

Temperature Dependence of Reinforcement in the Composites Polyurethane Rubber–Crosslinked Polymeric Filler

J. KOLAŘÍK, S. HUDEČEK, and F. LEDNICKÝ, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*, and L. NICOLAIS, *Istituto di Principi di Ingegneria Chimica, Università di Napoli, Napoli, Italy*

Synopsis

The temperature dependence of the components of the complex tensile and shear modulus of composites thermoplastic polyurethane rubber (Estan 5707)–crosslinked polymeric filler has been determined using torsional pendulum and Rheovibron viscoelastometer techniques. For comparison, dynamic mechanical properties of the system Estan 5707–glass beads were determined. The temperature dependence of the relative modulus (modulus of composite/modulus of matrix) of the former composites exhibited a pronounced maximum at about 50°C above the glass transition temperature of the matrix. This maximum of reinforcement was discussed in terms of (a) immobilized interfacial layer, (b) broadening of the spectrum of relaxation times, and (c) increase in the glass transition temperature of the matrix. From the excess reinforcement, i.e., the discrepancy between experimental data and theoretical prediction, an apparent thickness of the immobilized layer was calculated.

INTRODUCTION

The mechanical properties of polymer composites filled with a particulate filler or with short fibers are greatly dependent on the adhesion of phases. Insufficient interfacial adhesion is usually reflected in impaired ultimate properties^{1,2} and in a high loss factor $\tan \delta$ due to additional frictional mechanisms at the interface.^{3,4} On the other hand, strong interfacial adhesion, which is needed for the composite to possess good mechanical properties, may account for a depression of molecular mobility and for a change in the packing of matrix macromolecules adjacent to the interface. The existence of a surface layer with modified physical properties which is formed at the boundary polymer–solid support is borne out by the optical and mechanical anisotropy of thin cast films.^{5,6} The cause of a spontaneous formation of the layer is seen in interfacial forces and in the spatial limitation of the number of possible chain conformations in the proximity of the phase boundary.⁵ Both these effects are obviously operative also at the interface of the composites.

Luminescence spectra⁷ of the “probe” molecules dissolved in the polymer matrix have revealed that the boundary layer of the matrix with increased density (up to 4%) is 2–4 μm thick. Measurements of the solvent vapor sorption in composites with an inorganic filler (TiO_2) led to the conclusion^{8,9} that the filler particles are surrounded by a nonabsorbing polymer layer up to 0.15 μm thick. Likewise, in composites epoxy resin–glass beads a portion of the matrix is effectively immobilized and made relatively impermeable to liquid water; the

thickness of the ordered layer is 0.4 μm for beads 40 μm in diameter.¹⁰ Nuclear spin relaxation studies of filled polymers have indicated¹¹ that chain reorientation in the interphase is restrained compared to that in the unfilled matrix; fillers seem to affect the polymer mobility to a depth of about 10 nm. A strong interfacial interaction is believed to underlie the increase (ordinarily less than by 20°K) in the glass transition temperature T_g of the matrix with increasing of filler content.¹²⁻²⁰ The increase in T_g of a series of polymers filled with silica¹⁷ has turned out to be directly proportional to the polymer-filler interaction energy. The T_g and the effective network density of polyurethane rubber have been found¹⁹ to increase with the specific surface area of mineral fillers, i.e., with the fraction of adsorbed matrix molecules. The discrepancy between the modulus of particulate composites²¹⁻²³ and the prediction of the Kerner theory²⁴ was attributed to strong interfacial adhesion and immobilization of the matrix layer surrounding the filler particles. Similarly, the Smith-van der Poel theory^{25,26} fitted the experimental modulus of several particulate composites only when an effective filler volume fraction was introduced²⁷: $v_{\text{eff}} = v_f + k(v_f/d)^{2/3}$, where v_f is the filler volume fraction, d is the diameter of filler particles, and $k > 0$ is an empirical parameter. From v_{eff} and v_f for polyethylene filled with mineral fillers it has been calculated²⁸ that the thickness of an interphase layer is 190 nm. The thickness of the immobilized layer in polybutadiene (in the glassy state) filled with carbon black or fused silica has been estimated²⁹ from the decrease in the integral value of the mechanical damping with increasing filler content; the reported thickness is about 1.7 or 0.5 μm , respectively. The reviewed assessments are believed to be evidence of the existence of an immobilized layer in particulate composites; however, the available data on the layer thickness are not uniform. Model calculations^{30,31} using the finite element method show that the mechanical properties of the interfacial layer are of basic importance for the elastic and ultimate properties of the composites. Unfortunately, the results cannot be readily correlated with experimental data published to date.

