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The effect of carbon black and colloidal silica fillers on interfacial adhesion at polystyrene interfaces

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Abstract—We have shown that the addition of small amounts of carbon black can drastically reduce the interfacial fracture toughness between polymers. This is interpreted as being due to strong interactions between the filler particles and the polymer chains which hinder interfacial adhesion. The effect is less severe when graphitic carbon black particles are used. The fracture toughness was found to increase with time as $t^{1/2}$, regardless of filler concentration, indicating that interface formation was diffusion limited. A distinct minimum with filler concentration in the fracture toughness of interfaces annealed for times longer than 5 min was found. This feature could be explained as a balance between the increase in modulus and the decrease in polymer chain dynamics as a function of carbon black concentration. The addition of colloidal silica, where the surface interactions are screened, was found to reinforce the interface, as predicted by the Guth–Gold relationship. Mixing small quantities ($<2\%$) of inert fillers with interfacially active ones restored the fracture toughness. This observation has practical importance since one can now obtain optimum adhesion without compromising the mechanical integrity provided by the reactive filler.

Keywords: Interfacial adhesion; fracture toughness; polymer interface; carbon black; colloidal silica; filler.

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1. INTRODUCTION

Fillers are important in many industries since they can be used to control properties of materials, such as hardness, heat resistance and electrical conductivity simply by varying their concentration [1]. Fillers are also commonly used to reinforce the mechanical properties of polymers by increasing their modulus and impact resistance. Recently, Zhang *et al.* [2] have shown that, when strong interactions exist between the filler particles and the polymer matrix, the internal chain dynamics can be drastically slowed down. They reported that the interfacial width between layers of partially miscible polyolefin rubbers (brominated isobutylene methylstyrene and butadiene) decreased from 100 nm to 2 nm with the addition of only 2.5% commercial carbon black. This was interpreted as being the three-dimensional analogue of the behavior previously observed by Zheng *et al.* [3] for thin polymer films adjacent to an attractive substrate. Zheng *et al.* [3] showed that polymer/wall interactions could pin the chains in the layer adjacent to the interface and impede the motion of chains in subsequent layers for up to several hundred nanometers from the interface. When fillers are added, the amount of surface area available for polymer adsorption is greatly increased. If the filler/polymer interactions are as long ranged as those near planar surfaces, then the dynamics of the polymer chains can be reduced within a 'sphere of influence' as postulated by Zhang *et al.* [2] can extend several hundred nanometers around each particle. Since direct contact is not required, the amount of filler needed to affect the viscosity can be much smaller than expected. Furthermore, Zhang *et al.* [2] showed that when fillers such as colloidal silica, where the surface interactions are screened, were added, only a minimal reduction of the interfacial width was observed. No effect on the interfacial width could be detected when small amounts of colloidal silica filler were mixed with carbon black, indicating that 'free polymer' associated with the silica tended to segregate out of the regions physically cross-linked by the attractive carbon filler.

The interfacial width is a critical parameter in determining the adhesion between polymers. Hence, these concepts can also be tested by measuring the adhesion between polymer layers, when carbon black, colloidal silica, or their mixtures are added. The polymers used by Zhang *et al.* [2] have glass transitions, T_g approx. $-40°C$ and hence are rubbery at room temperature. This makes it difficult to quantify the interfacial strength as a function of annealing time using peel tests, since significant interdiffusion can occur during the measurements. We, therefore, chose to study polystyrene (PS) which can be annealed above its glass transition, $T_g = 100°C$, for joining and quenched to room temperature for measurement. The interfacial adhesion or fracture toughness, G_c, can then be measured, using the double cantilever beam method, as a function of annealing time, polymer/filler interactions and filler concentration.

In this paper, we report on interfacial adhesion (fracture toughness, G_c), measurements for molded PS slabs with colloidal silica, commercial carbon black, carbon black heated to 1100°C, carbon black heated to 2400°C, and mixtures of these fillers. The results are compared with those of Zhang *et al.* [2] and a simple model is presented to explain the time/concentration dependence.

