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Using the bond energy density to predict the reinforcing ability of a composite

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A model is proposed to predict the ability of a filler to reinforce a polymer. The model combines the effects of filler particle size, filler surface chemistry and filler volume fraction into one parameter called the bond energy density. Bond energy density is defined as the total interfacial bond energy per unit volume of a polymer composite. Bond energy density is determined by Fowkes's equation. The critical bond energy density, which is equivalent to the bond energy density of the composite when its tensile strength equals that of its matrix, determines whether a filler will reinforce or weaken a polymer. To get a filler reinforcing effect, the bond energy density of the composite must be greater than its critical bond energy density.

1. Introduction

The performance of a composite material is strongly dependent on the combined effects of filler particle size, filler surface chemistry, and volume fraction filler [1–32]. One should strive to find a single parameter that can describe the combined reinforcing effect of these three variables. Such a single parameter could be used to estimate the reinforcing ability of a filler used in a composite material.

The interfacial bond between the filler particle surface and the polymer matrix can be quantified in terms of the work of adhesion, W_a [32]. Work of adhesion can be calculated from the modified Fowkes's equation [32] by determining acid–base pair density and acid–base interaction energy [32]. The acid–base pair density can be determined from titration and the acid–base interaction energy by Fourier transform infrared spectroscopy (FTIR) [32]. Williams *et al.* [32] reported the effect of work of adhesion on both Young's modulus and the tensile strength of a silica-filled polymer composite with this approach. At fixed volume fraction filler, but with different filler surface areas, Young's modulus and tensile strength of silica-filled polymers increased with increased work of adhesion.

One can combine the effects of filler size, filler surface chemistry, and volume fraction filler into one parameter called the bond energy density (BED). BED can be determined by extending Fowkes's equation [27, 28] (Appendix). The object of this study was to test the hypothesis that the BED reflects the reinforcing ability of a filler dispersed in a polymer matrix.

2. Experimental Details

2.1. Materials

Spherical silica particles, either 0.6 μm or 0.014 μm in diameter, were used as filler particles in an ethylene-vinyl acetate (E-Va) copolymer (72 wt % ethylene and 28 wt % vinyl acetate) (Scientific Polymer Products, Inc., Ontario, NY). Spherical silica particles that had a diameter of 0.6 μm were prepared according to a method described by Stöber [33, 34]. The finer MS-7 grade fused silica was obtained from Cab-O-Sil Division (Cabot Corporation, Tuscola, IL).

2.2. Surface treatment

Amorphous fused quartz plates (Quartz Scientific, Inc., Fairport Harbor, OH) were used to characterize the surface properties of silica. The properties of the plates were assumed to be similar to the surface properties of the silica filler particles.

The surface treatment procedures we used for treating either the silica particles or the quartz plates comprised two main groups: (1) heat and (2) heat and chemical treatment with trimethylchlorosilane (TMCS) [35].

2.3. Surface properties determination

The surface properties were measured with a contact angle goniometer (NRL Model 100, Rame-Hart, Inc., Mountain Lake, NJ). We determined the number of hydroxyl groups and the extent of hydrogen bonding at the surface of silica powders. The number of hydroxyl groups was determined by titration with *n*-

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butylamine (Fisher Scientific Co.) [36], using neutral red as an indicator [37–39]. Diffuse reflection FTIR (DRIFT) was used to determine the extent of hydrogen bonding.

For the titration, we dissolved 1.5 g neutral red (Pfaltz & Bauer, Inc., Stamford, CT) in 40 ml benzene (Fisher Scientific Co.). This solution was used as an indicator dye. We also dissolved 0.1 M n-butylamine in benzene and used it to titrate the hydroxyl groups present on the silica surface. The indicator dye was added to the silica solution after we had equilibrated the hydroxyl groups of the silica surface with n-butylamine.

The type of bonding between the E-Va copolymer and the filler surface was determined with DRIFT. Non-hydrogen-bonded carbonyl groups of E-Va copolymer absorb at 1739 cm^{-1}, while the hydrogen-bonded carbonyl groups absorb at 1704 cm^{-1}.

