

Work of adhesion influence on the rheological properties of silica filled polymer composites

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As the work of adhesion, W_a , increases between a silica filler surface and a polymer matrix, the dynamic viscosity and the shear modulus of the composite material increase. The logarithms of these properties decrease linearly as W_a decreases. At lower dynamic test frequencies, a change in W_a has a more dramatic impact on these properties than at higher frequencies. An "effective silica particle size" model can be used to explain why W_a affects the viscosity and the shear modulus of a composite. According to that model, the thickness of the interphase layer increases as the W_a increases. An increase in effective particle size decreases the "free" polymer volume, and the decrease free volume polymer causes both the viscosity and the shear modulus to increase. Increasing the dynamic test frequency releases some of the immobilized polymer from the filler surface which causes the effective particle size to decrease. As the effective particle size decreases because of the increased testing frequency and approaches the mean size of the original filler, the impact of the W_a value on viscosity and shear modulus should decrease. However, the friction experienced between the filler interphase and the polymer, the so called "skin friction", depends on the magnitude of W_a and the more general term, bond energy density (BED). The skin friction determines the viscosity of the composite, particularly at lower frequencies. Higher W_a values induce higher skin friction and thereby higher flow resistance (viscosity) as polymer chains move along the filler surface.

1. Introduction

The effect of the interfacial bond on the mechanical properties of composites has been treated quantitatively in a limited number of publications [1–5]. In previous studies, where such a quantitative approach was used, a simplified silica filled ethylene vinyl acetate (EVA) composite system without a polymerized silane layer at the filler surface was analysed [1–3, 6]. Different interfacial bond strengths were determined in those papers and expressed quantitatively in terms of work of adhesion, W_a , values [1–3]. From those determinations it was shown that the W_a value correlated with the mechanical properties of the investigated composites. At a given volume fraction silica, both the interphase thickness, Young's modulus and the tensile strength increased as the W_a value increased [1–3]. Higher W_a values were related to thicker interphase regions of polymer bonded to the silica surface, and the hydrogen component, W_a^h , of the work of adhesion, W_a , equation was shown to have a dominant effect on that thickness [1–3]. The logarithms of the interphase thickness, Young's modulus and the tensile strength decreased linearly as W_a decreased [1–3].

Based on these results, the validity of these exponential relationships for the rheological properties

of the same materials is explored. The main goal of this study was to test the hypothesis that W_a is a valid predictive parameter of the rheological properties of composites.

The first objective was to correlate work of adhesion with the rheological properties of the silica filled composite by plotting the shear modulus and the viscosity values as functions of W_a . A correlation is expected because the interphase thickness is known to increase as W_a increases [1–3].

The second objective was to determine how the shear modulus and the viscosity depend on material characteristics, such as filler particle size, volume fraction filler and testing condition (the rheological dynamic frequency), for a given W_a value [7–22].

2. Experimental procedure

2.1. Materials

Spherical silica particles, 0.014 or 0.6 μm in diameter, were used as fillers in an ethylene vinyl acetate (EVA) copolymer (72 wt % ethylene and 28 wt % vinyl acetate) (Scientific Polymer Products, Inc., Ontario, NY). The finer MS-7 grade fused silica particles (0.014 μm) were obtained from Cab-O-Sil (Cabot Corporation, Tuscola, IL). The 0.6 μm silica

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particles were prepared according to a method described by Stöber [23] and Stöber and Tan [24].

2.2. Surface treatment

To characterize the properties of the silica particle surfaces, amorphous fused quartz plates were used as a model material. The surface properties of these plates were assumed to be similar to those of the silica particles. Two treatment procedures were conducted to modify the surfaces of the silica particles and the quartz plates. These two treatments consisted of:

1. heat treatment, and
2. heat treatment combined with a treatment with $(\text{CH}_3)_3\text{-SiCl}$ (trimethylchlorosilane, TMCS) [25, 26].

2.3. Determination of work of adhesion

To quantify the interfacial bond strength between the silica surface and the EVA copolymer matrix, work of adhesion, W_a , was determined from [1–3 27–35]

$$W_a = W_a^d + W_a^h \quad (1)$$

In Equation 1, W_a^d represents dispersion forces and W_a^h represents hydrogen bonds and polar forces. The detailed computation of W_a^d and W_a^h has been described previously [1, 2].

2.4. Composite sample preparation

Forty grams of EVA copolymer were thoroughly dissolved in 800 ml benzene at 40°C. Different volume fractions of pretreated silica powders (5, 10, 15 and 20 vol % silica) were then incorporated into the polymer solution. Before the Stöber silica or the Cab-O-Sil silica were added to the benzene–EVA solutions, these fillers were heated to either 110, 500 or 750°C, or were treated with TMCS after they were heated to these temperatures (110°C/TMCS, 500°C/TMCS and 750°C/TMCS groups). A magnetic stirrer was used to improve silica dispersion into the polymer solution. For the Cab-O-Sil silica composite solutions, sonication (model W-375, Heat Systems-Ultrasonic, Inc.) at 20 KHz for 15 min was used to enhance the Cab-O-Sil dispersion.

Benzene was chosen as a solvent because it is non-polar and a good solvent for the EVA copolymer. The silica particles were expected to disperse in the polymer solution since the solvent induces optimal polymer chain length expansion which stabilizes the silica powders in solutions. The polymer composite solution was cast over a large Teflon® pan and the solvent was rapidly evaporated to prevent an uneven filler precipitation.

2.5. Rheological measurement

The rheological properties of the silica filled EVA copolymer were measured with a Rheometrics Dynamic Spectrometer (model RDS-II). The dynamic viscosity and the shear storage modulus were both

obtained by using a set of 25 mm diameter parallel plates, and frequency sweeps were from 0.1 to 100 rad s^{-1} at a 100% strain level during testing [36–38].

Rheological measurements of the Stöber filled composites were made at 150°C with a 0.6 mm gap between the parallel plates, while the Cab-O-Sil silica composites were tested at 210°C with a 2.0 mm gap. These differences in testing were introduced because the Cab-O-Sil silica composites have more filler–polymer contact area than the Stöber composites containing the same silica volume. The spectra of either the dynamic viscosity or the shear modulus versus frequency were recorded.

2.6. SEM studies on brittle fracture surface

The morphology of fractured composite samples was studied with scanning electron microscopy (SEM) (model JSM-35CF). The composite sheets were first immersed in liquid nitrogen and then broken by a hammer to form brittle fracture surfaces. Such fractured surfaces were expected to reveal a true distribution and dispersion of silica fillers in the polymer matrix. The matrix and the Stöber silica particle interface, either heat or heat–TMCS treated, were examined in the SEM.

3. Results

3.1. Shear modulus of Cab-O-Sil and Stöber silica composites

Figs 1 and 2 show the logarithm of the shear modulus $\log G'$, versus the frequency, ω , of a composite containing 5 vol % Cab-O-Sil silica and 20 vol % Stöber silica, respectively. The composites containing 15, 10 and 5 vol % Stöber silica show similar plots. These plots indicate that the filled polymers had a higher shear modulus than the unfilled polymer and that their shear modulus increased with increased frequency [8, 9, 39].

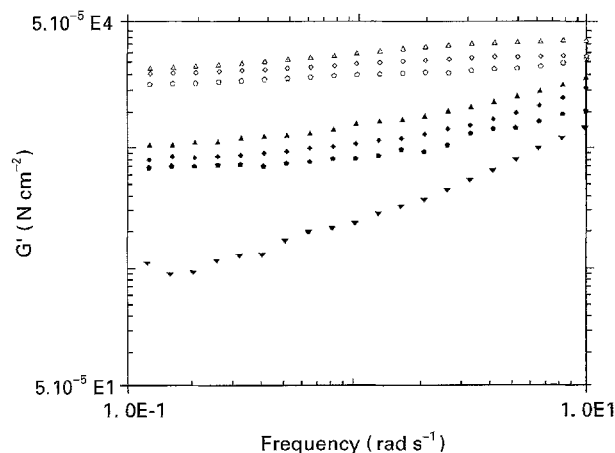


Figure 1 Shear modulus versus frequency of 5 vol % Cab-O-Sil silica filled EVA composites with various silica surface properties: (Δ) 110°C, (\diamond) 500°C, (\square) 750°C, (\blacktriangle) 750°C–TMCS, (\blacklozenge) 500°C–TMCS, (\clubsuit) 110°C–TMCS, (\blacktriangledown) EVA copolymer.