2. EXPERIMENTAL

The symmetric double cantilever beam method (SDCBM) [4, 5] was used to test the interfacial adhesion (fracture toughness, G_c) of the samples. In this geometry the polymers are molded into slabs and a slab is glued to a hard substrate. The interfacial adhesion (fracture toughness, G_c) is then determined from the equation:

$$G_c = \frac{3u^2EL^3}{8a^4[1 + 0.64(L/a)]^4}\ (\text{J/m}^2). \tag{1}$$

Here u is wedge thickness or the thickness of the razor blade, $E = 3.0 \times 10^9$ Pa is Young's modulus of PS (polystyrene) in the upper layer, L is the thickness of the upper layer and a is the crack length.

Polydisperse PS (Aldrich Chemical, $M_w = 280\,000$) was poured into rectangular stainless steel molds, 42 mm by 10.5 mm by 2 mm, and pressed for a total of four minutes at 150°C. In order to keep the surfaces of the strips molecularly flat, the steel mold was covered with heat resistant Kapton® film (Fig. 1). Monodisperse PS (Polymer Laboratories, $M_w/M_n < 1.05$, $M_w = 217\,000$) was dissolved in toluene together with different volume fractions of fillers. Films were initially spun cast onto Si wafers and their thickness, approximately 200–300 nm, was measured using ellipsometry. Films were spun cast directly onto the surface of one of the slabs of polymer or floated in water onto a polymeric slab. Two slabs were then pressed together with a pressure of 1500 kg/m^2 at 150°C for times ranging from 1 to 10 min. A small Kapton spacer was inserted for a distance of 0.5 mm between the slabs prior to annealing in order to define the position of the interface (Fig. 1). The joined slabs were then air cooled for 1 h at room temperature and glued with epoxy

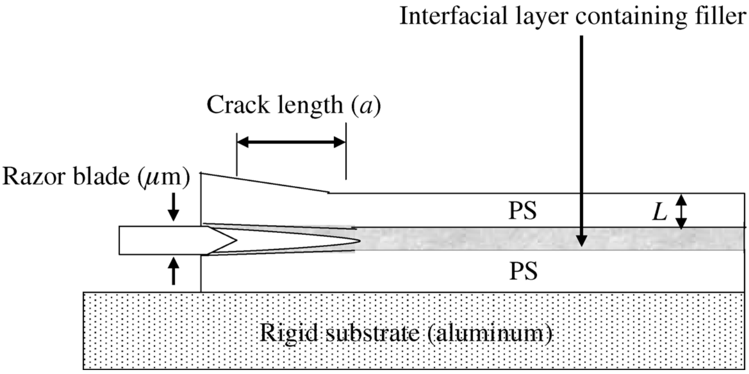
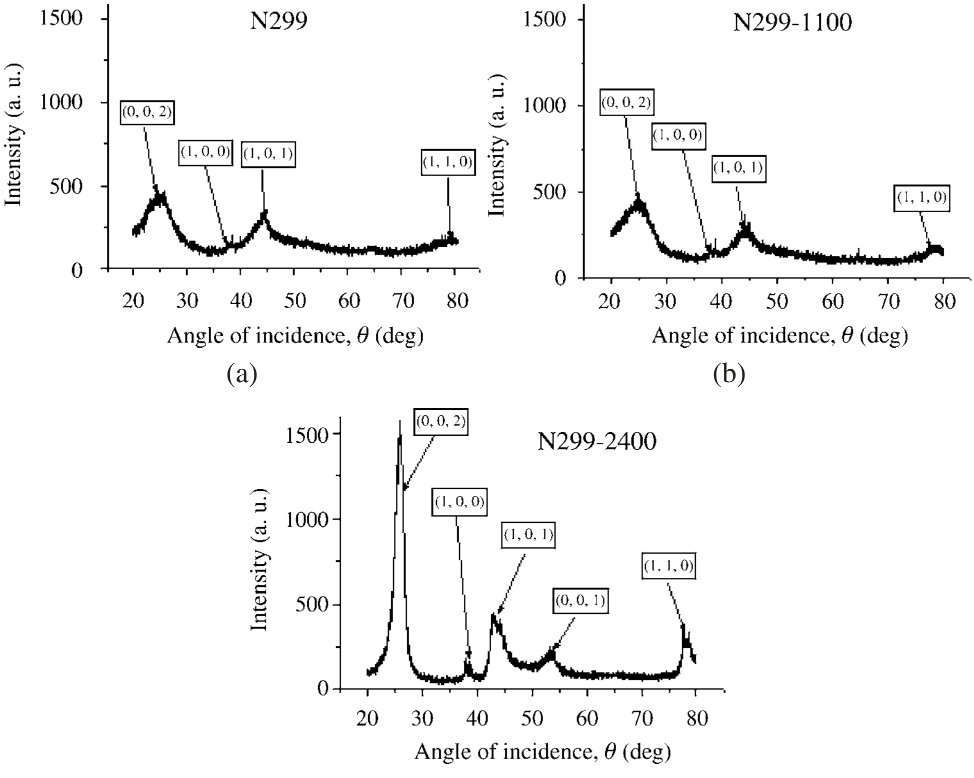