2.4. Composite sample preparation

E-Va composites sheets containing different volume fraction fillers (1,3,5,10,15 and 20%) were cast from benzene/E-Va solutions. Dumb-bell-shaped tensile specimens were then prepared from the cast sheets according to ASTM specification 1822 for compression moulded composite sheets. The composite specimens were annealed at 100 °C for 3 h and then conditioned at 25 °C for 3 days before they were tested in tension. The specimens were tested at a crosshead

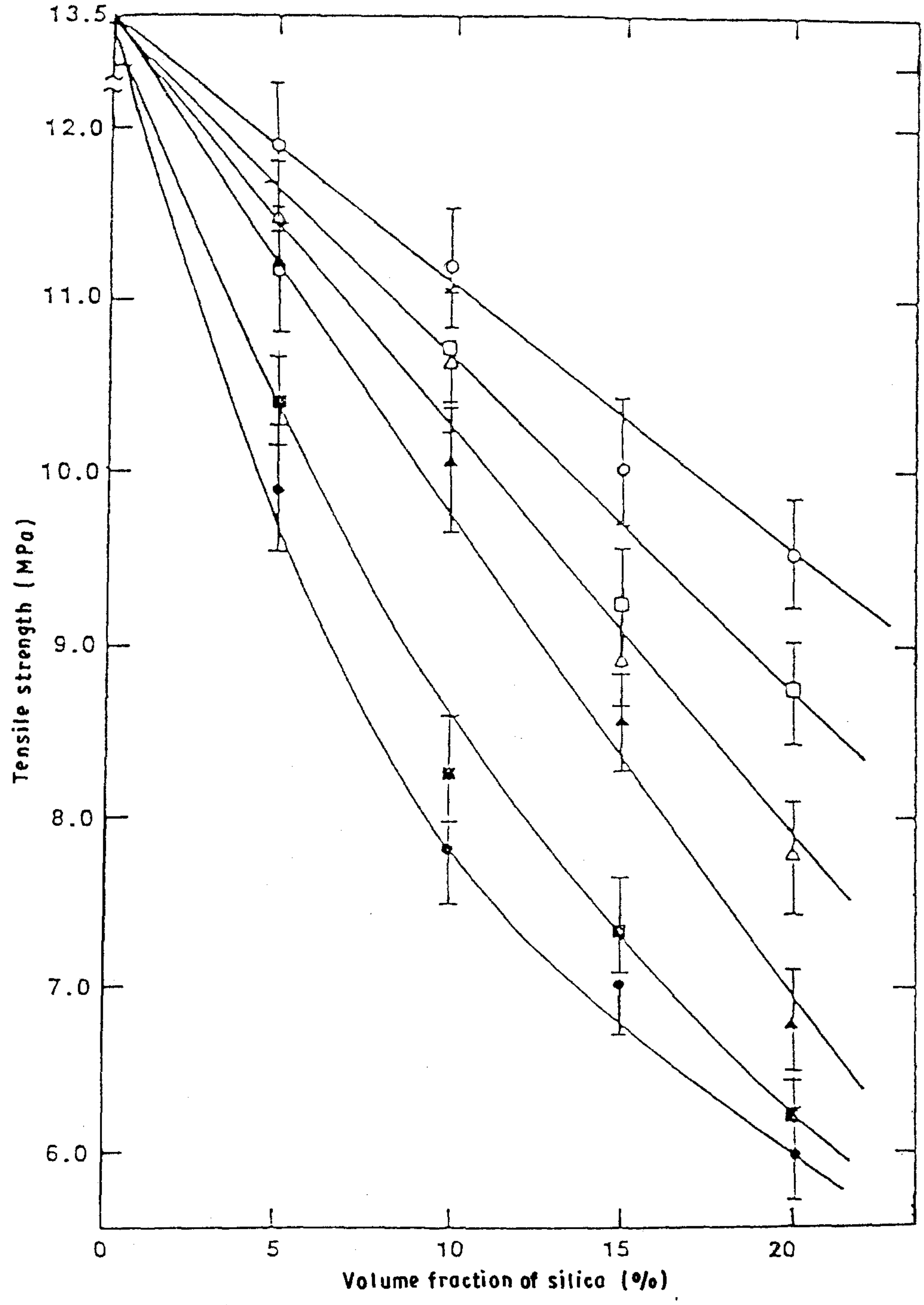

Figure 1 Effect of volume fraction and surface properties of Stöber silica filler on the tensile strength of polymer composites. Surface treatment (○) 110 °C, (□) 500 °C, (△) 750 °C, (▲) 750 °C/TMCS, (■) 500 °C/TMCS, (●) 100 °C/TMCS. Diameter of Stöber silica: 0.6 μm.

speed of 50.8 mm min^{-1} at 25 °C by using an Instron testing machine Model 1122. At least six specimens per group were tested.