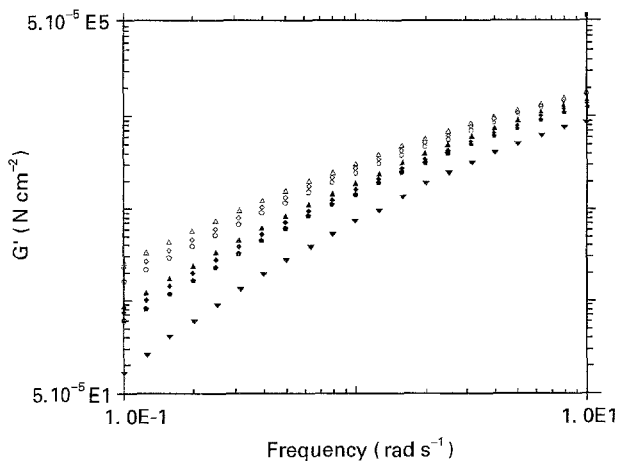


Figure 2 Shear modulus versus frequency of 20 vol % Stöber silica filled composites with various silica surface properties: (Δ) 110 °C, (\diamond) 500 °C, (\triangle) 750 °C, (\blacktriangle) 750 °C-TMCS, (\blacklozenge) 500 °C-TMCS, (\bullet) 110 °C-TMCS, (\blacktriangledown) EVA copolymer.

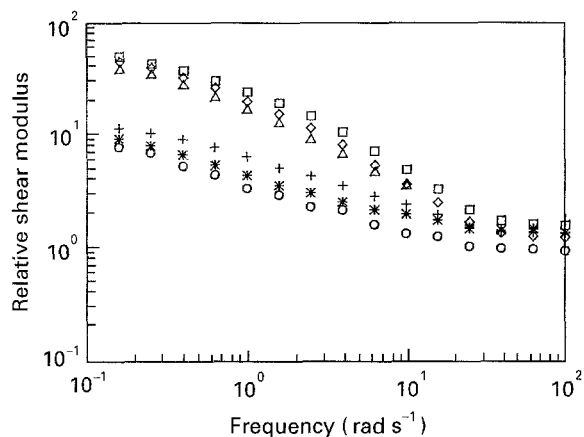


Figure 3 Effect of frequency and silica surface properties on the relative shear modulus of 5 vol % Cab-O-Sil filled EVA composites: (\square) 110 °C, (\diamond) 500 °C, (\triangle) 750 °C, (+) 750 °C-TMCS, (*) 500 °C-TMCS, (\circ) 110 °C-TMCS.

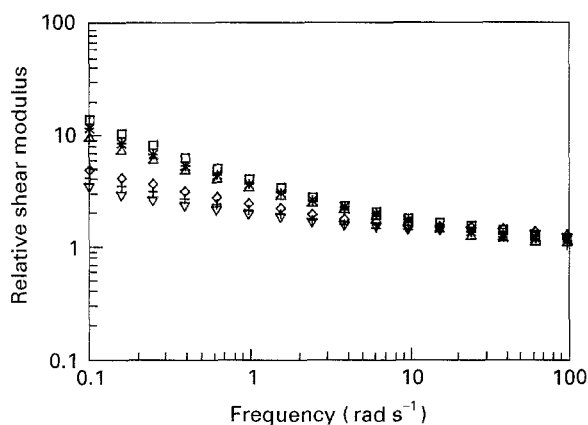


Figure 4 Effect of frequency and silica surface properties on the relative shear modulus of 20 vol % Stöber silica filled composites: (\square) 110 °C, (+) 500 °C, (\triangle) 750 °C, (\diamond) 750 °C-TMCS, (+) 500 °C-TMCS, (∇) 110 °C-TMCS.

The influence of the matrix on the rheological properties can be minimized if the relative value of a filled versus an unfilled polymer is introduced. Figs 3 and 4 show the relative shear modulus, G'_c/G'_p , of 5 vol % Cab-O-Sil and 20 vol % Stöber silica composites,

respectively. The $\log(G'_c/G'_p)$ versus ω plots at 15, 10 and 5 vol % Stöber silica composites are similar to Figs 3 and 4. Note that at 5 vol % filler, Cab-O-Sil composites had a higher G'_c/G'_p ratio than Stöber silica composites.

The composites containing heat treated silica had higher shear moduli, particularly at lower frequencies, than those containing heat-TMCS treated silica. Figs 3 and 4 show that the G'_c/G'_p ratio approached a constant value at higher frequencies and became independent of interfacial bond strength.

3.2. Dependence of work of adhesion on shear modulus

3.2.1. Effect of frequency

Figs 5–7 show the plots of G'_c/G'_p ratio versus W_a^{-1} of 5 vol % Cab-O-Sil silica composites and 20 and 5 vol % Stöber silica composites, respectively. At frequencies equal to either 0.1, 1.0 or 10 rad s^{-1} , exponential relationships between the G'_c/G'_p ratio and W_a^{-1} were observed. Similar exponential relationships were found for 15 and 10 vol % Stöber silica composites.

Figs 5–7 show that the G'_c/G'_p ratio increased as W_a increased, particularly at lower frequencies. Consequently, at a lower frequency, W_a had a greater effect on the shear modulus of a composite. At a higher frequency, W_a is not as effective in determining the shear modulus as it is at a lower frequency. To compare mechanical properties with rheological

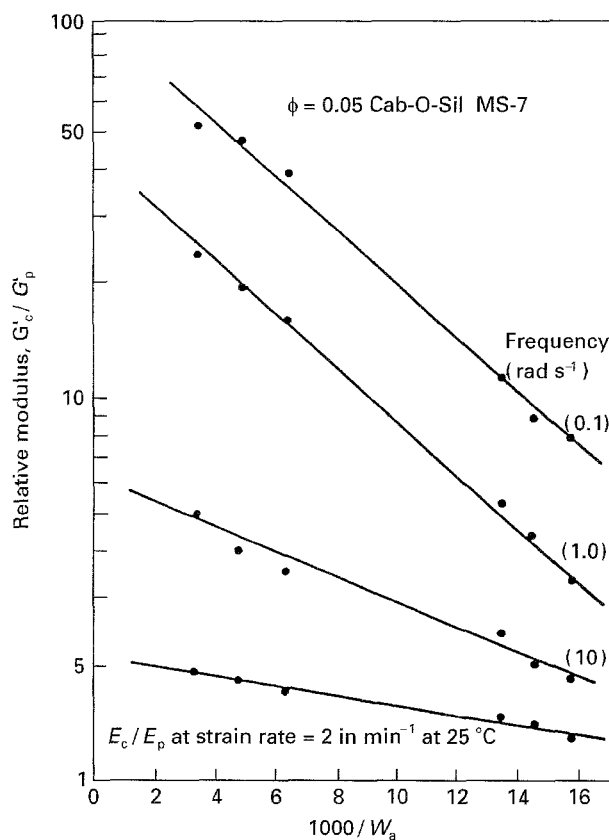


Figure 5 Effect of work of adhesion and frequency on the relative shear modulus of 5 vol % Cab-O-Sil silica filled EVA composites.

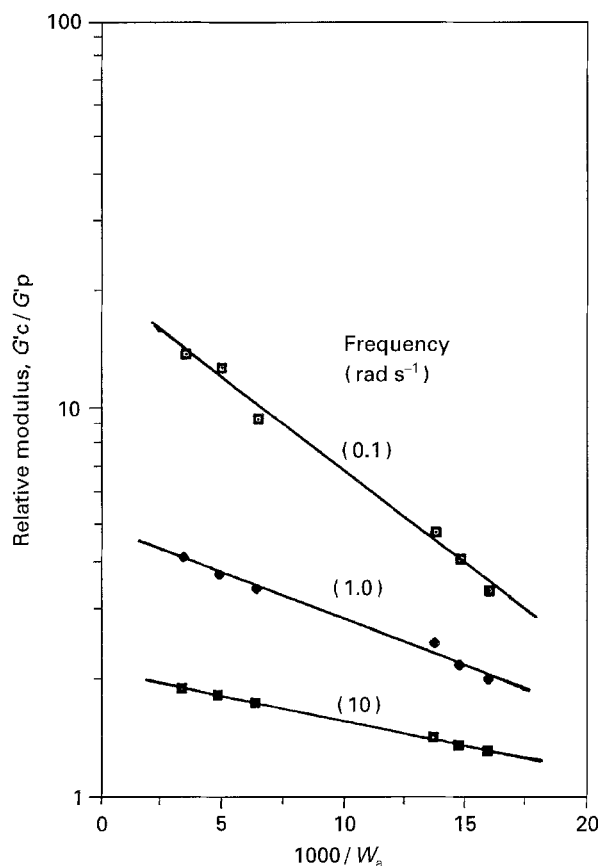


Figure 6 Effect of work of adhesion and frequency on the relative shear modulus of 20 vol % Stöber silica filled EVA composites.

