (G'_e/G'_m)$ representing the maximum reinforcing for a given filler concentration was obtained by extrapolation (hence index e) of the relative modulus G'_{rs} to the main transition temperature $T_\alpha = 104^\circ\text{C}$ (Fig. 2; Table I).²⁰ (T_α is some 15°C higher than the dilatometrically determined²³ T_g , so that the existing molecular mobility excludes the formation of thermally induced stress.) The values calculated by means of eq. (16) in reference 20 were used for the function $f(v_b)$. Although only approximate values of the above terms were used, the good agreement between the experimental and calculated $d(G'_{cs}/G'_m)/dT$ values (Fig. 3) suggests that the above causes of the temperature dependence of G'_{rs} included in eq. (1) can be regarded as real. The deviation of experimental data from the theoretical linear dependence (Fig. 2) in the region around 0°C can be qualitatively explained by the thermal dependence of the quantity $(\alpha_m - \alpha_b)$. Dilatometric measurements have revealed^{23,25} that the β_1 dispersion of PHEMA and of a number of other esters of poly(methacrylic acid) is accompanied by an increase in the thermal expansion coefficient. As shown by eq. (1), the increase in α_m leads necessarily to an increase in the slope of the temperature dependence of G'_{rs} , in agreement with the trend of the experimental data.

Effect of Filler on the Storage and Loss Moduli

A number of equations have been derived to calculate elastic properties of multiphase systems from the properties of the components.¹²⁻¹⁴ An equation derived by Kerner¹² and modified by Nielsen¹⁴ appeared to be best suited for the description of the reinforcement of glassy PHEMA filled with glass beads. Since in this paper the results of dynamic mechanical measurements are reported, the equation had to be used in complex form (cf.^{15,26,27}):

$$\frac{G^*_c}{G^*_m} = \frac{1 + AB^*v_b}{1 - B^*\psi v_b} \quad (2)$$

where $A = (7 - 5\nu_m)/(8 - 10\nu_m)$, $B^* = [(G^*_b/G^*_m) - 1]/[(G^*_b/G^*_m) + A]$, and the empirical function $\psi = 1 + [(1 - \nu_{\max})/v^2_{\max}]v_b$ represents correction for the maximum possible filling (for beads of the same size,^{14,16} $\nu_{\max} = 0.64$). Using simplifying assumptions $G''_b = 0$, $G'_b \geq 10 G'_m$, $G'_m \geq 10 G''_m$, one can with good accuracy write

$$B^* = B' + iB'' = [(G'_b/G'_m) - 1]/[(G'_b/G'_m) + A] - i[(A + 1)(G''_m/G'_b)]/[1 + (AG'_m/G'_b)]^2$$

and from eq. (2) derive approximate relationships:

$$G'_c = G'_m \frac{1 + AB'v_b}{1 - B'\psi v_b} \quad (3)$$

$$G''_c = G''_m \frac{1 + AB'v_b}{1 - B'\psi v_b} - G'_m \frac{(A + \psi)B''v_b}{(1 - B'\psi v_b)^2} \quad (4)$$

$$\text{tg } \delta_c = \text{tg } \delta_m - \frac{(A + \psi)B''v_b}{(1 + AB'v_b)(1 - B'\psi v_b)} \quad (5)$$

If all the three simplifying assumptions are fulfilled, the relative error of eqs.

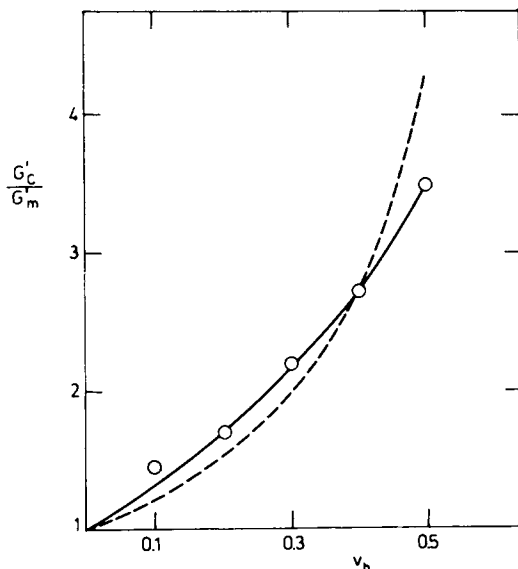


Fig. 4. Effect of filler content on relative modulus of composites. Full and broken lines respectively represent extrapolated G'_{re} and data calculated using eq. (3).

