Interfacial Phenomena in Macromolecular Systems. II. Relaxation Modulus of Uncross-linked Silica–Polydimethylsiloxane Composites[1]

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ABSTRACT: Relaxation modulus measurements on uncured silica-filled polydimethylsiloxane composites were correlated in terms of the polymer/filler interfacial energy. The heat of adsorption of a model compound (octamethylcyclotetrasiloxane) on the filler surface was taken as a measure of the interaction energy. The results on uncured composites containing these silicas revealed a strong correlation between the relaxation modulus and the net heat of adsorption. Roughly, 1.5 kcal/mol difference in the net heat of adsorption per siloxane bond caused a change in the relaxation modulus of two orders of magnitude. Dispersion of the fillers was examined with the electron microscope and revealed no significant difference in the dispersion of different silicas. The effect of interfacial energetics on the relaxation modulus can be entirely lost when cross-links are introduced into the system.

The addition of "reinforcing" filler in elastomers results in considerable enhancement of the modulus whether measured in tension or shear. To date, the physical properties of several filled systems have been extensively investigated in order to elucidate the mechanism of reinforcement. However, because of the enormous complexity of the problem which involves the interaction of several variables such as the particle size, dispersion, as well as the physical and chemical forces of interaction at the polymer–filler interface, the precise evaluation of the role played by each variable has remained obscured.

One of the earliest attempts to explain the results obtained with filled elastomers in terms of the hydrodynamic effects of the filler particles was that of Smallwood,[2a] who derived an equation for the Young's modulus of the filled composites

$$E = E_0(1 + 2.5\Phi)$$

where E and E_0 are the Young's moduli of the filled and unfilled mediums, respectively, and Φ is the volume fraction of the filler. This relationship is similar to Einstein's equation[2b] describing the viscosity of dilute suspension of spherical particles and has in common with Einstein's theory the condition that the filler particles must be wetted by the dispersing medium and must also be small enough to preserve the continuum nature of the supporting medium. Guth and Gold[3] had previously introduced a second-order term in Φ to the Einstein equation for composite viscosities to take account of the particle–particle interaction in more concentrated suspensions, and Guth[4] later applied this same equation

$$E = E_0(1 + 2.5\Phi + 14.1\Phi^2) \quad (2)$$

to the modulus of filled elastomers. He also introduced a shape factor for nonspherical filler particles

$$E = E_0(1 + 0.67f\Phi + 1.62f^2\Phi^2) \quad (3)$$

where f = length/width of the particle.

It is interesting to note that, apart from the condition of "wettability" of the filler, the above equations are independent of the size of the filler particle and of the quantitative nature of the interfacial bonding. It is therefore not surprising that these equations appear to explain only the results obtained with nonreinforcing fillers of large particle size, *e.g.*, calcium carbonate, glass beads, and thermal carbon black.[5,6] They are entirely inadequate, however, to explain the results obtained with even relatively poor reinforcing fillers of fine particle size, such as graphitized carbon black in polybutadiene rubbers.[5]

It is generally recognized that the interfacial bonding in filled systems has an important bearing on the rheological and mechanical properties of such systems.[6–13] The interaction between the polymer and the filler surface may be physical (mobile adsorption) or chemical (covalent bonding). Furthermore, the physical adsorption forces may be weak or strong. Different views are held by workers in this area regarding the nature of the interfacial bonding in many systems and of the relative importance of each type of interaction on the physical properties of composites.[5,14] The reason for this uncertainty is no doubt related to the difficulty involved in direct examination and measure-

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TABLE I

PROPERTIES OF THE SILICAS USED IN THIS INVESTIGATION

Treatment of the silica	Alkoxy groups per 100 Å^2	Net heats of adsorption[a] of octamethylcyclotetrasiloxane, kcal/mol
Untreated		12.4
Methanol	1.2	11.1
Methanol	2.5	9.9
Methanol	4.0	6.8
Methanol	4.1	6.3
Ethanol	2.8	7.8
Ethanol	3.0	7.2
Butanol	1.6	9.1

[a] Net heat of adsorption = $\Delta H - \Delta H_v$, where ΔH is the measured value of differential heat of adsorption at $\theta \rightarrow 0$ and ΔH_v is the heat of condensation of octamethylcyclotetrasiloxane.

ment of the type and the extent of interfacial bonding in the composite itself.