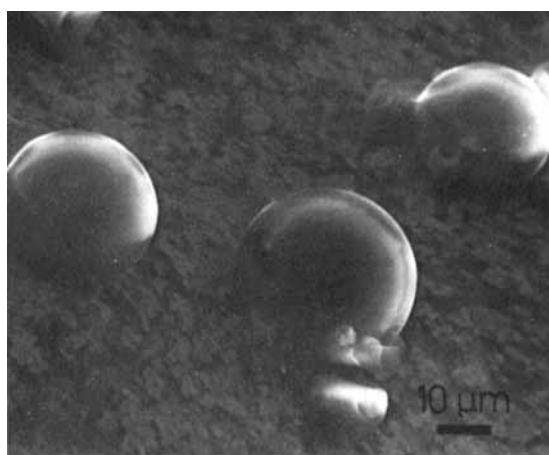
In investigating the mechanical properties of the system thermoplastic rubber matrix-crosslinked polymeric filler, we found that the temperature dependence of the relative tensile or shear modulus (modulus of composite/modulus of matrix) passed through a pronounced maximum, whereby the values of the relative modulus were distinctly higher than the theoretical prediction. In contrast, the temperature dependence of the relative modulus of the polyurethane rubber filled with glass beads was virtually immaterial. We have attempted to qualitatively analyze the grounds underlying the maximum of the relative modulus and to represent the excess reinforcement in terms of an apparent volume fraction of the filler and an apparent immobilized layer of the matrix.

EXPERIMENTAL

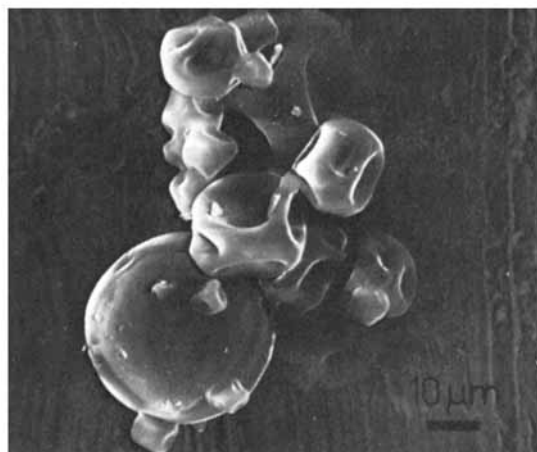
The polymeric filler was prepared³² by the crosslinking terpolymerization of divinylbenzene, acrylamide, and methacrylic acid (in a weight ratio of 30:53:17) in an aqueous emulsion stabilized with the emulsifiers Dowfax 2A1 (Dow Chemical Co., U.S.A.) and Slovafo1 909 (Chemical Works, Nováky, Czechoslovakia). The polymerization was initiated using the redox system ammonium persulfate-potassium pyrosulfite; the polymerization proceeded at 65°C for 3.5 hr. The filler was obtained by drying the latex in a spray-drying box (Niro-

Atomizer, Copenhagen, Denmark) at air temperatures ranging from 160° to 180°C.

The size and shape of the filler particles (without any surface treatment) were examined by means of a scanning electron microscopy. The spherical shape of droplets in the aqueous dispersion remained preserved only for a few percent of particles of the resulting filler (Fig. 1). The majority of the filler particles possessed a globular shape with dimples on their surface. The breakdown of the initial spherical shape was presumably caused³³ by contraction during the polymerization inside the droplets and during the drying process. The skin of the particles wrinkled and folded because it was not capable of shrinkage; the surface of the dimpled particle remained however compact (Fig. 1). In evaluating the size of the filler particles, we regarded the largest particle dimension observed as the diameter of the initial sphere.



(a)



(b)

Fig. 1. Scanning electron micrograph of polymeric filler particles: (a) spherical particles; (b) wrinkled and folded particles.

The polymeric filler was polydisperse. The diameter of the particles varied between 3 and 60 μm : the diameter of approximately 75% of the particles was between 5 and 25 μm , and the most frequent diameter of particles was about 7 μm . The average particle diameter calculated from the average particle surface was 15 μm . The diameter of the majority (more than 80%) of the glass beads (Ballotini Europe 3000 CP, Italy) was between 5 and 25 μm ; the largest fraction (approx. 40%) of particles was that with diameters of 12–18 μm .

The composites were prepared by mixing the filler with a thermoplastic polyurethane elastomer of the polyester type³⁴ Estan 5707 (B. F. Goodrich Chemical Co., U.S.A.) on a two-roll mill at about 160°C. To facilitate the processing on the rolls, 0.5% Advawax 280 lubricant (Deutsche Advance Production, BRD) was added to the mixture. The samples were annealed and dried for about one month at 70°–80°C (over P_2O_5 to constant weight). The temperature dependence of the components of the complex tensile modulus was determined with a Rheovibron DDV-II viscoelastometer at a frequency of 110 Hz. Measurement of the components of the complex shear modulus was carried out on a freely oscillating torsional pendulum at a frequency of about 1 Hz. The average temperature increase with time in both measurements was 1°C/min. The Poisson ratio was determined from the elongation and transverse contraction of samples measured under an XY microscope; its value was constant up to a strain of about 0.1, which is well above the strain used in the dynamic mechanical measurement.