(3)–(5) is not greater than 5%. Similar equations for the storage and Young's loss moduli, in which the parameter ψ was introduced in a different manner, were used to describe the dynamic mechanical properties of the polymer-polymer composites.¹⁵

Since the modulus G'_{rs} increases with temperature, an extrapolated G'_{re} was considered in the estimation of the reinforcing effect (Fig. 2). Ratios of $G'_c(T_\alpha)/G'_m(T_\alpha)$ are rather inaccurate, because at temperatures about T_α the moduli of both the composite and the matrix steeply decrease with increasing temperature (Fig. 1). With respect to the above extrapolation, the average value $G'_b/G'_m = 20$ was used, even though at T_α this ratio may be higher. The agreement between experimental and theoretical data is satisfactory up to the glass beads content $v_b = 0.4$ (Fig. 4; Table I). It can be said, therefore, that the shear modulus of the model composite PHEMA-glass beads is affected by the filler content in a standard manner. The probable cause of the low G'_{re} for $v_b = 0.5$ can be sought in the aggregation of the filler particles and in the possible formation of cavities,^{21,28,29} because the content of glass beads approaches the maximum random packing. Substitution of the modulus G'_c calculated according to eq. (3) into eq. (1) yielded the theoretical dependence of $d(G'_{cs}/G'_m)/dT$ on the filler content, also shown in Figure 3. In this case, too, it is obvious that the agreement between experimental and theoretical data is good up to $v_b = 0.4$; for $v_b = 0.5$, the theoretical value is higher than the experimental one.

The existence of thermally induced stress in the composites under investigation can also be documented by calculating the temperature dependence of the lower limit of the modulus of elasticity according to the following equation¹³ (on a simplifying assumption that in the glassy state the moduli G_c , G_m , and G_b can be approximated by the corresponding storage moduli):

$$G'_{c(-)} = G'_m + v_b/[1/(G'_b - G'_m) + D(v_m/G'_m)] \quad (6)$$

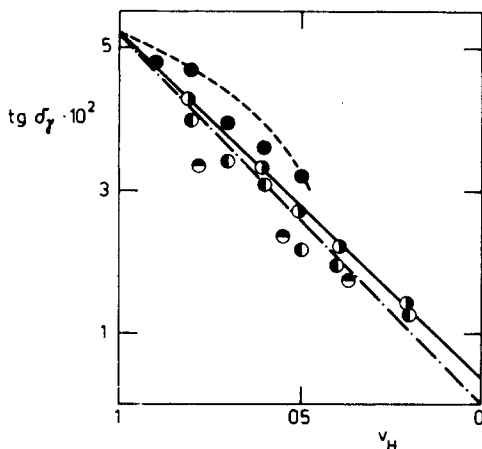


Fig. 5. Effect of volume fraction of poly(2-hydroxyethyl methacrylate) v_H in composites (●) and in copolymers with methyl methacrylate (○), methacrylamide (◐), and acrylamide (◑) on the height of low-temperature maximum. Broken and dash-and-dot lines respectively were calculated using eqs. (5) and (7); full line represents average linear dependence of damping on v_H for copolymers.

where v_m is the volume fraction of the matrix in the composite. $G'_b = 3 \times 10^{11}$ dyn/cm² was used,^{20,30} and approximate values of the bulk modulus of the matrix K_m involved in the constant $D = 6(K_m + 2G_m)/5(3K_m + 4G_m)$ were calculated from the modulus G'_m using the temperature independent Poisson's ratio $\nu_m = 0.35$. The curve given in Figure 2 was calculated for $v_b = 0.4$, because at such filling the experimental data agree well with the theoretical values G'_c/G'_m and $d(G'_c/G'_m)/dT$. Hence, one can see that owing to the thermally induced stress at low temperature the modulus of the composite can assume values lower than admitted by theory.