3. Results and discussion

3.1. Silica particle size and volume fraction on the composite's tensile strength

Figs 1 and 2 show the tensile strength values of composites containing either Stöber silica or Cab-O-Sil silica. The composites filled with Stöber silica had lower tensile strength than the unfilled E-Va copolymer, suggesting that Stöber silica had a weakening effect on the composite. In contrast, the composites filled with Cab-O-Sil silica were stronger than the unfilled polymer, at least for silica filler fractions of 15% or less. At lower filler fractions of Cab-O-Sil, the tensile strength of the composite increased with increased volume fraction silica, reaching a maximum around 4 vol % filler. The Cab-O-Sil composites retained their higher tensile strength values compared to the unfilled polymer up to 15 vol % filler.

The finding that maximal tensile strength occurs at a low filler fraction is not new. Similar findings have been observed for carbon-black-filled rubber [40–42]. The finding that the larger Stöber silica particles were less effective as a reinforcing filler than the finer Cab-O-Sil filler suggests that the reinforcing ability often decreases as the filler particle size increases. This finding is also in line with other results [42].

3.2 Effect of heat and/or TMCS treatment on the presence of reactive groups on the silica filler surface

Table I shows the number of hydroxyl groups on the silica surfaces treated differently. The different silica surface treatments consisted of either: (1) heat (110, 500 and 750 °C), or (2) heat and chemical treatments

TABLE I Surface hydroxyl groups per unit area. Indicator dye method/titrating with 0.1 M *n*-butylamine. Indicator dye: neutral red.

Treatment	Cab-O-Sil (OH nm^{-2})	Stöber silica (OH nm^{-2})
110 °C	4.39 ± 0.12	4.55 ± 0.04
500 °C	2.86 ± 0.08	2.96 ± 0.05
750 °C	1.88 ± 0.11	1.95 ± 0.05
750 °C/TMCS	0.13 ± 0.02	
500 °C/TMCS	0.27 ± 0.04	
110 °C/TMCS	0.39 ± 0.04	