Figure 1. Schematic of the symmetric double cantilever beam test geometry. The width of the razor blade inserted at the interface of the 2 slabs was measured in μm.

Table 1.
Summary of fillers used and their properties

Filler type and manufacturer	Description	Treatment
Carbon black (Vulcan)	N299	None
Carbon black (Special Production, Cabot)	N299-1100	Heated to 1100°C
Carbon black (Special Production, Cabot)	N299-2400	Heated to 2400°C
Colloidal silica (Aerosil)	R812	Surface modified with silamine 1,1,-trimethyl-N-(trimethyl-silyl)



(a) (b)

(c)

Figure 2. X-ray diffraction patterns of powder carbon black samples. (a) Untreated N299, (b) N299-1100 heated to 1100°C, (c) N299-2400 heated to 2400°C.

to an aluminum plate for testing. A razor blade was inserted into the joint at a rate of 10 μm/s. The length of the crack that propagated along the interface was measured with an optical microscope. An average of 5 sets of 10 measurements each was taken for every sample in order to determine the mean crack length, which was inserted in equation (1). The surfaces of the fractured samples were then imaged with a Veeco (Santa Barbara, CA, USA) DI-3000™ scanning probe microscope in the contact mode.

The fillers used in these experiments were N299 carbon black (Sid Richardson, Akron, OH, USA) and colloidal silica (Aerosil, R812). Some of the carbon black samples were further annealed to 1100°C and 2400°C in an induction furnace under argon atmosphere. The specifications of the fillers used are listed in Table 1.

The carbon black samples were further analyzed using X-ray diffraction (XRD). The diffraction patterns obtained, using a Phillips AP3520 PW 1729 X-ray generator, for N229, N229-1100, and N299-2400 are shown in Fig. 2a, 2b and 2c, respectively. From Fig. 2, we can see that N299 and N299-1100 show only a broad peak at an angle of incidence $\theta = 26°$, while N299-2400 shows relatively sharp peaks at $\theta = 26°, 38°, 44°, 54°$ and 77°, corresponding to the [0, 0, 2], [1, 0, 0], [1, 0, 1], [0, 0, 4] and [1, 1, 0] Bragg reflections in graphite, respectively. Our data indicate that heating to 1100°C does not change the predominantly turbostatic structure of the N299 carbon black particles, while heating to 2400°C induces a large degree of crystallinity. This is in agreement with the results reported by Zerda *et al.* [6] where they found that heating carbon black N299 to 2730°C under nitrogen atmosphere reduced the amorphous fraction to 3% and produced graphitic crystallites.

3. RESULTS AND DISCUSSION

3.1. Carbon black fillers

The interfacial adhesion (fracture toughness, G_c), of the PS/PS interface, annealed for 2 min, as a function of carbon black concentration is shown on linear plots in Fig. 3a for the three types of carbon black listed in Table 1.