RESULTS AND DISCUSSION

The temperature dependence of the storage and loss moduli shows (Fig. 2) that the matrix exhibits a low-temperature dispersion (transition, relaxation) at -155°C (1 Hz) and a main dispersion (glass transition) at -26°C (1 Hz) or at about -15°C (110 Hz). The low-temperature transition reflects the onset of a short-range molecular motion, while the main transition from the glassy into the rubber-like state is due to long-range segmental motion of the backbones.³⁵ Incorporation of the polymeric filler slightly raises the main transition temperature, while the temperature position of the low-temperature dispersion does not vary to any perceptible extent. The reinforcing effect of the filler is conveniently represented (Fig. 3) by the temperature dependence of the relative modulus $E_r = E_c/E_m$, or $G_r = G_c/G_m$ (where subscripts *c*, *m*, and *f* denote composite, matrix, and filler, respectively). The increase in the relative modulus with temperature in the main transition region is primarily due to the fact that the modulus of the matrix decreases by two orders of magnitude, while the modulus of the filler remains constant. [The modulus of the filler could not be determined directly, but it may be approximated by that of polyacrylamide³⁶ and poly(methacrylic acid)³⁷ given in Fig. 2(b).]

Above 25°C, there is a drop in the relative modulus with temperature (Fig. 3), though the moduli G'_f and G'_m are virtually temperature independent; the phenomenon is the more pronounced the higher the filling. A similar maximum of the temperature dependence of the relative modulus has also been observed for composites epoxy resin–silica,²³ epoxy resin–mica flakes,¹⁸ and butadiene–acrylonitrile rubber–glass beads.³⁸ The reference composite with glass beads does not reach such a high E_r values, and its temperature dependence above the glass transition temperature is immaterial (Fig. 4).

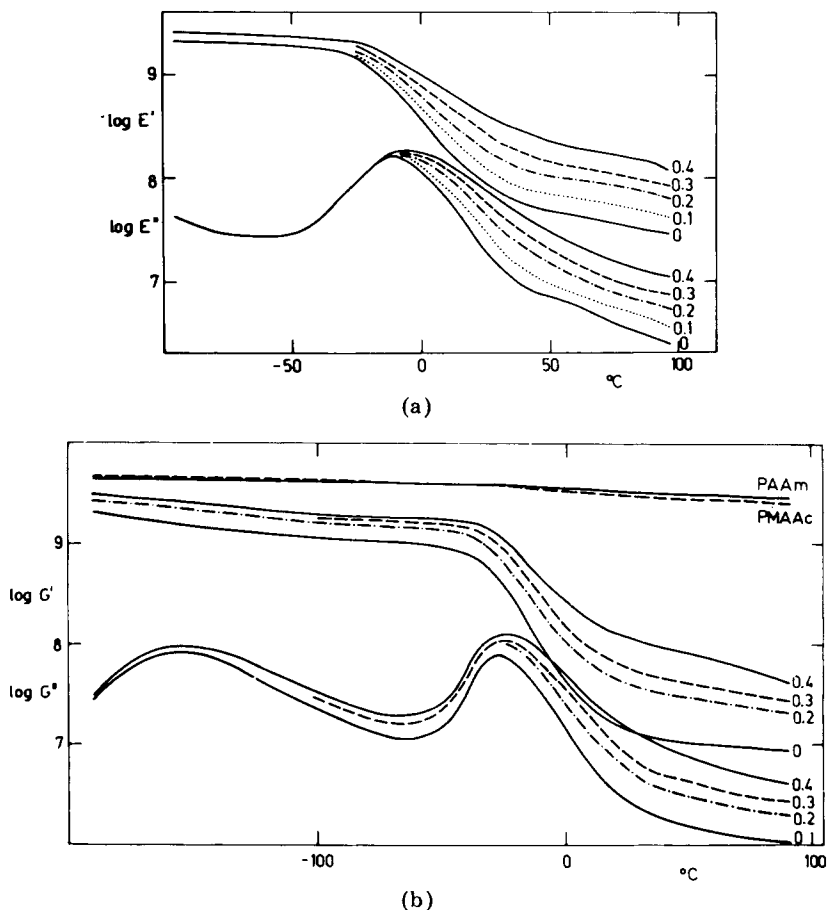


Fig. 2. Effect of volume fraction (indicated at curves) of polymeric filler on the temperature dependence of the storage and loss moduli: (a) E' , E'' (Pa); (b) G' , G'' (Pa). Temperature dependence of the modulus of polyacrylamide or poly(methacrylic acid) stands for that of the polymeric filler.