The present investigation was undertaken to correlate a physical property of the uncross-linked silica–polydimethylsiloxane composites in terms of the interaction energy of the two constituents.

The heat of adsorption of a model compound of the polymer (octamethylcyclotetrasiloxane) on the silica surfaces was taken as a measure of the interfacial energy[15] and, since the surface properties of silica can be changed[15] without affecting the particle size, it was possible to control the interfacial energies. We were thus able to determine the effect of interfacial energy on the physical properties of the composites. The property measured was the relaxation modulus and the results revealed a strong correlation between the interfacial energies and this property.

Experimental Section

The System. Polydimethylsiloxane, SE-76, supplied by the General Electric Co., Waterford, N. Y., was used as the polymer. It was devolatilized by pumping at 120° and 1 μ pressure. The viscosity average molecular weight of the devolatilized material was 5×10^5 g/mol.

An amorphous silica, Cab-o-Sil, ultimate particle size 12 mμ, manufacturer's quoted surface area 200 m^2/g, was used as the filler (the measured value of the surface area by nitrogen adsorption was 199 ± 10 m^2/g).

Characterization and Surface Modification of the Silica. The interfacial interaction energies were expressed in terms of the heat of adsorption of a model compound of the polymer (octamethylcyclotetrasiloxane) and were measured by vapor phase chromatography at surface coverages approaching zero. The values obtained on several surfaces were reported earlier.[15] The modification of the silica surface was accomplished by treating it with normal alcohols in the vapor phase. The desired characteristics were obtained by a suitable choice of the number and size of the alkoxy groups chemisorbed per unit surface area of the silica sample. The surface coverage was controlled by the temperature and pressure of the reaction and was calculated on the basis of the total carbon analysis and the surface area.[15] The pertinent information regarding the silicas used in this investigation is given in Table I.

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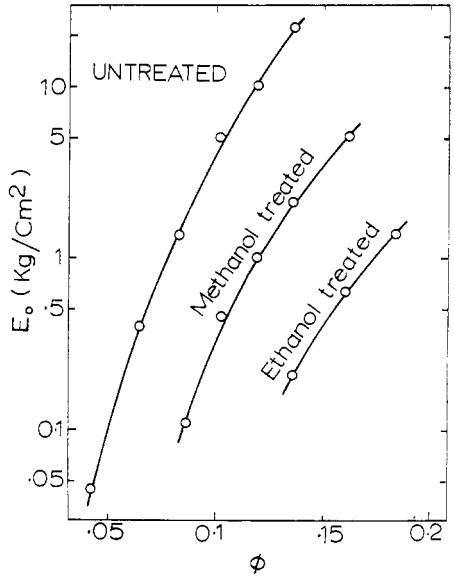

Figure 1. Relaxation modulus of uncross-linked composites as a function of Φ, the volume fraction of the filler.

Preparation of Composites. A solution of polydimethylsiloxane, approximately 20%, was prepared in *n*-hexane. Silica samples which had been dried at 130° and 1 μ pressure were mixed into the solution and the mixture was then stirred with a spatula until it was almost dry. It was held at 0.01 μ pressure at room temperature for 6–8 hr in order to remove the solvent. Spectroscopic and gravimetric analyses had shown that this treatment was sufficiently rigorous to remove completely *n*-hexane from silica and from the polymer. The dried samples were then worked with a rolling pin until the air pockets were removed and were tested mechanically shortly after their preparation.

Mechanical Measurements. The dried silica–silicone composites were sheeted out in a mold 4 × 3.5 in. and 0.09 in. deep, at a pressure of 1500 psi. Test samples were then cut from the sheets in the form of 1-in. wide strips. The stress relaxation tests were carried out on an Instron tensile tester. The samples were clamped in smooth plate jaws, allowing 4.0 cm between the jaws with 10% extensions being employed. Extension was applied at the rate of 50 cm/min. The decay in stress was then observed over an extended period of time. From the straight line portion of the plots of log E *vs.* time, the relaxation modulus (E_0) at zero time was obtained. The reported values are the average of two to three individual tests with fresh samples used for each test.