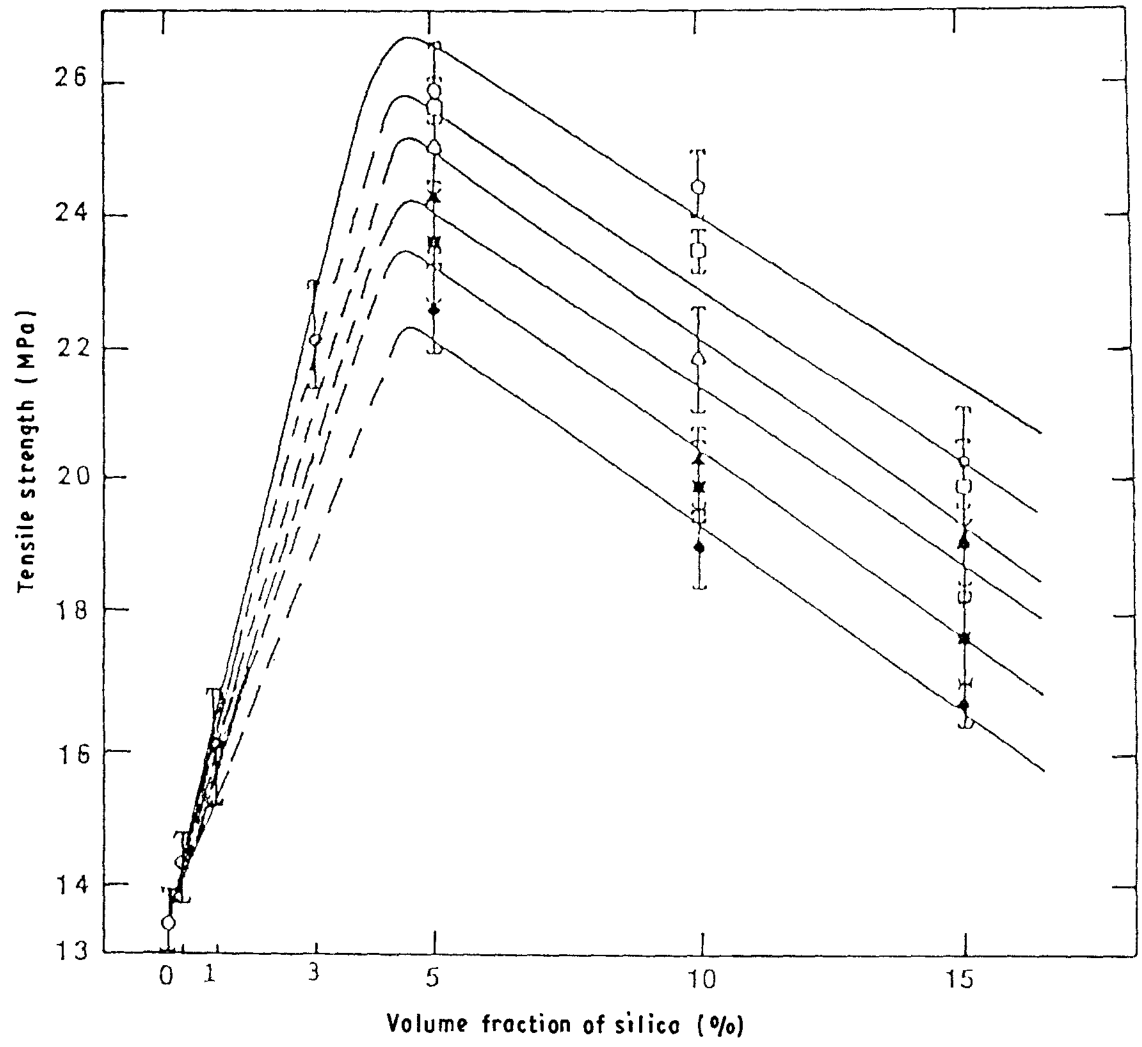

Figure 2 Effect of volume fraction and surface properties of Cab-O-Sil silica filler on the tensile strength of polymer composites. Surface treatment: for key see Fig. 1. Diameter of Cab-O-Sil silica: 0.014 μm.

(110, 500, and 750 °C/TMCS). Both heat and heat combined with TMCS treatments reduced the number of hydroxyl groups on the silica surfaces. This has also been shown by others [36]. Thus there were 4.39 hydroxyl groups per nm^2 on Cab-O-Sil silica surfaces which were treated at 110 °C, but only 0.39 OH groups per nm^2 on the silica surface heated at 110 °C and treated with TMCS (Table I). Consequently, heat and/or TMCS treatments reduce the number of hydrogen and polar bonds. This reduction in bond sites occurs at the interface of the silica surface, between the OH groups of the silica and the carbonyl groups of the polymer chains. The reduced number of bond sites results in weaker interfacial bonding.

Figs 1 and 2 show that silica composites pretreated at 110 °C had higher tensile strength than silica composites that were both heat treated at 110 °C and then TMCS treated. If we compare composites containing the same silica content (Figs 1 and 2), we find that the tensile strength decreases when the work of adhesion decreases.

3.2.1. Poor interfacial bonding

The W_a^d and W_a^h values were calculated from the τ_s^d and τ_s^h values (Appendix) and determined for the three composites that were first heat treated and then treated with TMCS (750, 500, and 110 °C/TMCS). We selected these composites since they had few or no hydrogen bonds.

Table II shows the calculated τ_s^d, τ_s^h, and τ_s values of heat and/or TMCS modified silica and E-Va copolymer. We observed a decrease in τ_s^h when the silica surfaces had been heated and coated with TMCS. Such a treatment also caused a lower τ_s value. Table III shows the calculated W_a^d, W_a^h, and W_a values of the silica-filled composites (heat and TMCS treated). As seen from this table, the value of W_a^h was small and its contribution to W_a was low.

3.2.2. Good interfacial bonding

For systems that exhibited strong hydrogen and polar bonds, we calculated the W_a^h values of the silica-filled composites (treated at 110, 500 and 750 °C) from the modified Fowkes's equation (Appendix). We calculated the W_a^d values from the τ_s^d and τ_s^h values. Table III shows that there is a great change in W_a^h after heat treatments of silica surfaces. The W_a increased as the interfacial bonding increased. Most of the changes in W_a of the heat treated silica interface came from W_a^h. Table III further shows that the W_a^h values of heat-treated silica are higher than those of silica that had been heat treated and coated with TMCS.

TABLE IIa Surface energy of heat and/or TMCS treated silica (10^{-5} N cm^{-1}). Evaluated by contact angles.

Surface energy	110 °C	500 °C	750 °C	750 °C TMCS	500 °C TMCS	110 °C TMCS
τ_s	74 ± 1	72 ± 1	60 ± 2	40 ± 1	33 ± 2	27 ± 1
τ_s^h	60	56	38	17	10	6
τ_s^d	14	16	22	23	23	21

TABLE IIb Surface energy of E-Va copolymer (10^{-5} N cm^{-1}). Evaluated by contact angles

Surface energy	E-Va copolymer	H_2O	MI
τ_s	35 ± 1	72.8	50.8
τ_s^h	7	50.7	6.7
τ_s^d	28	22.1	44.1

3.3. Bond energy density (BED)

Table IV shows the calculated BED values of the silica-filled E-Va composites. This table shows that for matching silica concentrations and surface treatments, the Cab-O-Sil composites had a higher BED than the Stöber composites.