From Fig. 3, we can see that the interfacial adhesion (fracture toughness, G_c) decreases drastically with carbon black content. The most dramatic change occurs when only 2.9% untreated carbon black, N299, is added and G_c decreases from approximately 400 J/m^2 to 100 J/m^2. Increasing the carbon black concentration further to 17.6%, the actual amount used in most carbon filled compounds, causes a much smaller reduction to G_c approx. 50 J/m^2. These results are similar to those reported by Zhang *et al.* [2] and others [7–10] where the largest rate of decrease in the interfacial width also occurred around 2.5% carbon black. The open circles in Fig. 3 correspond to the interfacial adhesion of the slabs with carbon black annealed to 1100°C. From Fig. 3 we can see that the decrease in G_c with concentration is still large with N229-1100, but slightly more gradual than with untreated N299 carbon black. At a concentration of 2.9%, $G_c = 200$ J/m^2, which is twice as high as G_c for the same concentration of untreated carbon black. The largest effect though is clearly seen to occur when carbon black heat treated to 2400°C is added to the interface. In this case the decrease is much more gradual. At a concentration of 2.9%, G_c is only decreased to 350 J/m^2 while at a concentration of 16.0%, $G_c = 150$ J/m^2 which is still three times larger than G_c for the same concentration of N299.