The glass beads in PHEMA also considerably influence the magnitude of energy losses (Fig. 1): the height of the γ maximum increases from 15.7×10^8 dyn/cm² for PHEMA to values around 20×10^8 dyn/cm² for composites with the filler fraction $v_b \geq 0.2$ (Table I). At temperatures above -100°C , one can see an increase in the level of the loss modulus with the filler content; for samples having $v_b \geq 0.3$, the β_1 maximum is overlapped by the left branch of the much higher main loss maximum situated at 104°C .

To compare the experimental values of the loss modulus and $\text{tg } \delta$ with the theoretical ones, calculations were carried out using eqs. (4) and (5) for three characteristic temperatures: $T_{\gamma_1} -60^\circ\text{C}$, (at which the loss modulus passes through a minimum) and T_α . As follows from Table I, calculated \bar{G}''_γ values increase with filler content and are all higher than the experimental ones. However, the experimental values of G''_γ are affected by thermally induced stress similarly to the corresponding values of G' . To eliminate this effect, calculated \bar{G}''_γ values were multiplied by the factor $G'_{rs}(T_\gamma)/G'_r(T_\alpha)$ expressing the decrease in the relative modulus of the composite owing to the thermally induced stress. The corrected loss moduli $(\bar{G}''_\gamma)_{\text{cor}}$ then agree well with the experimental data (Table I).

A similar situation is found for the loss modulus $\bar{G}''(-60^\circ\text{C})_{\text{cor}} = \bar{G}''(-60^\circ\text{C})[G'_{rs}(-60^\circ\text{C})/G'_r(T_\alpha)]$ at the minimum of mechanical losses. It

can be said consequently that the thermally induced stress depresses the corresponding moduli G'_{cs} and G''_{cs} to the same extent. This is also indicated by the fact that $\text{tg } \delta_c = G''_{cs}/G'_{cs}$ (Table I) fits in fairly well with the theoretical data without any correction. Figure 1 also shows that with increased filler content the β_1 maximum becomes flat and, for $v_b = 0.5$, virtually disappears. Besides the overlapping of the β_1 maximum with the α maximum, the cause should be looked for in the increasing effect of thermally induced stress. It should be taken into account that the correcting factor $G'_{rs}(T)/G'_r(T_\alpha)$ increases with filler content; as a consequence, the resulting temperature dependence of the loss modulus of composites becomes flatter.

While for the evaluation of the effect of the filler content on the storage modulus extrapolated values had to be used (Fig. 2), in the case of the loss modulus one can start with values determined experimentally (Fig. 1). As follows from Table I, the relative magnitude of the α loss maximum $G''_r(T_\alpha) = G''_c(T_\alpha)/G''_m(T_\alpha)$ increases with the filler content virtually identically with the extrapolated relative modulus G'_{re} . Only for $v_b = 0.5$ the $G''_r(T_\alpha)$ value is higher than G'_{re} and approaches the theoretical value. (Even though at T_α the simplifying assumption $G'_m \geq G''_m$ is not fulfilled any more, the relative error of eqs. (3)–(5) does not exceed 10% on the average.) The satisfactory agreement between the experimental and calculated data for $G''_r(T_\alpha)$ also justifies the assumption that thermally induced stress is negligible at T_α .

Data in a number of papers^{14,21,22,28,31,32} indicate that $\text{tg } \delta_c$ values of filled systems are higher than corresponds to the volume fraction of the matrix in composites in which the filler particles do not participate in the dissipation of mechanical energy. In other words, it means that the empirical equation^{14,31}

$$\text{tg } \delta_c = v_m \text{tg } \delta_m \quad (7)$$

is not fulfilled. An analogous linear relationship approximately holds for a number of copolymers of HEMA with other methacrylic comonomers (Fig. 5), which do not exhibit low-temperature dispersions above the liquid nitrogen temperature. (A certain level of energy losses in the second component has as its consequence that, with decreasing volume fraction of HEMA, v_H , the $\text{tg } \delta$ values do not drop to zero.) For the two-phase system PHEMA–glass beads, all the values of $\text{tg } \delta$ are higher than corresponds to eq. (7) (Fig. 5), and their concentration dependence is rather described by eq. (5). It can be inferred that the inequality $\text{tg } \delta_c > v_m \text{tg } \delta_m$ cannot generally be regarded as a sufficient proof of the presence of additional dissipation mechanisms in composites (interparticular friction, friction at the interphase boundary, etc.). It seems that before these mechanisms are used, more or less speculatively, to interpret the experimental data, one should find out, if possible, whether the changes in G' , G'' , and $\text{tg } \delta$ due to the filler are or are not correlated with each other.