Dispersion. The dispersion of silicas in the composites was determined by means of electron microscopy. Replicas of freshly prepared surfaces were obtained by depositing on them a 20% solution of gelatin in water at 80°.[16,17] After drying, the gelatin wafer was stripped and a layer of carbon was evaporated onto it. It was then shadowed with platinum and the gelatine dissolved away by floating the wafer on hot distilled water.

Results and Discussion

The relaxation moduli (E_0) at zero time are plotted as a function of the volume fraction (Φ) of the filler (Figure 1). The data cover the region above Φ = 0.04 loading since samples filled below that level were too weak to be tested in the manner described.

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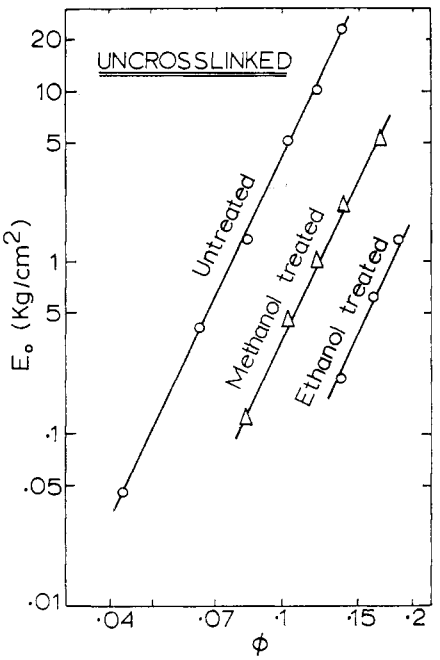

Figure 2. Relaxation modulus of uncross-linked composites as a function of log Φ, the volume fraction of the filler.

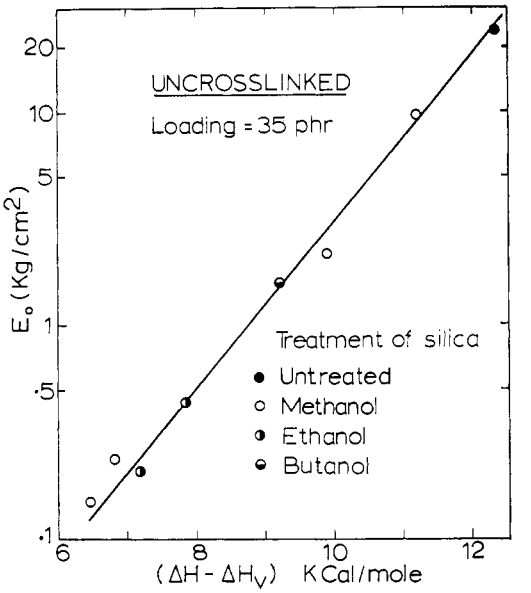

Figure 3. Relaxation modulus of uncross-linked composites as a function of the net heat of adsorption of octamethylcyclotetrasiloxane on the filler surface, at a constant filler concentration.

It is quite obvious from Figure 1 that the relaxation modulus is not a unique function of the volume fraction of the filler as might be expected from the Guth–Gold relationships. According to those equations, which neglect interfacial energetics, the results due to all three surface treatments of the silica should have fallen on the same curve. Replotting of the data from Figure 1 on a log Φ scale yields linearity in the relationship between the zero time relaxation modulus and volume fraction of the filler (Figure 2).