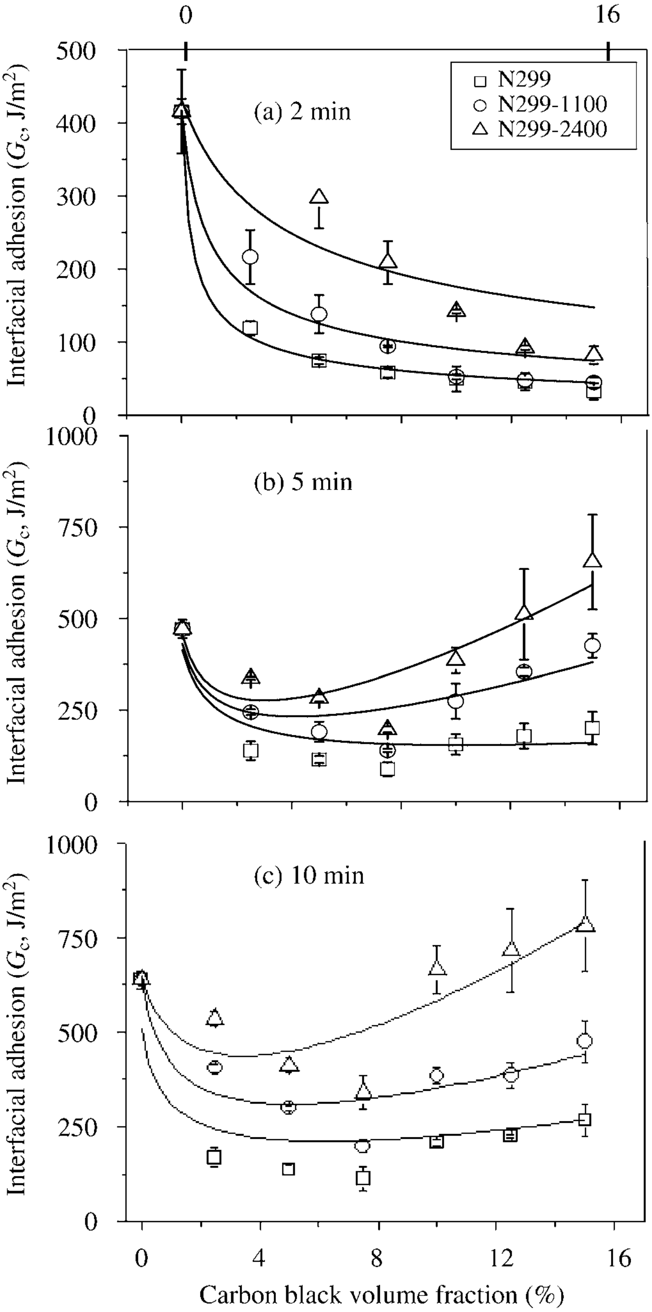


Figure 3. Interfacial adhesion (fracture toughness, G_c) of the PS/PS interface as a function of volume fraction for the three different types of carbon black tested. The samples were annealed at 150°C for (a) 2 min, (b) 5 min and (c) 10 min. The solid lines are just to guide the eye. The solid lines in (b) and (c) are fits to equation (8) with the best fit parameters presented in Table 2.

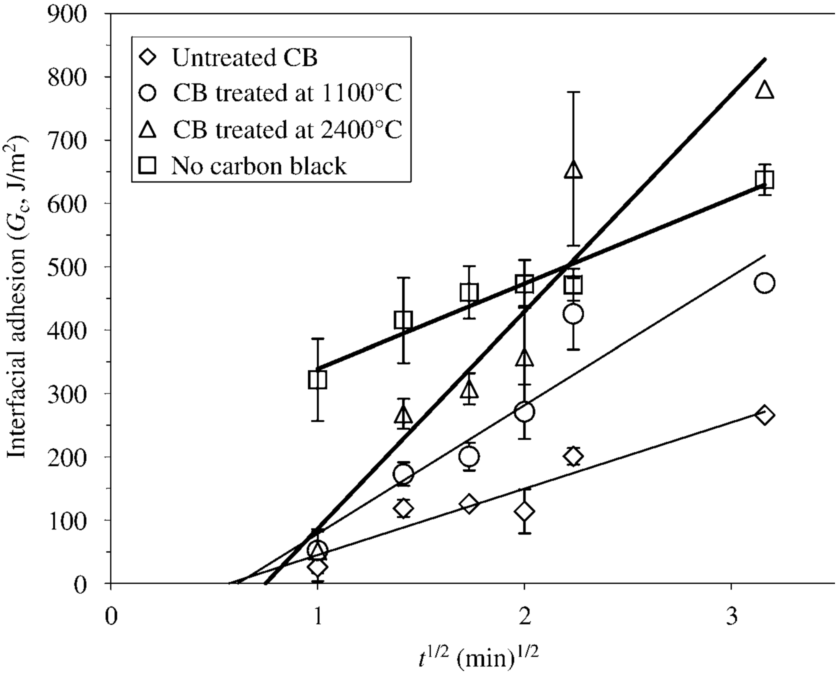


Figure 4. Interfacial adhesion (fracture toughness, G_c) of PS/PS samples without carbon fillers (□) and with volume fraction, $\phi = 16\%$ for all three types of carbon black, as shown, plotted *versus* the square root of the annealing time.

Even though these results are consistent with those of Zhang *et al.* [2], the decrease in fracture toughness with increasing carbon black concentration is contrary to the expectation that carbon black should reinforce the polymer interface against crack propagation. The decreased adhesion may, therefore, be a non-equilibrium effect due to the reduced mobility of the polymer chains when strongly interacting fillers are present, rather than a change in an intrinsic property of the composite material.

In order to determine the effects of dynamics on adhesion, we plot in Fig. 4 the interfacial adhesion (fracture toughness) *vs.* the square root of the annealing time for all three types of carbon black at a volume fraction, $\phi = 16\%$. The square block curve obtained from a bare PS/PS interface is drawn for comparison. From Fig. 4 we can see that the data are well fitted by a linear curve, indicating that G_c scales as $t^{1/2}$ for all interfaces, regardless of carbon black content. This scaling has been reported previously for bare polymer interfaces by Jud *et al.* [11], as well as by others [12, 13], where it was interpreted as an indication that G_c was diffusion limited. Hence, we conclude that in filled systems as well G_c is initially determined by polymer interdiffusion, with a reduced diffusion coefficient.