Of the existing theories^{4,24-26,39-42} of composite materials, we used the Kerner equation²⁴ modified by Nielsen,⁴ which is simple and versatile, to confront experimental data with theoretical prediction:

$$\frac{G_c}{G_m} = \frac{1 + ABv_f}{1 - B\psi v_f} \quad (1)$$

where $A = (7 - 5\nu_m)/(8 - 10\nu_m)$ is a function of the Poisson ratio of the matrix ν_m , $B = [(G_f/G_m) - 1]/[(G_f/G_m) + A]$, v_f is the volume fraction of the filler, and the empirical function $\psi = 1 + [(1 - v_{\max})/v_{\max}^2]v_f$ represents a correction for the maximum packing fraction of the filler, v_{\max} , determined as the ratio of the true and sedimentation volume of the filler. The experimentally found v_{\max} for the polymeric filler and the glass beads was 0.55 and 0.65, respectively. Using the relationship $E = 2(1 + \nu)G$, eq. (1) assumes the following form for the tensile modulus:

$$\frac{E_c}{E_m} = K \frac{1 + AB_E v_f}{1 - B_E \psi v_f} \quad (2)$$

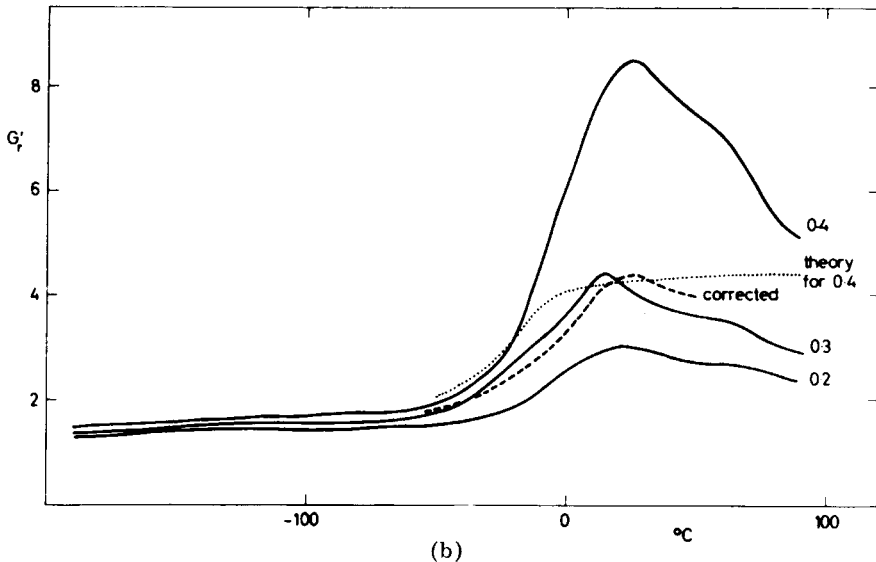
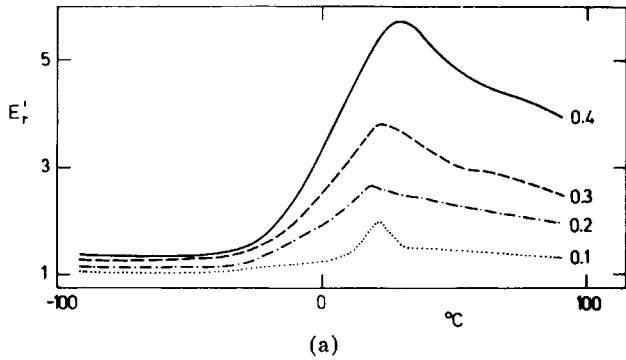


Fig. 3. Effect of volume fraction (indicated at curves) of polymeric filler on temperature dependence of relative modulus: (a) E_r ; (b) G_r .

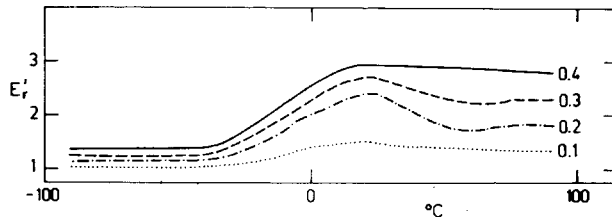


Fig. 4. Effect of volume fraction (indicated at curves) of glass beads on temperature dependence of relative modulus E_r .

where $K = (1 + \nu_c)/(1 + \nu_m)$, $B_E = [(CE_f/E_m) - 1]/[(CE_f/E_m) + A]$, and $C = (1 + \nu_m)/(1 + \nu_f)$; B is primarily determined by the ratio E_f/E_m and only slightly influenced by C . For the system rubbery matrix-glassy filler, it has been shown^{43,44} that the tensile and shear moduli can be approximated by the respective storage moduli.