We introduced "work of adhesion per unit volume composite" to combine the effects of filler particle size and filler volume fraction. We called this new unit "bond energy density" (BED). BED was defined as the total interfacial bond energy per unit volume of a

TABLE IIIa Calculated work of adhesion (W_a (10^{-7} J cm^{-2})) of Cab-O-Sil-silica/E-Va composites

Work of adhesion	110 °C	500 °C	750 °C	750 °C TMCS	500 °C TMCS	110 °C TMCS
W_a	292	205	154	73	68	63
W_a^h	251	163	105	20	17	13
W_a^d	41	42	49	53	51	50

TABLE IIIb Calculated work of adhesion (W_a (10^{-7} J cm^{-2})) of Stöber silica/E-Va composites

Work of adhesion	110 °C	500 °C	750 °C	750 °C TMCS	500 °C TMCS	110 °C TMCS
W_a	301	210	158	73	68	63
W_a^h	260	168	109	20	17	13
W_a^d	41	42	49	53	51	50

TABLE IVa Calculated bond energy density ($10^{-5}E(10^{-7}$ J cm^{-3})) of Cab-O-Sil silica/E-Va composites

Silica volume	110 °C	500 °C	750 °C	750 °C TMCS	500 °C TMCS	110 °C TMCS
5 %	313	220	165	78	73	68
10 %	626	440	330	156	146	135
15 %	939	659	495	235	219	203

TABLE IVb Calculated bond energy density ($10^{-5}E(10^{-7}$ J cm^{-3})) of Stöber silica/E-Va composites

Silica volume	110 °C	500 °C	750 °C	750 °C TMCS	500 °C TMCS	110 °C TMCS
5 %	7.3	5.1	3.8	1.8	1.7	1.6
10 %	14.0	10.0	7.7	3.6	3.4	3.2
15 %	22.0	15.0	12.0	5.5	5.1	4.7

polymer composite. BED will increase as the filler particle size becomes smaller for a composite of fixed filler fraction. This increase relates to the increase in total filler surface area, A, per volume fraction of filler that occurs with decreased filler particle size. An increase in filler volume fraction of a fixed particle size also will cause a higher BED value. Increased interfacial bonding also increases the BED value. In terms of quantitative changes in BED values determined in this study, we found that the A/V ratio was the dominant term.

3.4. Reinforcement of a composite

Fig. 3 shows the tensile strength versus BED values at 5 vol %, 10 vol %, and 15 vol % silica. This figure shows that the Stöber silica cannot reinforce the E-Va copolymer, and that the Cab-O-Sil composites gradually lose strength when the silica concentration increases.

Fig. 4 shows that the tensile strength increased with an increase in BED values. For a fixed BED value, the tensile strength decreases as the volume fraction of silica increases. This finding suggests that the reinforcing ability gradually disappears as the filler content increases. For a particular surface treatment, e.g. a 110 °C heat treatment of Cab-O-Sil particles, there is a decrease in tensile strength (reinforcing ability) as the volume fraction of silica filler increases after it exceeds 4 vol %.

Fig. 5 shows a plot of the critical bond energy density (CBED) against silica concentration. We defined CBED arbitrarily as the BED of the filled composite when its tensile strength equals that of its unfilled polymer (Fig. 4). Based on this definition, a polymer composite with a lower BED value than its CBED value will have lower tensile strength than the unfilled polymer. Therefore, the BED/CBED ratio of a filled composite can be used to estimate the reinforcing ability of a filled polymer system. Fig. 5 suggests