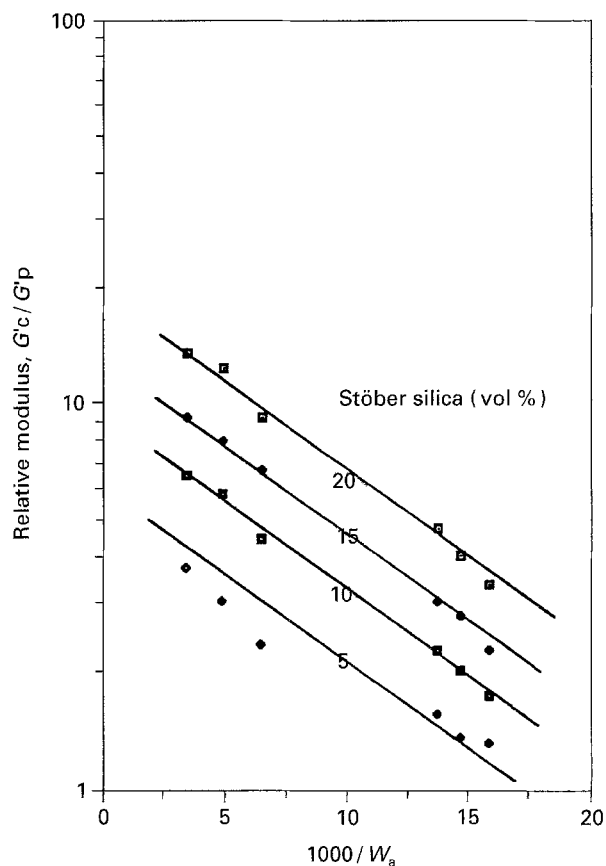


Figure 8 Effect of work of adhesion and Stöber vol % on the relative shear modulus of EVA composites measured at 0.1 rad s⁻¹.

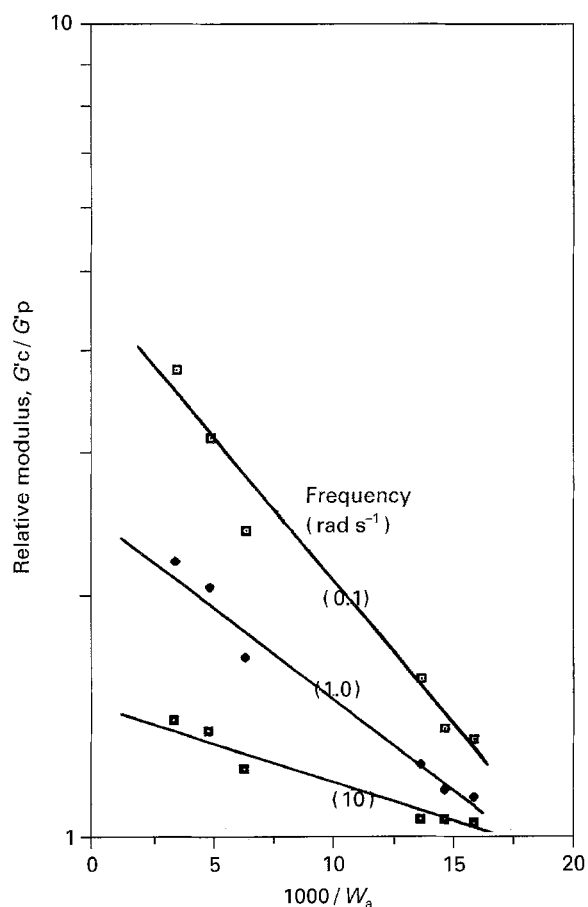


Figure 7 Effect of work of adhesion and frequency on the relative shear modulus of 5 vol % Stöber silica filled EVA composites.

properties, Fig. 5 includes Young's modulus of the 5 vol % Cab-O-Sil composites.

The relationships discussed above between the W_a and the G'_c/G'_p ratio can be described by a mathematical equation as

$$\frac{G'_c}{G'_p} = C \cdot \exp^{-K_{G'}(1/W_a)} \quad (2)$$

where G'_c and G'_p are the shear moduli of the composite and the polymer, and C and $K_{G'}$ are constants. The $K_{G'}$ term represents the slope of $\log G'_c/G'_p$ versus W_a^{-1} , and is determined from the experimental data. The $K_{G'}$ term is known as the apparent surface energy barrier of the shear modulus of a composite.

For the same volume fraction silica, but with different silica surface properties of the composites, the constant C in Equation 2 can be deleted and the ratio of two shear moduli can be written as

$$\frac{G'_c}{G'_{co}} = \exp^{-K_{G'}\left(\frac{1}{W_a} - \frac{1}{W_{a0}}\right)} \quad (3)$$

where G'_{co} is the shear modulus of the silica composite having the weakest interfacial bond (110°C-TMCS treatment, $W_{a0} = 63 \times 10^{-7} \text{ Jcm}^{-2}$). The W_{a0} is the work of adhesion of the composite material with the weakest interfacial bond. When the shear modulus of a composite with its corresponding W_a is known, Equation 3 can be used to predict the shear modulus of other composites with another W_a but with the same silica content.

3.2.2. Effect of volume fraction

Fig. 8 shows the G'_c/G'_p versus W_a^{-1} values measured at a 0.10 rad s^{-1} frequency of the 5, 10, 15 and 20 vol % Stöber silica composites. As silica content increased, the G'_c/G'_p value increased too. The $K_{G'}$ values, which were the slopes in Fig. 8, were approximately the same.

The independency of $K_{G'}$ values to silica content was similar for the K_{Ec} values, as reported in previous publications [1, 3]. The K_{Ec} is the apparent surface energy barrier for Young's modulus of composites [1, 3]. Furthermore, the plots of G'_c/G'_p versus W_a^{-1} values measured at 1.0 and 10 rad s^{-1} also show that the $K_{G'}$ values were independent of silica content.

When the $K_{G'}$ values obtained at 0.1 rad s^{-1} were plotted against Stöber silica volume fraction, a group of horizontal lines were obtained, as shown in Fig. 9. At other frequencies, such as 0.4, 1.0, 2.5 and 10 rad s^{-1} , each frequency yielded data represented as a horizontal line.

When the G'_c/G'_p versus W_a^{-1} values at 0.1 rad s^{-1} of 5 vol % Cab-O-Sil silica composites (Fig. 5) were compared with those of 5 vol % Stöber silica composites (Fig. 7), the two $K_{G'}$ values were different. This finding suggests that the $K_{G'}$ values were dependent on the silica filler particle size.

All these results suggest that the $K_{G'}$ values were dependent on frequency (testing condition) and filler particle size (material characteristics), but independent of the silica volume fraction (material characteristics).

Fig. 9 shows that for the Stöber silica composites, each testing frequency had its own $K_{G'}$ value (intercept point A at the y-axis). When these $K_{G'}$ values were plotted against the logarithm of frequency, a straight line was obtained in Fig. 10. Thus, the $K_{G'}$ values were linearly dependent on the logarithm of frequency. This can be expressed as

1. at a constant frequency

$$K_{G'} \neq f(V_f) \quad (4)$$

$$K_{G'} = A + B \times V_f \quad B = 0 \quad (5)$$

2. at varied frequencies

$$A = C + m \times \log \omega \quad (6)$$

$$K_{G'} = C - m \times \log \omega \quad (7)$$

3. from Fig. 10, the Stöber silica composites show that

$$K_{G'} \times (-1000) = 26.6 - 16.8 \times \log \omega \quad (8)$$

where ω is frequency, while C and m are dependent of the particle size of the filler. Equation 7 can be used to predict $K_{G'}$ of Stöber silica composites when C and m are known.