A question now arises as to the effect of the temperature dependence of the

parameters A and B . As the Poisson ratio ν_m is approximately 0.3 in the glassy state, 0.47 at 25°C (Table I), and approaches 0.5 with increasing temperature, it is obvious that the corresponding increase of A from 1.1 to 1.5 accounts for a monotonic increase in the relative modulus with temperature. Using the moduli of the filler and of the matrix given in Figure 2(b), one can calculate that at -20°C, B or B_E is about 0.9 and approaches unity with increasing temperature. The resulting temperature dependence of the relative modulus G_r for $\nu_f = 0.4$ calculated using eq. (1) passes much below the level of experimental data and does not exhibit any extreme [Fig. 3(b)]. The maximum of the relative modulus can be explained—in terms of eqs. (1) and (2)—only by assuming an anomalous temperature dependence of A and/or ν_f .

Recently, a semiquantitative interpretation of the modulus jump has been offered³⁸ assuming that if the filler particles tend to form agglomerates, e.g., due to poor mixing or poor wetting by matrix, the coefficient A may amount up to 5. In essence, it is hypothesized³⁸ that below T_g the motion of the particles at the contact points is enforced by high shear forces produced by the glassy matrix ($A < 1.5$). Near above T_g , particle-particle motion in agglomerates ceases because of a substantial decrease in the matrix modulus; the agglomerates then behave as though they were completely rigid, and the produced increase in A (over 1.5) accounts for the major part of the jump in the relative modulus. At higher temperatures, the rubbery matrix expands more rapidly than the filler so that polymer-filler and/or filler-filler slippage may occur which presumably brings about a decrease in A with temperature. The relative modulus jump is expected to occur just above T_g . However, the maximum of the relative modulus of our system is located more than 50°K above the T_g of the matrix, and its shape is different from that predicted.³⁸ Model calculation³⁸ of the relative modulus jump for a composite characterized by $\nu_f = 0.4$ and $\nu_{\max} = 0.55$, which accidentally coincide with the parameters of our system, predicts a jump much smaller than that given in Figure 1. Conversely, if the maximum values of the shear relative modulus [Fig. 3(b)] are put into eq. (1), the calculated A is 6.21, 5.47, and 5.57 for $\nu_f = 0.2, 0.3,$ and 0.4 , respectively. Such values of A are too high, and furthermore they do not rise with ν_f (while in Ref. 38 they do) which would be evidence of increasing agglomeration with filler content.

Though such effects may partly occur in our systems (but we did not assess any detrimental effect of agglomerates on the ultimate properties⁴⁵), the pronounced maximum of the relative modulus necessitates that the phenomena associated with adsorption at the interface be also taken into account. Existing "self-consistent" models^{24,25,40} of particulate and short-fiber composites assume that filler particles are embedded in a matrix shell whose elastic properties coincide with properties of unfilled matrix; outside this shell lies a body with the properties of the composite. However, if the matrix is firmly adsorbed on the filler surface, it is obvious that mobility of the segments adjacent to the interface is suppressed and that the spectrum of relaxation times is deformed.⁴⁶

The quality of the interfacial adhesion at small strains can be estimated from the magnitude of the mechanical damping $\tan \delta$ of the composite. By solving eqs. (1) and (2)—which were derived²⁴ under the assumption of good interfacial adhesion—for complex moduli, an exact but rather complicated expression for the $\tan \delta$ -versus- ν_f dependence can be obtained.^{43,44} For rubber-like matrix and glassy filler of $0 < \nu_f \leq 0.4$, the solution can be reasonably well approximated

TABLE I
Effect of Volume Fraction of Polymeric Filler on Parameters of Composites

v_f^a	ν_c^b	K^c	25°C		90°C		0°C					
			$\left(\frac{E_r}{G_r}\right)_{25^\circ\text{C}}$	$\left(\frac{E_r}{G_r}\right)_{90^\circ\text{C}}$	$(v_{f,a})_{G_r}^d$	$(v_{f,a})_{E_r}^e$	$(v_{f,a})_{G_r}^d$	$(v_{f,a})_{E_r}^e$	$t, \mu\text{m}$	$t, \mu\text{m}$		
0.2	0.28	0.87	0.88	0.87	0.34	0.34	0.27	0.27	1.45	0.79	0.31	1.18
0.3	0.22	0.83	0.84	0.85	0.40	0.40	0.33	0.33	0.75	0.24	0.39	0.68
0.4	0.18	0.80	0.67	0.80	0.48	0.48	0.42	0.42	0.47	0.12	0.45	0.30
										0.36		

^a Volume fraction of polymeric filler.

^b Poisson ratio at 25°C (= 0.47 for matrix).