From Fig. 4 we can also see that G_c for all the interfaces with carbon black is initially less than the value for the bare interface. On the other hand, the slope or rate of increase of G_c is larger for the filled systems, with the one for N299-2400 being the highest. Hence, with sufficient annealing time, the interfaces reinforced with carbon black will be stronger than the bare PS/PS interface. In fact for an annealing time, $t > 2$ min, G_c for N299-2400 already surpasses that for the bare interface, confirming the expected interfacial reinforcement due to the carbon black particles.

In Fig. 3b and 3c, we plot G_c as a function of carbon black concentration after annealing the slabs for 5 and 10 min, respectively. From Fig. 3 we can see that the fracture toughness is no longer a monotonically decreasing function of the carbon black concentration. Rather, G_c exhibits a distinct minimum at low volume fractions, and increases with concentration thereafter. The minimum is most pronounced for samples annealed for 5 min and becomes shallower after annealing for 10 min.

These results can be explained qualitatively if we realize that the increase in modulus with filler concentration is counterbalanced by the decrease in the interfacial dynamics due to interactions between the polymer chains and the filler surfaces. At very short annealing times, the reinforcing effect of the fillers will not be felt, since only a very few chain segments and associated fillers have interpenetrated the two interfaces. Hence, as seen in Fig. 3a, the monotonic decrease in interfacial adhesion reflects only the decrease in the diffusion coefficient with filler concentration. For longer annealing times, entire chain segments and fillers penetrate across the interface and form entanglements. Consequently, the interfacial adhesion will be more sensitive to the filler concentration. We can then write an approximate relationship [12–14]

$$G(\phi, t) - G(\phi)\frac{\Delta x}{\mathrm{Rg}}, \quad \text{for } \frac{\Delta x}{\mathrm{Rg}} < 1 \tag{2}$$

and

$$G(\phi, t) - G(\phi), \qquad \text{for } \frac{\Delta x}{\mathrm{Rg}} \gg 1,$$

where Δx is the interfacial width. Equation (2) is derived from the Einstein relationship for the bulk viscosity, η, for a system with fillers. Since D approx. kT/η, it would appear that D is inversely proportional to the modulus, E. It is important to note at this point that the Einstein relationship refers to the viscosity of the entire system, which includes both fillers and polymer chains. Since we are examining such short time scales the motion of the polymer chains is not yet coupled to that of the particles. At this molecular level it is more correct to express the local viscosity in terms of the monomer friction coefficient. Numerous authors have shown [15] that for an entangled polymer, G_c reaches its maximum value when the interfacial width is on the order of the polymer radius of gyration, Rg. When this occurs it is assumed that several entanglements across the interface have formed. If we assume that the interfacial width grows by Fickian diffusion at this time, then

$$\Delta x = [4D(\phi)t]^{1/2}. \tag{3}$$

Here $D(\phi)$ is the tracer diffusion coefficient of the polymer chains in the filled system. When the size of the filler is large compared with the polymer radius of gyration, one can approximate that introduction of fillers into a system as increasing the number of interfaces that interact with the polymer chains. This assumption is valid in our case, since Rg is approx. 14 nm and the carbon (N299) aggregate size from Zhang *et al.* [2] is 100 nm.

We can then refer to the formalism developed by Zheng *et al.* [3] who derived a simple expression for the tracer diffusion coefficient for a melt consisting of chains with N monomers and an effective friction coefficient, F, given by;

$$F = \delta N_{\mathrm{s}} + \delta_0 N, \tag{4}$$

where δ is the monomer surface friction coefficient, N_{s}, is the number of monomers in contact with the surface and δ_0 is the monomeric bulk friction coefficient. In our case the number of monomer particle contacts is proportional to the filler concentration, ϕ, and the conformation of the chains adjacent to the filler. Since this is not as yet known for our system, we can only parameterize equation (4) as;

$$F = \phi\omega + \delta_0 N, \tag{5}$$

where ω is a constant for a given system that contains information as to the number of contacts and the polymer/filler interactions. Substituting for F into the equations for motion within a tube [16], where D_0 is the self-diffusion coefficient of pure PS, we find;