The above results clearly demonstrate that the lower polymer–filler interaction energy systems give lower values for the relaxation modulus at any given concentration of the filler. The effect of the polymer–filler interaction energy on the relaxation modulus may perhaps be better illustrated by examining the values of the relaxation moduli as a function of the interaction energies at constant concentration of the filler. In Figure 3 are plotted the logarithms of zero time relaxation moduli at a fixed loading of 35 phr of silica as a function of the net heats of adsorption of octamethylcyclotetrasiloxane on the filler surfaces. The relaxation moduli decreased linearly with decreasing interaction energy. Furthermore, the results obtained with all the fillers, whether untreated or covered with methoxy, ethoxy or the butoxy groups, fell on a common line.

The dependence of the relaxation modulus on the filler concentration (Figure 2) can be expressed by

$$E_0 \propto \Phi^{5.05}$$

which is obeyed by all the composites regardless of the nature of the surface treatment of the filler or its interaction energy. For a completely quantitative description of the results obtained with systems involving fillers of different interaction energies, it is however necessary to include a term expressing the dependence of E_0 on the interaction energy of the filler (Figures 2 and 3).

The results depicted in Figures 2 and 3 can be described by

$$E_0 \propto \Phi^{5.05} e^{b(\Delta H - \Delta H_V)}$$

where b is a constant and $(\Delta H - \Delta H_v)$ is the net heat of adsorption of octamethylcyclotetrasiloxane on the filler surface. In the following sections we will attempt to interpret these results in terms of the molecular phenomena leading to this behavior. The dependence of E_0 on Φ will be discussed first.

According to the theory of stress relaxation in elastomeric systems,[18,19] the straight line portion of the log stress *vs.* time plot is described by the equation $E(t) = E_0 e^{-t/\tau}$. The slope of this line is a measure of the nature and the extent of the viscoelastic phenomenon responsible for the observed relaxation behavior. The slope of the above-mentioned relaxation plot equals $-1/\tau$. τ is thus the relaxation time in the expression $\tau = \eta/E_0$, where E_0 is the relaxation modulus and η the viscosity. It was found in the present work that τ was constant, within experimental error, irrespective of the filler treatment or concentration. τ values were found to be in the range of 1.7–2.2 $\times$ 10^3 min. The constancy of τ in a system where $E_0 \propto \Phi^{5.05}$ implies a viscosity relationship of the form

$$\eta \propto \Phi^{5.05}$$

This relationship for the viscosity further suggests the application of the $\eta = M^\nu$ equation. It could well be argued that the filler particles act as cross-link points and in effect increase the molecular weight (M) of the polymer, resulting in the behavior described by this equation. The value of 5.05 for ν is, however, much

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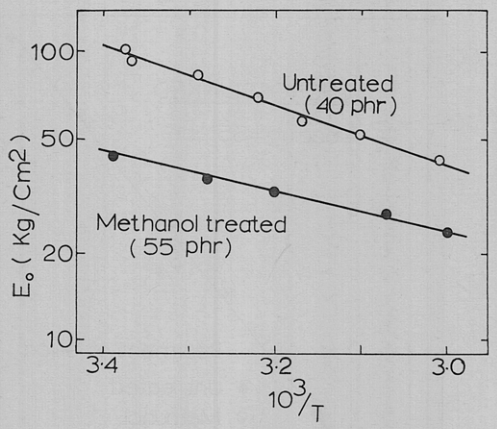

Figure 4. Activation energy of the relaxation modulus of composites containing untreated and treated filler.

higher than the expected value of 3.4 based on entanglement effects.[18,20] It is entirely plausible, however, that the strongly adsorbing silica surface results in multisegmental adsorption of entangled molecules and that this effect, along with the inclusions of solid particles, could complicate the rheology of the system. In view of this, a value of ν higher than the theoretical value may be expected. Indeed, values of ν as high as 4[20] and 5.8[21,22] have been reported.

Notwithstanding all this, the relatively constant value of τ found in these experiments fails to lend support to this simplified approach. This, because of the theory of stress relaxation,[18-20] predicts a relationship of the form $\tau = M^{\nu+1}$ for the variation in the relaxation times as a function of the molecular weight of the polymer in which the relationship $\eta = M^{\nu}$ is applicable.