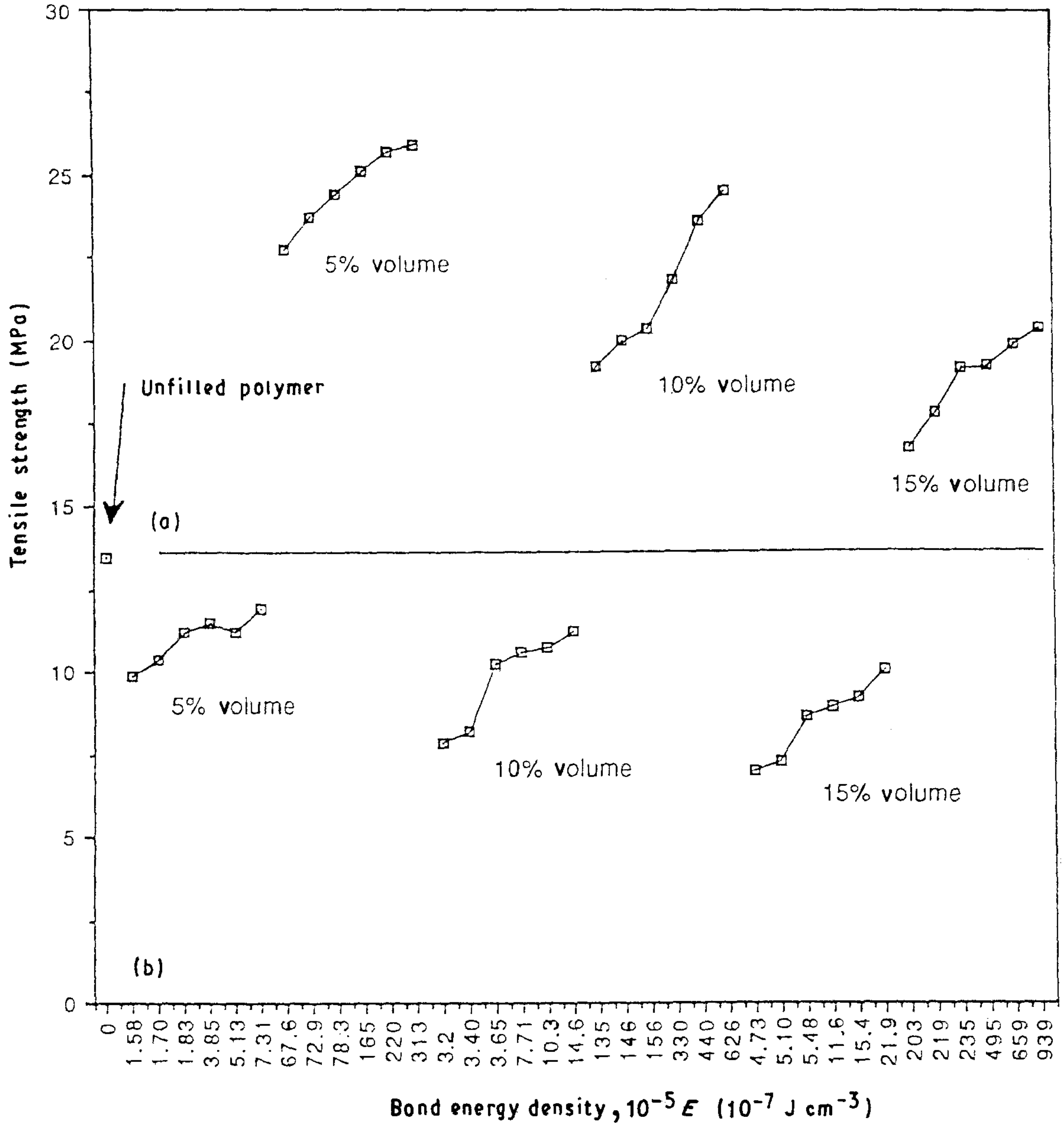

Figure 3 Effect of bond energy density on the tensile strength of polymer composites. (a) Cab-O-Sil silica-filled composites. (b) Stöber silica-filled composites.