3.3. Viscosity of Cab-O-Sil and Stöber Silica filled polymer

Figs 11 and 12 show the logarithm of the dynamic viscosity, $\log \eta_c^*$, versus the frequency, ω , of a composite containing 5 vol % Cab-O-Sil silica and

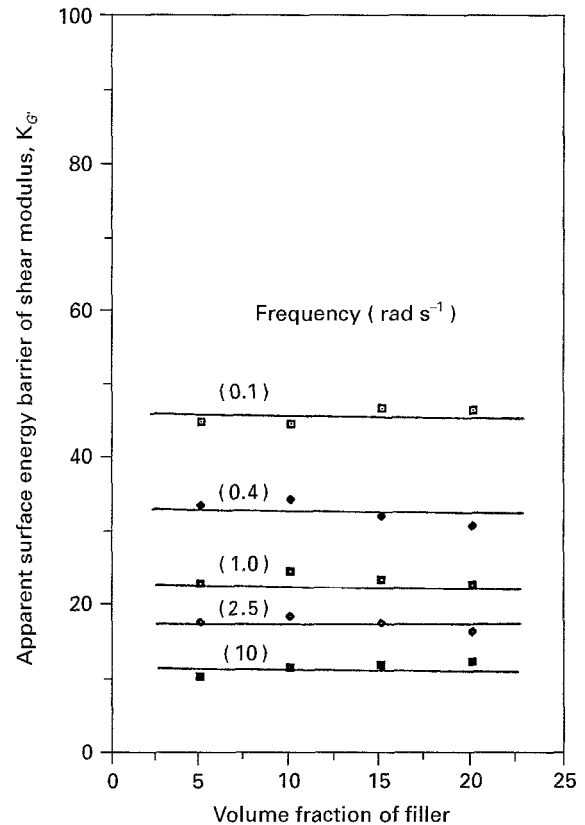


Figure 9 Effect of Stöber silica vol % and testing frequency on the apparent surface energy barrier of shear modulus from the (slope of G'_c/G'_p versus $1000/W_a$) $\times 1000$.

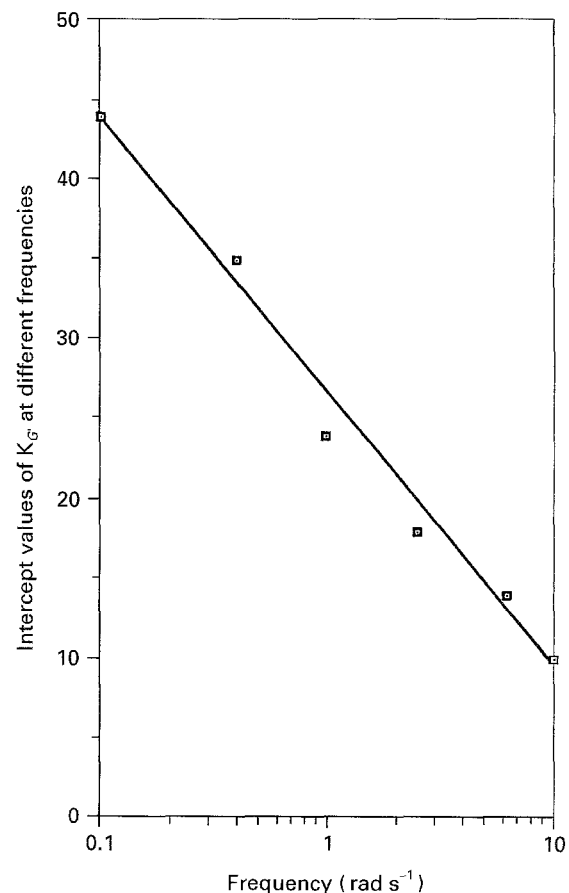


Figure 10 Effect of testing frequency on the y-intercept values in Fig. 9.

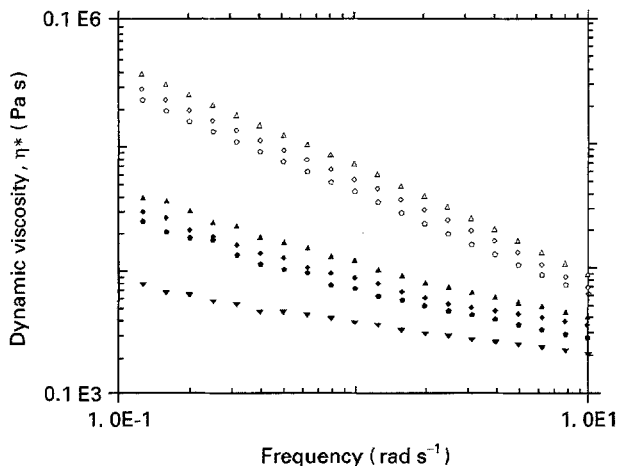


Figure 11 Dynamic viscosity versus frequency of 5 vol % Cab-O-Sil silica filled EVA composites with various silica surface properties: (Δ) 110°C, (\diamond) 500°C, (\square) 750°C, (\blacktriangle) 750°C-TMCS, (\blacklozenge) 500°C-TMCS, (\blacktriangleleft) 110°C-TMCS, (\blacktriangledown) EVA copolymer.

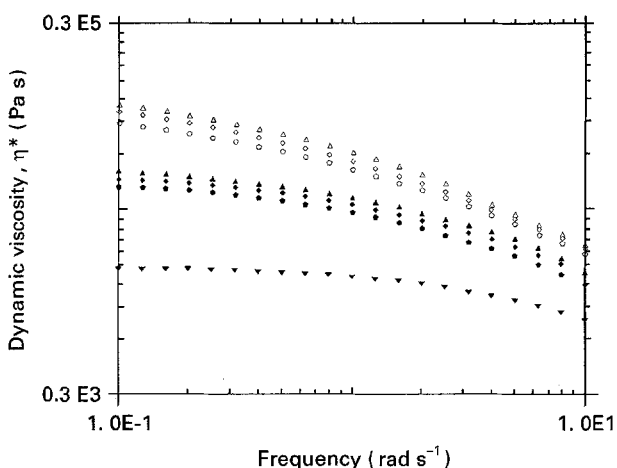


Figure 12 Dynamic viscosity versus frequency of 20 vol % Stöber silica filled composites with various silica surface properties: (Δ) 110°C, (\diamond) 500°C, (\square) 750°C, (\blacktriangle) 750°C-TMCS, (\blacklozenge) 500°C-TMCS, (\blacktriangleleft) 110°C-TMCS, (\blacktriangledown) EVA copolymer.

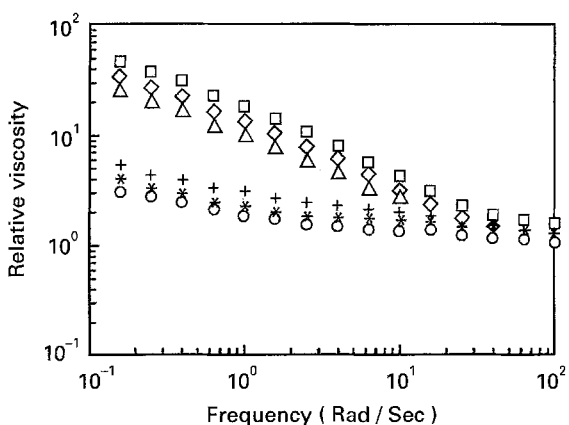


Figure 13 Effect of frequency and silica surface properties on the relative viscosity of 5 vol % Cab-O-Sil filled EVA composites: (\square) 110°C, (\diamond) 500°C, (Δ) 750°C, (+) 750°C-TMCS, (*) 500°C-TMCS, (O) 110°C-TMCS.

20 vol % Stöber silica, respectively. The composites containing 15, 10 and 5 vol % Stöber silica show similar plots. All of these show that the filled polymers had a higher viscosity than the unfilled

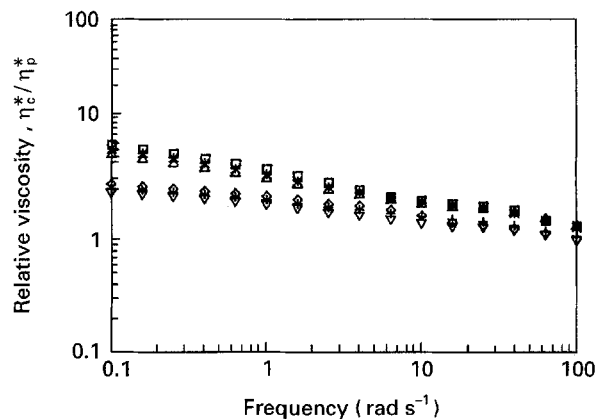


Figure 14 Effect of frequency and silica surface properties on the relative viscosity of 20 vol % Stöber silica filled composites: (\square) 110°C, (*) 500°C, (Δ) 750°C, (\diamond) 750°C-TMCS, (+) 500°C-TMCS, (∇) 110°C-TMCS.

polymer, and their viscosity decreased with increased frequency.

Figs 13 and 14 show the relative dynamic viscosity, η_c^*/η_p^* , of 5 vol % Cab-O-Sil and 20 vol % Stöber silica composites, respectively. The $\log(\eta_c^*/\eta_p^*)$ versus ω plots at 15, 10 and 5 vol % Stöber silica composites are similar to Figs 13 and 14. It is noted that at 5 vol % filler, Cab-O-Sil silica composites had a higher η_c^*/η_p^* than Stöber silica composites, because Cab-O-Sil had a higher ratio of surface area per volume.