It should be emphasized that the $E \propto \Phi^{5.05}$ relationship can safely be applied only to the range of the filler concentration investigated here. There could well be a critical concentration of filler beyond which this relationship changes. Such behavior was observed by Kambe[23] on polyethylene melts containing calcium carbonate and barium sulfate as filler. The dynamic moduli and viscosities (at 0.02 cps) of the suspensions containing calcium carbonate (coated with calcium stearate) and barium sulfate of particle sizes in the range of 40–265 mμ increased quite suddenly as a function of Φ after a certain critical concentration was reached. This critical concentration depended on the particle size and increased with the size. In the present investigation, since the log E_0 *vs.* Φ plots (Figures 1 and 2) are displaced toward higher concentration with successive decrease in the heat of adsorption, it could well be that the lower critical concentration of the filler occurs below the range investigated and in which the $E_0 \propto \Phi^{5.05}$ relationship is applicable.

The $E_0 \propto e^{b(\Delta H - \Delta Hv)}$ relationship at constant Φ (Figure 3) would imply that the number of the effective chain links increases exponentially with the interfacial energy, thus assuming that all links are equally effective

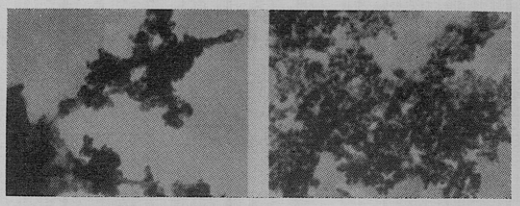

Figure 5. Electron micrographs of filler dispersed in hexamethyldisiloxane: a, untreated silica; b, silica covered with 4.1 methoxy groups per 100 Å².

in supporting the stress. These links may include (a) direct interparticle chain links, (b) those provided by entangled chains adsorbed on adjacent filler particles, and (c) by the conventional chain entanglements in the polymer not adsorbed on the filler. It would be expected that the filler particles will primarily influence the a and b type of links. It appears from the above results that under these experimental conditions the surface interaction energy determines only the number of such links and not their relaxation behavior or more specifically the slip or movement of the polymer chains adsorbed on the filler surface. This is because the relaxation time τ as mentioned earlier was constant within experimental error. It is not suggested, however, that these links will not relax under any other circumstances. Further evidence, indicating that the above results due to fillers with different interaction energy cannot be attributed to differences in the relaxation or slip mechanism at the polymer filler interface, was obtained from the activation energy plots of log E_0 as a function of $10^3/T$, where T is the absolute temperature.

The results for untreated and methanol-treated silica (surface coverage of 4.1 groups 100 Å²) filled composites are given in Figure 4. The loading was 40 and 55 phr, respectively. The activation energy was 4.8 kcal/mol for the untreated and 2.9 kcal/mol for the treated silica-filled samples. These values are comparable to the value of 3.55 kcal/mol found for the activation energy for viscous flow of high molecular weight polydimethylsiloxane.[24,25] It may therefore be concluded that the relaxation phenomenon in filled composites takes place primarily in the gum phase. Similar conclusions were also reached by Cotten[26] and Kambe[23] in filled SBR-1500 and polyethylene systems, respectively.

The possibility that the results of this investigation were perhaps affected by nonuniform dispersions or other structural effects of the filler associated with its interfacial energy was also examined. The dispersion of the unmodified and modified silicas in hexamethyldisiloxane and the gum was investigated. Figures 5a and b are the electron micrographs of the untreated silica and the silica covered with 4.1 methoxy groups per 100 Å² dispersed in hexamethyldisiloxane, respectively. Obviously the treated silica is dispersed more uniformly with less aggregation as compared to the untreated silica. This is indicated by the fact that the ultimate aggregate structures of roughly 25 to 120 mμ

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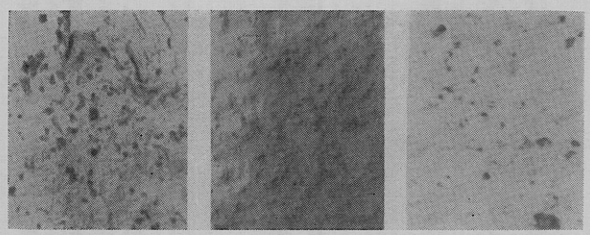

Figure 6. Electron micrographs of filler dispersed in the polymer: a, untreated silica, concentration 40 phr; b, silica covered with 2.5 methoxy groups per 100 Å², concentration 40 phr; c, silica covered with 4.1 methoxy groups per 100 Å², concentration 55 phr.

in size are distinctly visible in Figure 5b while Figure 5a simply represents a large cluster of smaller aggregates with very little finer detail.