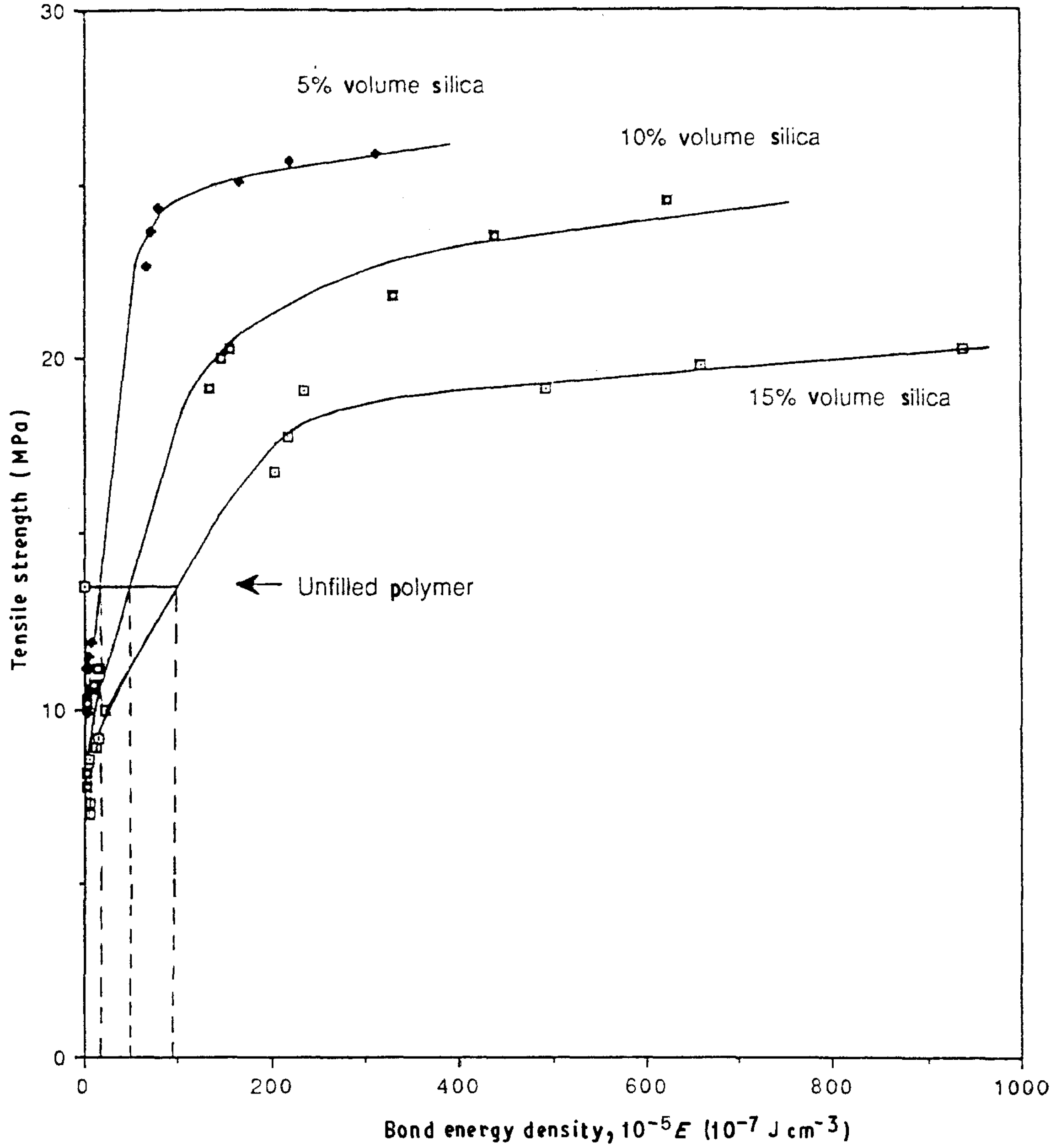

Figure 4 Effect of bond energy density on the tensile strength of different volume fraction of silica-filled polymer composites.

that the CBED value increases linearly with an increase in volume fraction of filler.

4. Conclusion

BED is a single parameter that includes the combined effects of filler particle size, filler interfacial bonding, and filler volume fraction. When the surface-to-volume ratio of a filler increases and interfacial bonding improves, the BED increases. Thus BED reflects the reinforcing ability of a filler dispersed in a polymer system.

The CBED reflects the reinforcing ability of a filler used in a composite. CBED is the BED of a filled composite whose tensile strength equals that of its unfilled polymer. The BED of a composite must be greater than its CBED to get a filler reinforcing effect. The CBED of a composite increases linearly with an increase in volume fraction filler.

5. Appendix

5.1. Definitions

BED is the total interfacial bond energy per unit volume of a polymer composite. We can express BED as

$$E = W_a A/V \qquad \text{(A1)}$$

In Equation A1, we express E in J cm^{-3}. 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 (1) volume of silica and (2) volume of E-Va matrix.