The composites containing heat treated silica had higher viscosities, particularly at low frequencies, than those containing heat-TMCS treated silica. Figs 13 and 14 show that the η_c^*/η_p^* approached a constant value at higher frequencies, and became independent of interfacial bond strength.

3.4. Dependence of work of adhesion on viscosity

3.4.1. Effect of frequency

Figs 15–17 show the plots of η_c^*/η_p^* versus W_a^{-1} of 5 vol % Cab-O-Sil silica composites and 20 and 5 vol % Stöber silica composites, respectively. At frequencies equal to either 0.1, 1.0 or 10 rad s^{-1} , exponential relationships between the η_c^*/η_p^* ratio and W_a^{-1} were observed. Similar exponential relationships were found for 15 and 10 vol % Stöber silica composites.

Figs 15–17 show that the η_c^*/η_p^* increased as W_a increased, particularly at a low frequency. This result indicates that at a low frequency, W_a had a greater effect on the composite viscosity. At a high frequency, W_a was not as effective in determining viscosity as at a low frequency.

The relationships discussed above between the W_a and η_c^*/η_p^* can be described by a mathematical equation. It can be expressed as

$$\frac{\eta_c^*}{\eta_p^*} = C \cdot \exp^{-K_\eta \left(\frac{1}{W_a} \right)} \quad (9)$$

where η_c^* and η_p^* are the dynamic viscosities of the composite and polymer, respectively. The C and

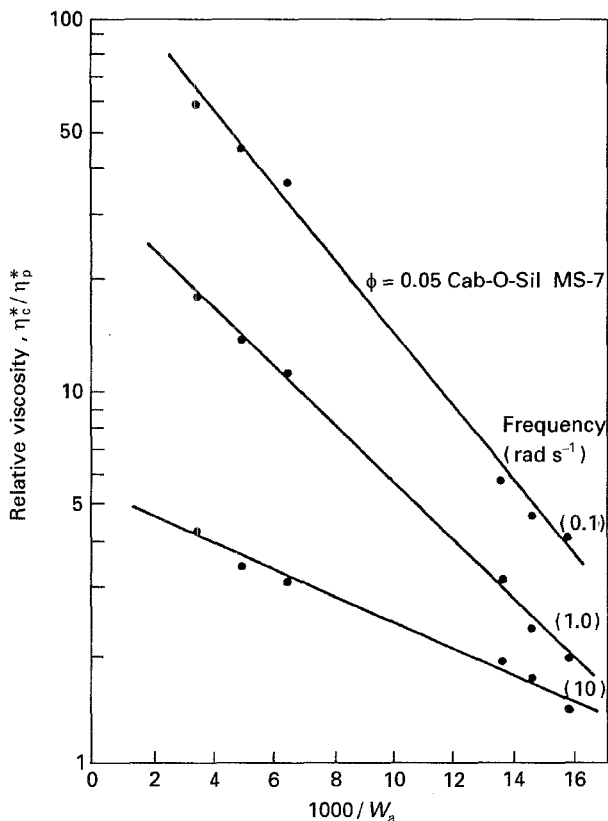


Figure 15 Effect of work of adhesion and frequency on the relative viscosity of 5 vol % Cab-O-Sil silica filled EVA composites.

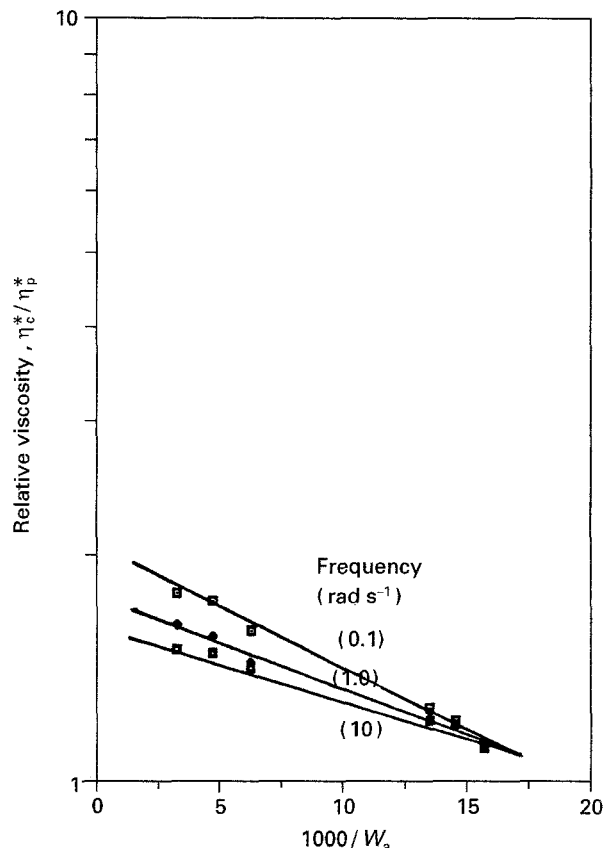


Figure 17 Effect of work of adhesion and frequency on the relative viscosity of 5 vol % Stöber silica filled EVA composites.

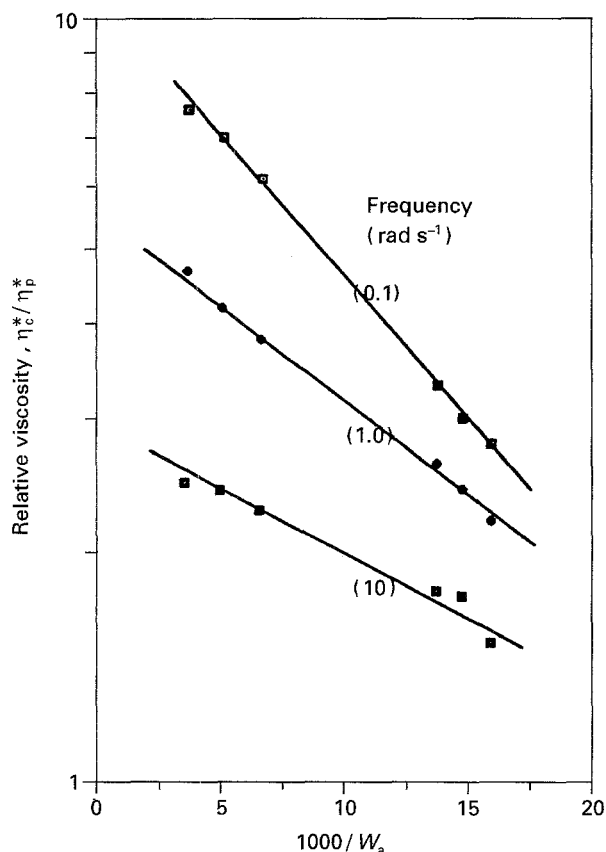


Figure 16 Effect of work of adhesion and frequency on the relative viscosity of 20 vol % Stöber silica filled EVA composites.

K_η are constants. The K_η term represents the slope of η_c^*/η_p^* versus W_a^{-1} , and is determined from the experimental data. The K_η decreased with increased frequency. The K_η term is known as the

apparent surface energy barrier of the dynamic viscosity of a composite.

For the same volume fraction silica, but with different silica surface properties of composites, the constant C in Equation 9 can be deleted and the ratio of two composite melt viscosities can be written as

$$\frac{\eta_c^*}{\eta_{co}^*} = \exp^{-K_\eta \left(\frac{1}{W_a} - \frac{1}{W_{ao}} \right)} \quad (10)$$

where η_{co}^* is the melt viscosity of the silica composite with the weakest interfacial bond (110°C-TMCS treatment, $W_{ao} = 63 \times 10^{-7} \text{ J cm}^{-2}$). When the viscosity of a composite with its corresponding W_a is known, Equation 10 can be used to predict the viscosity of other composite with another W_a but with the same silica content.

3.4.2. Effect of volume fraction

Fig. 18 shows the relationship between η_c^*/η_p^* and W_a^{-1} , measured at 0.10 rad s⁻¹ frequency, of 5, 10, 15 and 20 vol % Stöber silica composites. As the silica content was increased, η_c^*/η_p^* increased. The K_η values, which were the slopes in Fig. 18, increased as with an increase in silica content.

The increase in K_η values with silica volume fraction was different from that shown by K_G values in Fig. 8, which were independent of silica content. Furthermore, the plots of η_c^*/η_p^* and W_a^{-1} value measured at 1.0 and 10 rad s⁻¹ also show that the K_η values were dependent on Stöber silica volume fractions.