^c Constant of eq. (3).

^d Apparent volume fraction of filler from the relative shear modulus.

^e Apparent volume fraction of filler from the relative tensile modulus.

^f Apparent thickness of the immobilized layer.

by the following empirical equation which has been assessed^{4,15} to fit many experimental data:

$$\tan \delta_c = v_f \tan \delta_f + (1 - v_f) \tan \delta_m \quad (3)$$

If the interfacial adhesion is insufficient, new damping mechanisms may arise at the interface,⁴ e.g., particle-particle or particle-matrix frictions, which raise the mechanical damping. The contribution of the excess damping can be expressed by using the parameter³ $I = (\tan \delta_c)_{\text{exp}} / (\tan \delta_c)_{\text{theor}}$. Since for the system Estan-polymeric filler $I = 1.03$ (Fig. 5), it is obvious that the interfacial adhesion is strong enough to prevent any additional frictional mechanisms and, presumably, to cause immobilization. On the other hand, $I = 1.36$ for the system Estan-glass beads indicates an imperfect adhesion between the components.

Resulting overall reinforcement has been expressed by means of an apparent (effective) volume fraction $v_{f,a}$ of the filler (Table I). From the corresponding pairs $v_{f,a}$ and v_f an increment t , i.e., apparent immobilized layer, of the radius r of the filler particles has been calculated. The implicit assumption that the modulus of the immobilized layer is equal to the filler modulus is obviously unreal. The values $v_{f,a}$ or t should therefore be viewed as tools of a simplified numerical representation of the assessed reinforcement. The agreement between data ensuing from torsional and tensile measurements (Table I) is very good at both the temperature of the apparent maximum of reinforcement (25°C) and at 90°C (t is given for the average diameter of 15 μm). Similarly, the values $K = (1 + \nu_c) / (1 + \nu_m)$ calculated from the experimentally determined ν_m, ν_c data at 25°C are in accordance with $K \approx E_r / G_r$ obtained from dynamic mechanical measurements.

The decrease in t with filler concentration may be regarded as a consequence of diminishing relative effect of the filler on the segmental mobility. (One can only speculate that t approaches a limiting value with decreasing filler content. This is difficult to prove because the reinforcement markedly diminishes with decreasing filler content so that ordinary inaccuracy of mechanical measurement can produce a large error in the estimate of t ; for this reason, t is not given for $v_f = 0.1$ in Table I). Regardless of the volume fraction of the filler in composites,

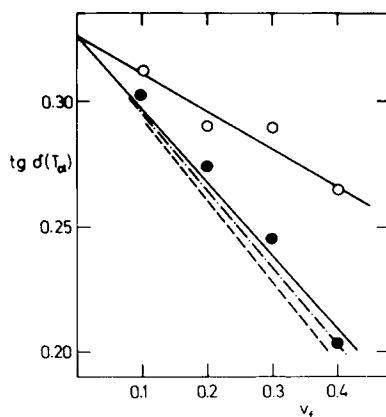


Fig. 5. Effect of volume fraction of polymeric filler (●) and of glass beads (○) on the height of the main (α) maximum of the loss factor. Corresponding dependences calculated from eq. (3) are represented by dash and dot-dash lines.

the value of t increases within the interval from -20° to 25°C (Table I), while above 25°C it decreases with temperature. Although the phenomenological description is satisfactory, the consequences are unreal, for it is unlikely that the extent of the chain immobilization at the interface increases with rising temperature and/or passes through a maximum. Therefore, one has to conclude that the maximum (not all the excess reinforcement) of G_r , E_r , and t is primarily due to modification of the viscoelastic properties of the matrix in the composite (Fig. 6). The relative modulus of the composites with glass beads is almost constant from 25° to 90°C ; since it is very close to the theoretical prediction (Fig. 7), the values of $v_{f,a}$ and v_f would be virtually identical and t negligible.

The incorporation of the filler causes broadening of the main loss maximum (Fig. 6) toward higher temperatures (which is equivalent to broadening of the spectrum of relaxation times toward longer times) and therefore a rise in the T_g if this is read off as the temperature of the peak of the loss maximum. The broadening of the spectrum necessarily brings about an increase of the relative modulus at temperatures above the T_g of the matrix, which is noticeable even at 90°C , i.e., about 120°C above the T_g of the matrix (Fig. 7).