Figures 6a, b and c are the electron micrographs of replicas of the composites containing untreated and methanol treated silicas with 2.5 and 4.1 methoxy groups per 100 Å², respectively. Both Figure 6a and b contain 40 phr of silica while Figure 6c contains 55 phr of silica. Upon comparison, it is obvious that the dispersion is close to uniform in all the three samples and that the average particle size corresponds to the aggregates observed in Figure 5b and not those observed in Figure 5a. Thus, while the particle structure which was noticed in Figure 5a has been broken down as a result of the shear forces encountered upon working the filler into the gum, the milling action was not severe enough to break up the ultimate aggregate structures.

The results shown in Figure 7 lend further support to the hypothesis put forward above that it is the interparticle linkages, whether direct or through the entanglements, which determine the enhancement in the strength properties of the filled composites over and above that of the unfilled gum. The results of Figure 3 have been replotted in Figure 7 along with some results obtained on samples cross-linked with γ radiation as well as with benzoyl peroxide. (Benzoyl peroxide was dissolved in the gum in *n*-hexane solution prior to the addition of the filler. The curing was done in an oven at 135° for 2 hr.)

It is apparent that while the addition of cross-links increased the E_0 of the composites containing untreated silicas (those with the largest interaction energy, $\Delta H - \Delta H_v = 12$ kcal/mol), maximum increase in E_0 was obtained in the case of samples containing modified silicas with lowest heats of adsorption. The

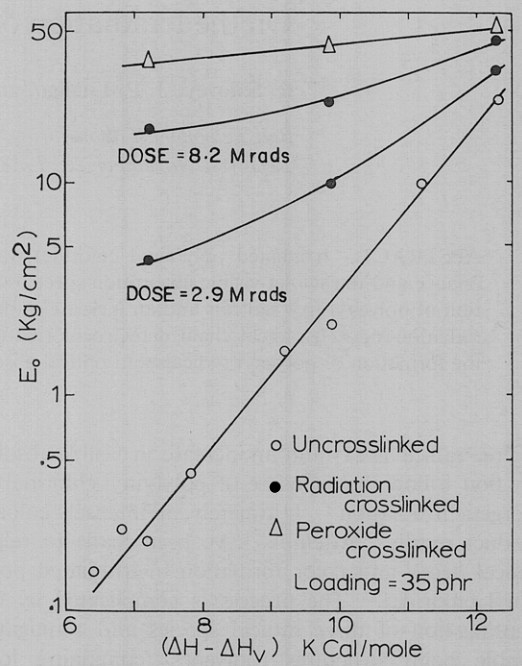

Figure 7. Relaxation modulus of uncross-linked and cross-linked composites *vs.* the net heat of adsorption of octamethylcyclotetrasiloxane, at constant filler concentration.

higher the cross-link density, the less important is the nature of the surface. In the case of the peroxide cross-linked samples (benzoyl peroxide concentration was 2.25 g/100 g of gum), the relaxation modulus was practically the same regardless of the nature of the surface treatment. Evidence has been presented elsewhere[27] that polydimethylsiloxanes are cross-linked to the silica surface by γ radiation. Furthermore, there is a sufficient amount of reactive species in the gum capable of reacting with the silica surface on heat treatment during the peroxide curing.[28] Under these circumstances, it can be imagined that the cross-linking of the chains between the filler particles would eventually establish direct covalently bonded links between the particles. The number of these interparticle links would tend to become equal at the optimum cure of the composites regardless of the physical interaction energy of the filler surface and would therefore explain the results of Figure 7.

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