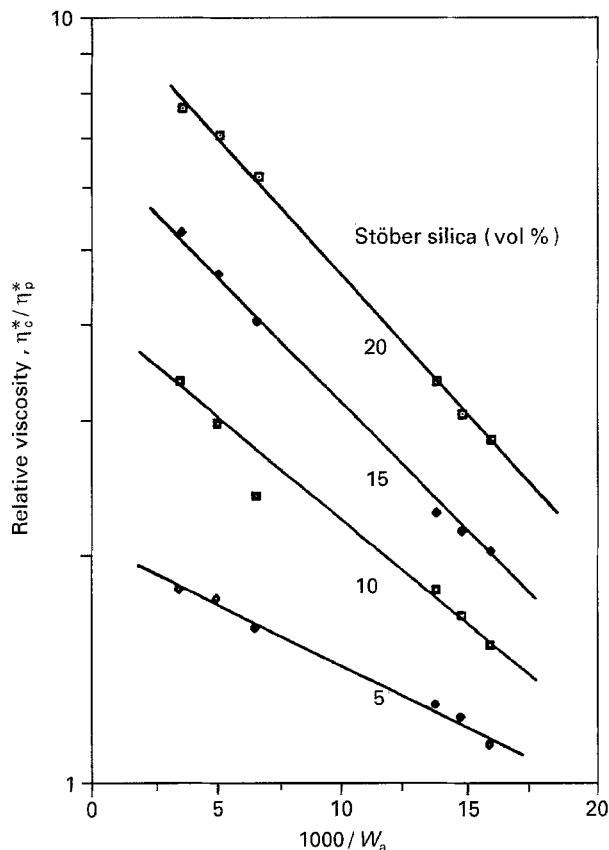


Figure 18 Effect of work of adhesion and Stöber vol % on the relative viscosity of EVA composites measured at 0.1 rad s^{-1} .

When these K_η values obtained at 0.1 rad s^{-1} were plotted against silica volume fractions, a linear relationship was observed as shown in Fig. 19. At other frequencies, such as 0.4, 1.0, 2.5 and 10 rad s^{-1} , each frequency corresponded to similar linear plots.

As the η_c^*/η_p^* versus W_a^{-1} at 0.1 rad s^{-1} of 5 vol % Cab-O-Sil silica composites (Fig. 15) was compared with that of 5 vol % Stöber silica composites (Fig. 17), the two K_η values were different. This result indicates that the K_η values were dependent on the silica filler particle size.

These results suggest that the K_η values are a function of testing condition (frequency) and material characteristics (filler particle size and volume fraction).

Furthermore, when the slopes of each linear line (slope of K_η at a specific frequency) in Fig. 19 were plotted against logarithm of their own frequency, linear behaviour was observed, as shown in Fig. 20. Fig. 20 shows that at a given frequency the slope, Q , of K_η versus silica volume fraction linearly decreased with the logarithm of frequency. This can be expressed as

1. at a constant frequency

$$K_\eta = f(V_f) \quad (11)$$

$$K_\eta = P + Q \times V_f \quad (12)$$

2. at variable frequencies

$$Q = R - n \times \log \omega \quad (13)$$

$$K_\eta = P + (R - n \times \log \omega) \times V_f \quad (14)$$

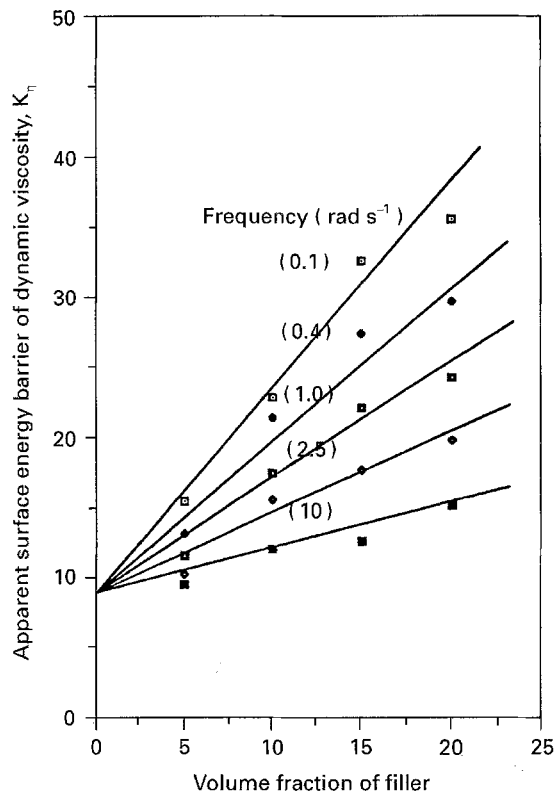


Figure 19 Effect of Stöber silica vol % and testing frequency on the apparent surface energy barrier of dynamic viscosity (from the slope of η_c^*/η_p^* versus $1000/W_a$) $\times 1000$.

3. from Fig. 20, the Stöber silica composites shows

$$K_\eta \times (-1000) = 8 + (88 - 53 \times \log \omega) \times V_f \quad (15)$$

where ω is the frequency, R and n are dependent on the filler particle size, and P is the intercept point at $V_f = 0$ in Fig. 19, which is equal to -0.008 in this study. The value of P should equal zero when the polymer contains no filler particles. Reasonably good agreement between the experimental data and the theoretical value was obtained in this study.

3.5. Dispersion of silica particles in polymer matrix

Figs 21 and 22 show the SEM micrographs of 15 vol % Stöber silica dispersed in the EVA polymer at different magnifications. Figs 21 and 22 show the dispersion of Stöber silica treated at 110°C and 110°C-TMCS silica, respectively. These two groups encompass the silica fillers with the highest and lowest interfacial bond strengths in the present study.

4. Discussion

4.1. Frequency dependence of effective silica particle size

The effective silica particle size increases as W_a increases [1–3]. Earlier studies showed that Young's modulus and tensile strength increase with increased effective particle size. However, in earlier reports, the effect of W_a on Young's modulus and tensile strength was studied at a constant testing rate [1–3].

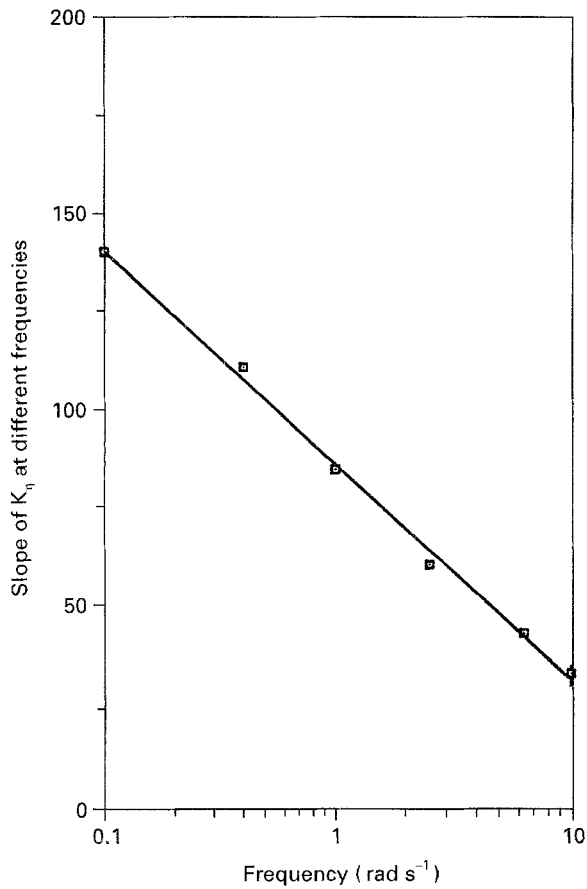


Figure 20 Effect of testing frequency on the slope values in Fig. 19.

Fig. 23 shows how the effective silica particle size changes with testing frequency. The effective particle size is larger at a low frequency. As the frequency increases, the adsorbed polymer gradually loses its entanglements through decoupling at the silica surface [39]. When the polymers disentangle, the interphase layer becomes thinner and the effective particle size becomes small.

The change in effective particle size with frequency depends on the magnitude of W_a . At low frequency regions, the effective particle size decreases much faster as the testing frequency increases for the higher W_a silica than for the lower W_a silica. As the frequency further increases, the effective silica particle size of the high W_a finally approaches a constant size, which is equal to that of low W_a silica particles.