The latter effect is difficult to estimate in dynamic mechanical measurements carried out as a function of temperature. Although it is not rigorous, the following procedure was used to eliminate the effect of the broadening of the

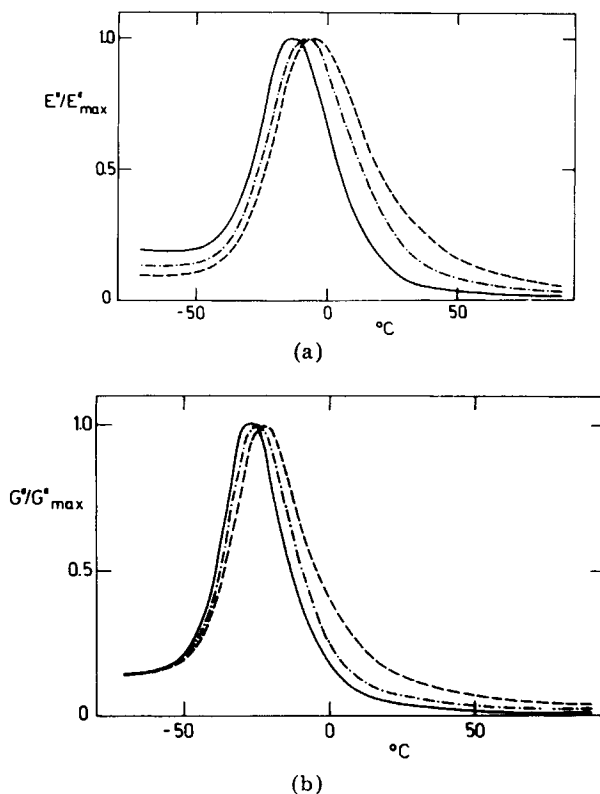


Fig. 6. Effect of polymeric filler on temperature dependence of the normalized (a) tensile loss modulus and (b) shear loss modulus in the glass transition region. Volume fraction of filler $v_f = 0$ (—), 0.2 (- - -), and 0.4 (- · -).

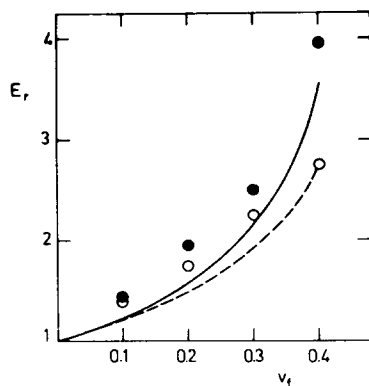


Fig. 7. Effect of volume fraction of polymeric filler (●) and of glass beads (○) on relative modulus of composites at 90°C. Theoretical dependences represented by solid and dashed lines, respectively, were calculated using eq. (2) and the K values in Table I.

spectrum of relaxation times: The normalized G''/G_m'' values [Fig. 6(b)] of the $v_f = 0.4$ composite were shifted toward lower temperatures so as to superimpose over the same values for the unfilled matrix; the shifts read off along the temperature axis were applied to corresponding values of the G' modulus, and a corrected temperature dependence of the relative modulus was then calculated [Fig. 3(b)]. The corrected relative modulus assumes values closer to the theoretical prediction, which indicates that the modification of the viscoelastic properties due to filling may to a large extent account for the excess reinforcement.

Summarily, a maximum on the temperature dependence of relative modulus above the T_g of the matrix is likely to be a general characteristic of particulate composites not associated with a particular structure, size, and shape of filler particles. To avoid misjudgment of the reinforcing effect of a filler, which may occur in the case of measurements carried out at one temperature, it is inevitable to assess the composite material moduli over an appropriate interval of temperatures. Besides the shape and size of particles, which affect the maximum possible packing, also interfacial interaction polymer–filler is obviously of crucial importance for the resulting reinforcement. Thus, the reinforcement of rubbery or leathery matrix produced by a polymeric filler may be apparently higher than that produced by an inorganic filler possessing a much higher modulus. If a system is characterized by strong interaction of phases, the habitual theoretical prediction of reinforcement may be far below the actual values.

None of the existing theories of composite materials, whatever the shape of inclusions,^{4,24–26,39–42} can explain the jump and subsequent decrease in relative modulus with increasing temperature above the T_g of the matrix. As long as the filler modulus is constant and the matrix modulus decreases with temperature, only increase in relative modulus can be anticipated. The introduction of adjustable parameters into current equations to fit experimental data is suitable for a particular composite, but it does not impart any versatility to the equations, for the procedure always requires experimental data. The values of effective filler fraction or apparent immobilized interface layer should be viewed as simplified representation of the excess reinforcement. The resolution of encompassed effects, i.e., actual immobilization, broadening of the spectrum

of relaxation times, increase in the glass transition temperature, agglomeration, and others, if any, would require a comprehensive study of composite systems combining results of pertinent physical methods.