Effect of Water

The effect of water on the temperature dependence of the storage and loss moduli was investigated only for samples with the highest volume fraction of the filler $v_b = 0.5$ (Fig. 6). All the changes observed due to increasing water content are similar to those for unfilled PHEMA⁵: the main (α) dispersion is shifted to lower temperatures and overlaps the β_1 dispersion; the γ maximum

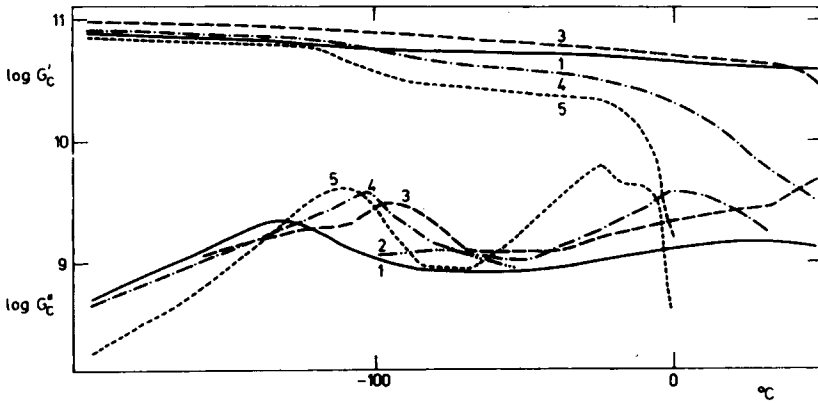


Fig. 6. Effect of water on temperature dependence of moduli G'_c and G''_c (dyn/cm²) of composites with volume fraction of filler $v_b = 0.5$. Volume fraction of water in matrix: (1) 0.00; (2) 0.01 (only loss modulus from -100° to -50°C is given; outside this interval, curves are identical with those for dry composite); (3) 0.07; (4) 0.30; (5) 0.40.

is reduced and eventually disappears; while the β_{sw} maximum increases and is shifted toward lower temperatures. The temperature interval of the β_{sw} dispersion, i.e., -70° to -110°C , coincides with this interval for PHEMA. As the increased magnitude of the γ maximum leads to a higher β_{sw} maximum (compared to unfilled PHEMA), it seems obvious that also in composites the incorporation of water brings about a transformation of the γ process into the β_{sw} process. The data indicate that the effect of water is reflected only by standard changes in the energy dissipation patterns of the polymer matrix.

CONCLUSIONS

The above results allow us to conclude that the filler enhances the capacity of the matrix both to store and to dissipate mechanical energy. The dependence of the moduli of composite, G'_c and G''_c , on the filler content is described satisfactorily by the corresponding eqs. (3) and (4); at temperatures below the glass transition temperature, the agreement between theory and experiment is good only after correction for the effect of thermally induced stress has been carried out. It should be stressed that the character of molecular motion giving rise to the dispersions remains unchanged, because the temperature position of the loss maxima is independent of the filler content. In the case of the γ dispersion, the proportionality between the height of the loss maximum and the corresponding decrease in the modulus $\Delta G'_\gamma = G'_{cs}(-196^\circ\text{C}) - G'_{cs}(-60^\circ\text{C})$ is preserved, so that the ratio $Q_\gamma = 2G''_\gamma/\Delta G'_\gamma$ practically does not vary with the filler content (Table I). As the parameter Q thus defined can with a certain licence be considered¹ the parameter of the distribution of relaxation times, it can be said that the filler does not affect the distribution of relaxation times of the γ dispersion to any considerable degree. Consequently, it seems that the effect of the filler leads predominantly to changes in the quantitative parameters, primarily in extent, of the molecular motion in the glassy state. Also, the data obtained do not indicate that at the interphase boundary immobilization takes place of the side chains

or of backbone segments whose motion is responsible for the dispersions observed.

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Received February 21, 1965

Revised May 28, 1975