4.2. Interphase dependence of composite viscosity and shear modulus

As stated earlier, to minimize the matrix effect, the effect of W_a on the rheological properties can be understood better by studying the relative viscosity and the relative shear modulus. The relative viscosity and the relative shear modulus decrease less with W_a^{-1} at a higher frequency than they do at a lower frequency, because at a high frequency the effective particle size instantly becomes smaller. At a lower frequency, however, the greater effective silica particle size remains, explaining why the relative viscosity and the shear modulus become more dependent on W_a value for lower frequencies. Fig. 23 shows that at

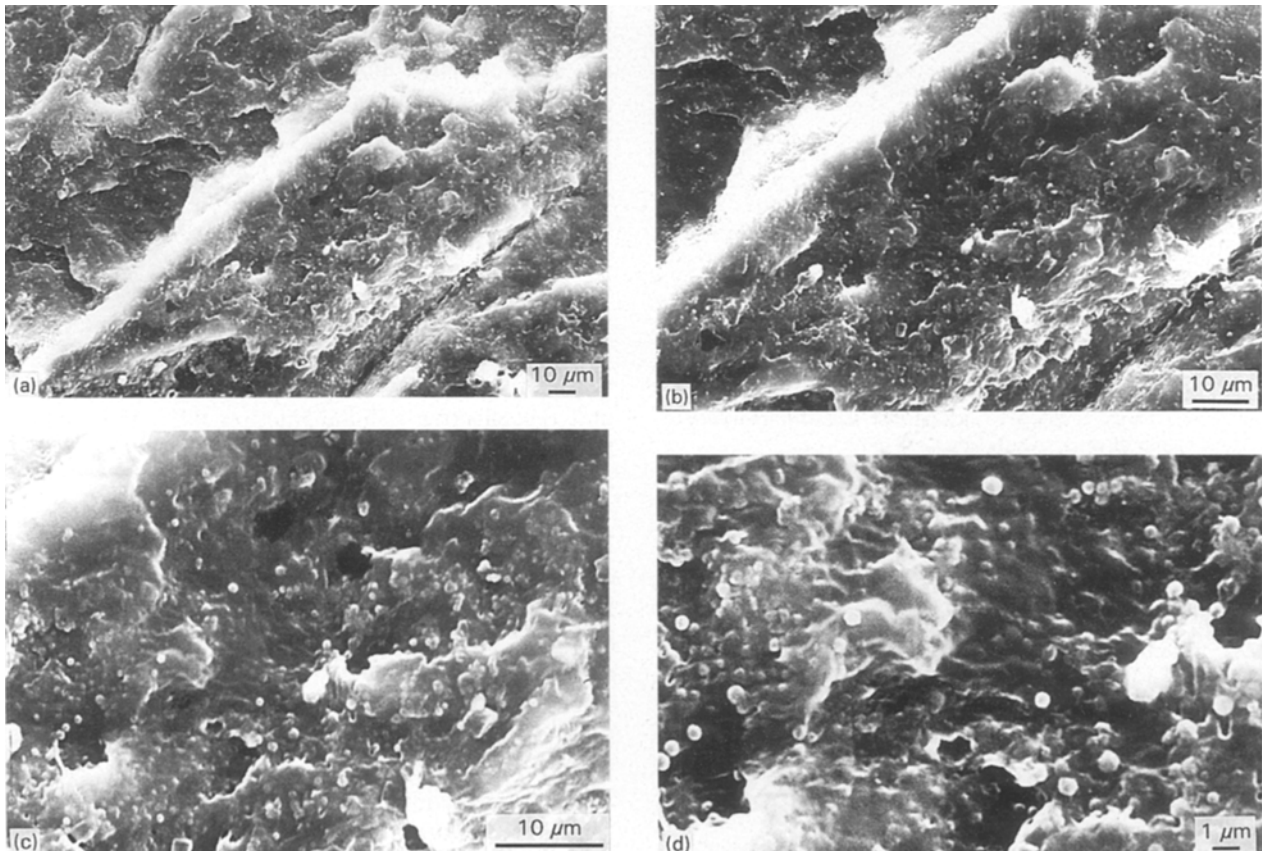


Figure 21 SEM micrographs of 15 vol % Stöber silica particles dispersion in the EVA matrix. Silica treated at 110 °C.

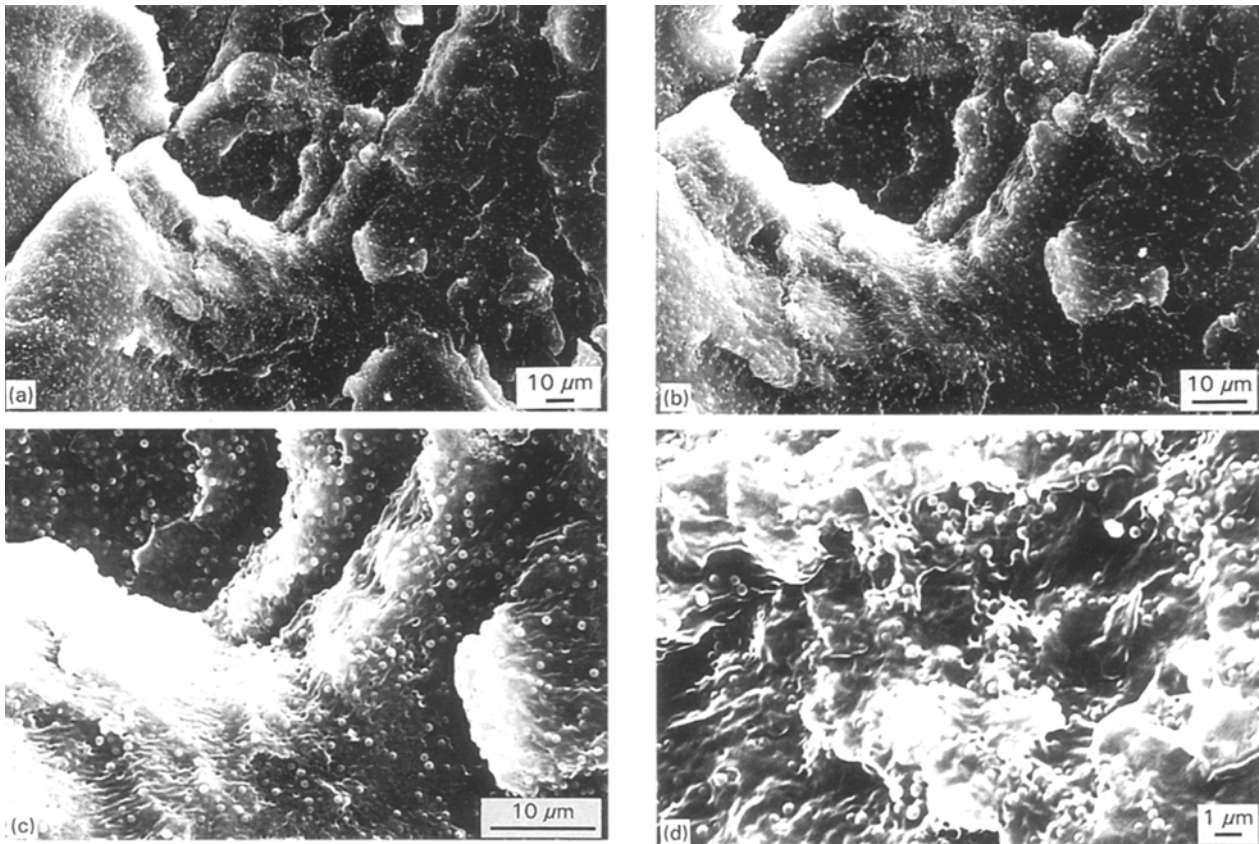


Figure 22 SEM micrographs of 15 vol % Stöber silica particles dispersion in the EVA matrix. Silica treated by 110°C-TMCS.

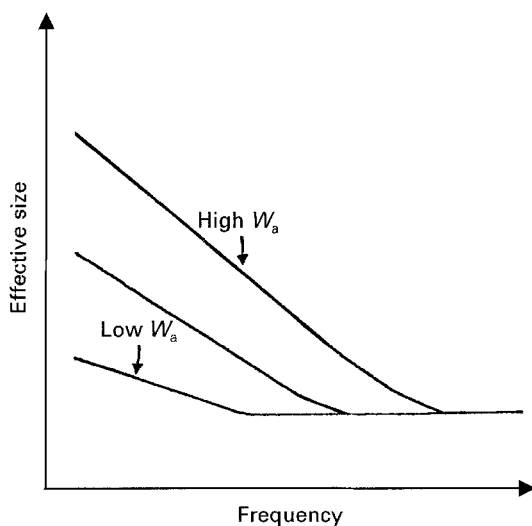


Figure 23 Change of effective silica particle size with frequency at various values of work of adhesion.

a given W_a , the change in effective particle size is more pronounced at a low frequency than at a higher frequency. It also shows that the effective silica particle size of a high W_a silica decreases much faster at a low frequency than at a high frequency. Thus, the K_η and K_G , which represent the changes of viscosity and shear modulus with W_a , were larger at a low frequency than at a high frequency.