References

1. T. L. Smith, *Trans. Soc. Rheol.*, **3**, 13 (1959).
2. L. Nicolais, E. Drioli, and R. F. Landel, *Polymer*, **14**, 21 (1973).
3. J. L. Kardos, W. L. McDonnel, and J. Raison, *J. Macromol. Sci.-Phys.*, **B6**, 397 (1972).
4. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974.
5. Yu. M. Malinskii, *Uspekhi Khim.*, **39**, 1511 (1970).
6. A. N. Cherkasov, J. Kolařík, and J. Janáček, *Int. J. Polym. Mater.*, **5**, 295 (1977).
7. Yu. S. Lipatov, E. G. Moisy, and G. M. Semenovich, *Polymer*, **16**, 582 (1975).
8. T. K. Kwei and C. A. Kumins, *J. Appl. Polym. Sci.*, **8**, 1483 (1964).
9. T. K. Kwei, *J. Polym. Sci. A*, **3**, 3229 (1965).
10. J. A. Manson and E. H. Chiu, *J. Polym. Sci. C*, **41**, 95 (1973).
11. D. H. Droste, A. T. DiBenedetto, and E. O. Stejskal, *J. Polym. Sci. A-2*, **9**, 187 (1971).
12. C. A. Kumins and J. Roteman, *J. Polym. Sci. A*, **1**, 527 (1963).
13. K. C. Rush, *J. Macromol. Sci.-Phys.*, **B2**, 421 (1968).
14. D. H. Droste and A. T. DiBenedetto, *J. Appl. Polym. Sci.*, **13**, 2149 (1969).
15. L. E. Nielsen, *J. Polym. Sci. C*, **12**, 249 (1969).
16. G. Kraus and J. T. Gruver, *J. Polym. Sci. A2*, **8**, 571 (1970).
17. A. Yim, R. S. Chahal, and L. E. St. Pierre, *J. Colloid Interface Sci.*, **43**, 583 (1973).
18. K. Iisaka and K. Shibayama, *J. Appl. Polym. Sci.*, **20**, 813 (1976).
19. J. Seto, *Rubber Chem. Technol.*, **50**, 333 (1977).
20. R. J. C. Rowson and R. G. C. Arridge, *J. Mater. Sci.*, **12**, 2154 (1977).
21. K. D. Ziegel and A. Romanov, *J. Appl. Polym. Sci.*, **17**, 1119 (1973).
22. K. D. Ziegel and A. Romanov, *J. Appl. Polym. Sci.*, **17**, 1133 (1973).
23. Yu. S. Lipatov, V. F. Babich, and V. F. Rosovizky, *J. Appl. Polym. Sci.*, **18**, 1213 (1974).
24. E. H. Kerner, *Proc. Phys. Soc.*, **69B**, 808 (1956).
25. C. van der Poel, *Rheol. Acta*, **1**, 198 (1958).
26. J. C. Smith, *J. Res. Natl. Bur. Stand.*, **79A**, 419 (1975).
27. R. A. Dickie, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2073 (1976).
28. J. Gähde, A.-E. Carius, Yu. S. Lipatov, *Plaste Kautsch.*, **23**, 875 (1976).
29. R. J. Morgan, *J. Mater. Sci.*, **9**, 1219 (1974).
30. L. J. Broutman and B. D. Agarwal, *Polym. Eng. Sci.*, **14**, 581 (1974).
31. R. G. C. Arridge, *Polym. Eng. Sci.*, **15**, 757 (1975).
32. F. Juračka and S. Hudeček, Czech. Pat. Application PV 4058-75, June 10, 1975.
33. L. M. Barclay, *Angew. Makromol. Chem.*, **52**, 1 (1976).
34. J. H. Saunders and K. C. Frisch, *Polyurethanes*, Part II, Interscience, New York, 1964.
35. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London, 1967.
36. J. Kolařík and K. Dušek, *J. Macromol. Sci.-Phys.*, **B10**, 157 (1974).
37. J. Kolařík and M. Štol, *Polym. J.*, **5**, 158 (1973).
38. B. Lee and L. E. Nielsen, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 683 (1977).
39. Z. Hashin, in *Mechanics of Composite Materials*, F. Neudt, H. Liebowitz, and N. Perone, Eds., Pergamon Press, New York, 1970.
40. J. C. Halpin and J. L. Kardos, *Polym. Eng. Sci.*, **16**, 344 (1976).
41. U. Zorll, *Gummi-Asbest-Kunstst.* **30**, 436 (1977).
42. R. F. Fedors, in *The Stereo Rubbers*, W. M. Saltman, Ed., Wiley, New York, 1977.
43. R. A. Dickie, *J. Appl. Polym. Sci.*, **17**, 45 (1973).
44. J. Kolařík, J. Janáček, and L. Nicolais, *J. Appl. Polym. Sci.*, **20**, 841 (1976).
45. J. Kolařík, S. Hudeček, and F. Lednický, *Faserforsch. Textiltech.*, to appear.
46. R. J. Landel, *Trans. Soc. Rheol.*, **11**, 53 (1958).

Received December 14, 1976

Revised February 13, 1978