Work of adhesion, W_a, between the silica surface and the surrounding polymer matrix can be calculated from Fowkes's equation. Contributions to the work of adhesion are derived from dispersion forces, hydrogen bonds and polar forces. We express the work of adhesion, W_a, as

$$W_a = W_a^d + W_a^h \qquad \text{(A2)}$$

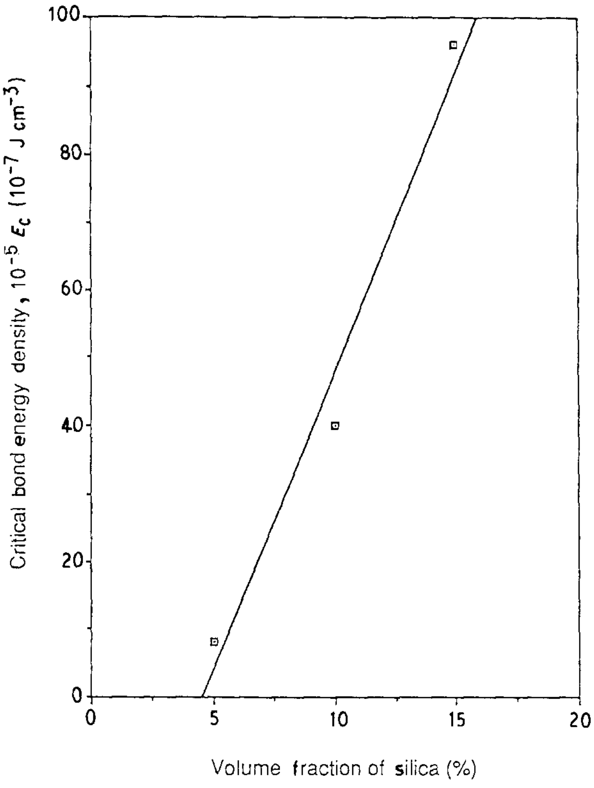

Figure 5 Effect of volume fraction of silica on CBED.

where W_a^d represent the dispersion forces. W_a^h represents both hydrogen bonds and polar forces.

5.1.1. Poor interfacial bonding

When few or no hydrogen bonds are present, we determined the W_a^d and W_a^h values from Equations A3 and A4

$$W_a^d = 2(\tau_f^d \tau_p^d)^{1/2} \qquad \text{(A3)}$$

$$W_a^h = 2(\tau_f^h \tau_p^h)^{1/2} \qquad \text{(A4)}$$

In these equations, τ refers to surface free energy, *d* the dispersion forces and *h* the hydrogen and polar bonds. Subscripts *f* and *p* represent filler particles and polymer, respectively. We determined the τ^h and τ^d values from the following equation [43]:

$$1 + \cos\theta = 2(\tau_s^d)^{1/2}(\tau_l^{d\,1/2}/\tau_l) + 2(\tau_s^h)^{1/2}(\tau_l^{h\,1/2}/\tau_l) \qquad \text{(A5)}$$

In Equation A5, θ represents the contact angle, *l* a liquid, and *s* a solid. τ_s^d symbolizes the dispersion component of the surface energy of the solid. τ_s^h symbolizes the hydrogen and polar components of the surface energy of the solid. τ_l refers to the surface energy of the liquid used to measure the contact angle of the solid surface.

We can calculate the surface energy of a solid by adding the τ for each component: $\tau_s = \tau_s^d + \tau_s^h$.

The W_a^d and W_a^h values of composites with little or no hydrogen bonding were calculated from Equations A3 and A4.

5.1.2. Good interfacial bonding

For systems exhibiting strong hydrogen and polar bonding, we calculated the W_a^d value from Equation A3. In this case, we used Fowkes's equation [27, 28] to calculate W_a^h. This equation is written as

$$W_a^h = f \cdot \Delta H^{ab} \cdot \text{moles of acid–base pairs/unit area} \qquad \text{(A6)}$$

$$\Delta H^{ab}(\text{kJ mol}^{-1}) = 1.00 \cdot \Delta v_{c=0}\ (\text{kJ mol}^{-1}\text{cm}^{-1}) \qquad \text{(A7)}$$

where $\Delta v_{c=0}$ is the wave number shift of the carbonyl stretching band of the polymer that occurs upon hydrogen bond formation [24, 28], and *f* is a conversion factor (here *f* is equal to 1). Moles of acid–base pair per unit area refer to the number of hydrogen bonds that can be formed between the surface of silica and the polymer.

Since the non-hydrogen-bonded carbonyl groups of the E-Va polymer absorb at 1739 cm^{-1}, while its carbonyl groups bonded to the OH groups of the silica absorb at 1704 cm^{-1}. $\Delta v_{c=0}$ is 35 cm^{-1} and ΔH becomes 35 kJ per mole of acid–base pairs.

The calculated W_a^d and W_a^h values of composites with strong hydrogen and polar bonding were also determined from Equations A3, A6 and A7.

The BED can be computed (Equation A1) after the work of adhesion has been determined (Equation A2). With the BED available, the reinforcing ability of the filler can be estimated as outlined in the paper.

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