4.3. Surface friction factor on composite viscosity

The “surface friction factor” can be used to throw light on how the effective silica particle size influences the

viscosity of the composite. The surface friction factor can be separated into

1. the form friction factor, and
2. the skin friction factor [40, 41].

These two frictional factors are different from segmental friction, which comes from the entanglements of matrix polymer molecular chains.

The form friction factor is determined by the shape of the filler particles [40, 41]. The spherical Stöber silica particle will not change shape after it has been surface modified. It remains spherical after the polymer has been bonded and adsorbed on the silica surface. The form friction factor accordingly remains the same regardless of the silica surface modification. In contrast, the skin friction factor is determined by particle size and/or the contact surface area of the particle. Because of the change in silica particle size and the effective volume fraction filler, the friction factor per unit composite changes after the polymer adsorption to the Stöber silica surface.

The skin friction factor depends on the magnitude of the W_a value and strongly reflects the adhesion quality, particularly at a low frequency. A large effective silica particle has more polymers bonded and adsorbed onto the silica surface. These bonded and adsorbed polymers introduce a strong skin friction when the polymers would like to pass between the silica particles. The resistance the polymer experiences when it moves over the silica particles is increased as W_a increases, which causes the viscosity to increase. The skin friction factor can accordingly be used to explain why the thickness of an interphase layer can control the viscosity of a composite.

4.3.1. Low frequency dependence of surface friction factor

The skin friction factor increases as W_a increases because the effective particle size increases with W_a . The η_c^*/η_p^* is high at a very low frequency. The polymer being bonded and/or adsorbed around silica particles is essentially not disentangled from the bulk polymer. At this low frequency, the effective silica particle size is approximately the same as it is at rest.

Regardless of silica surface modification, the segmental friction of the matrix polymer far away from the silica surface remains identical and will not affect the relative viscosity. Skin friction is thus the dominant factor in determining the relative viscosity of a composite. Since the skin friction factor is inversely proportional to the matrix velocity in fluid mechanics [40–45], the skin friction is higher at a low frequency. Thus, at a higher W_a the relative viscosity is higher, particular at a low frequency.

The skin friction factor of a unit volume composite increases as the contact surface area of the filler particles increases. This result is associated with the polymer becoming more strongly linked to the interphase layer and explains why at 5 vol % silica, the Cab-O-Sil silica composites shown in Fig. 15 have higher viscosities than the Stöber silica composites shown in Fig. 17.

The skin friction factor increases with increased filler concentration of a composite since more contact surface area is experienced. Fig. 18 shows that the K_η (slope of relative viscosity versus W_a^{-1}) becomes higher at a higher silica volume fraction. From Figs 18 and 19, it shows that the influence of the silica content on the K_η values gradually decreases as the testing frequency increases. From the above facts, it is concluded that the skin friction factor of a composite at a given frequency depends on silica particle size, volume fraction and the magnitude of W_a at the interface.

The effects of filler size, filler surface chemistry and volume fraction filler can be combined into a single parameter called the bonding energy density (BED) [2]. Since the skin friction factor of a unit volume composite depends on W_a , filler particle size and volume fraction, the skin friction factor is thereby determined by BED. The BED is defined as

$$\text{BED} = \frac{W_a \times A}{V} \quad (16)$$

where BED (J cm^{-3}) is bond energy density. W_a (J cm^{-2}) is the work of adhesion between filler and matrix, A (cm^2) is the total filler surface area and V (cm^{-3}) is the summation of (a) volume of silica and (b) volume of EVA matrix. The value of BED represents the total interfacial bonding energy per unit volume of a polymer composite [2]. Consequently, at a given frequency the skin friction factor is a function of the BED of that composite. The BED of a composite thus depends on its own material characteristics.

4.3.2. High frequency dependence of surface friction factor

The adhesion at the interface diminishes as the frequency increases. At a high testing frequency, the extent of entanglement of the polymer molecules within the interphase decreases [45]. The skin friction factor becomes less significant because the resistance of polymer movements decreases. Thus, the skin friction factor is not a dominant factor at higher frequencies.

Meanwhile, at a higher frequency most of the polymer becomes orientated and disentangled. The response of a polymer at a high frequency occurs only in the segmental (or local) portion of a polymer chain. This explains why the viscosity of an unfilled polymer is lower at higher frequencies. The response of the polymer is localized and experiences less polymer entanglements. At a high frequency the effect of entanglements on the viscosity of a composite becomes less significant.

Interfacial bonds may also be broken at a higher testing frequency. Accordingly, the skin friction factor at the interface does not play an important role. The segment friction factor of both unfilled and filled polymer at the matrix is similar. Therefore, the η_c^*/η_p^* of Stöber silica composites at a very high frequency is not much different. Since segmental friction of the polymer decreases at higher frequencies, the viscosity of the composite becomes lower at higher frequencies. The segmental friction is the dominant factor at higher frequencies in determining the viscosities of silica filled composites.

The above statement is confirmed by the experimental results shown in Figs 16 and 17. Even though the η_c^*/η_p^* at higher frequencies increases with W_a , the K_η is much smaller at higher frequencies.

Furthermore, since the skin friction factor does not play an important role at higher frequencies, the K_η at higher frequencies would not be so responsive to an increase in silica volume fraction. This is supported by the experimental result shown in Fig. 19. The segmental friction is thus the dominant factor at higher frequencies in controlling the viscosity of a silica filled composite.

4.4. Silica dispersion and silica interfacial bonding

Figs 21 and 22 show that the state of dispersion of Stöber silica in a polymer matrix is essentially the same, regardless of the silica filler surface modifications. This finding suggests, at least in this simplified silica filled EVA polymer system, that the W_a values have little influence on the dispersion of the silica particles in the polymer matrix. This finding, however, may be related to the sample preparation process.

The composites in this study were prepared by mixing the silica powders in the polymer solution instead of in a melt polymer. The individual silica particles were first wetted by the solvent before the EVA polymer was bonded and adsorbed on the silica surfaces. The silica agglomerates, if present, were swollen by the solvent and the silica particles were gradually separated individually from the agglomerates during the stirring process.

The rheological properties of a silica filled polymer are known to be dependent on both filler interfacial bonding and filler dispersion. Since the dispersion is essentially the same regardless of the W_a values, the effect of the W_a value on the rheological properties of this composite does not seem to be influenced by the dispersion factor.

By examining Figs 21 and 22 closely at a higher magnification, one can see that most of the 110°C treated Stöber silica particles remain embedded in the polymer matrix, while only a few 110°C-TMCS treated silica filler particles are embedded in the polymer matrix. This indicates that silica surface properties affect the interfacial bond strength since the locus of impact fracture of composites varies with different W_a values, even at very low temperatures. This observation is consistent with the results reported in previous publications, where the effect of W_a on the mechanical properties of silica filled polymer composites were studied [1–3].

5. Conclusions

This study supports the authors' hypothesis that both the dynamic viscosity and shear modulus of particulate filled composites are related to the work of adhesion, W_a , values of the filler particles. Both the dynamic viscosity and the shear modulus of the particulate composites decrease with W_a^{-1} in a semilogarithmic co-ordinate system.

The effect of W_a on the viscosity depends on both particle size and filler fraction (material characteristics), but also on testing frequency (testing conditions). Shear modulus depends on particle size and frequency only.

An increase in effective filler particle size caused by an increase in W_a can be used to explain why the viscosity and shear modulus increase as the interfacial bond strength increases. As the frequency increases, the effective particle size becomes smaller because of a release of less tightly bonded polymer from the filler surface. The reduced effective particle size causes the relative viscosity and the shear modulus of the composite to decrease at the higher frequencies.

The skin friction factor at the filler surface can also be used to examine the viscosity of a composite. As W_a increases, the skin friction factor increases simultaneously as the effective particle size increases. Since a lower frequency yields a higher skin friction factor, W_a has more pronounced effect on the viscosity at a lower frequency. For a unit volume composite tested at a given frequency, a high skin friction factor exists for smaller filler particle sizes, higher volume fraction fillers and higher W_a values. These variables can be combined and defined as bond energy density (BED). A composite with high BED thus has a high skin friction factor and a high viscosity.

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