$$D(\phi) = \frac{D_0}{(1 + \phi\omega)}. \tag{6}$$

If we follow the model of Brown [17] for the interfacial energy at the crack tip of a symmetric system, then E in equation (1) corresponds to the elastic tensile modulus in front of the propagating crack. This is also the region where the filler is located and hence, where we can approximate the modulus, E, by the Guth–Gold relationship for a filled system [18],

$$E = E_0(1 + 2.6f\phi + 14.1f^2\phi^2), \tag{7}$$

where f is a numerical coefficient that was later added by Donnet [18] to account for polymer/filler interactions and E_0 is the modulus of the unfilled system.

Substituting for E and Δx in equations (1) and (2) above, we find

$$G(\phi, t) = \frac{A[(1 + 2.6f\phi + 14.1f^2\phi^2)]}{(1 + \omega\phi)^{1/2}}, \text{ where } A = \frac{G_0 2(D_0 t)^{1/2}}{\mathrm{Rg}}, \tag{8}$$

where G_0 is the fracture toughness of the unfilled system. The solid lines in Fig. 3b and 3c are fits to the data for the 5 and 10 min annealing times, with three free

Table 2.
The best-fit parameters to equation (8)

		f	ω	A
5 min	Untreated	1.3 ± 1.0	150 ± 47	413 ± 72
	1100°C	2.6 ± 0.4	134 ± 40	421 ± 62
	2400°C	3.2 ± 0.4	107 ± 34	434 ± 60
10 min	Untreated	1.9 ± 0.9	100 ± 45	507 ± 66
	1100°C	2.3 ± 0.7	72 ± 34	641 ± 90
	2400°C	2.9 ± 0.7	32 ± 16	645 ± 90

parameters, A, f and ω. The fitting results are presented in Table 2. From Table 2 we see that A is independent of the nature of the filler and scales roughly with $t^{1/2}$, in agreement with equation (8). The value of f, on the other hand, is constant with time, but decreases with increasing annealing temperature of the N299 carbon black. The magnitude of f, $1 < f < 3.5$, is consistent with that reported by Donnet [18] for elastomers. The values of f required to fit the data imply that the interactions with carbon black reduce the tracer diffusion coefficient, $D(\phi)$, by approximately two orders of magnitude for the most attractive surface. Zheng *et al.* [3] reported a reduction of this magnitude for PS within 50 nm of an attractive planar Si interface. From the data of Zhang *et al.* [2], we estimate that the inter-particle distance varies between 30 and 100 nm over the filler concentration used. Hence, on average, the average surface-to-chain distance is in the same range as that measured by Zheng *et al.* [3]. Despite the good agreement, one must still be cautious in comparing the two experiments, since we do not know whether the magnitude of the surface interaction with Si is similar to that with carbon black, if the interaction propagates as far from a spherical interface as from a planar one, or if the particles simply provide physical hindrance. Experiments are currently in progress to determine where the diffusion coefficient in the filled system is being measured as a function of time, molecular weight and filler concentration.

3.2. Colloidal silica fillers and mixtures

In order to prove that the slowing down of the dynamics near an interface was indeed due to polymer-surface interactions, Zheng *et al.* [3] showed that when the planar silica surface was screened by 2-nm-thick polymer films, the reduction in the tracer diffusion coefficients for chains near the interface was much smaller. In analogy to the planar system, Zhang *et al.* [2] have shown that when silica fillers coated with silamine 1,1,-trimethyl-N-(trimethyl-silyl), were substituted for carbon black, the interfacial width between partially miscible rubbers was unaffected. This was interpreted as evidence that the decreased polymer dynamics in filled systems was indeed caused by surface interactions. In the uppermost curve (square symbols) of Fig. 5 we plot the interfacial adhesion (fracture toughness) as a function of colloidal silica concentration for samples annealed for 2 min. In contrast to Fig. 3 where

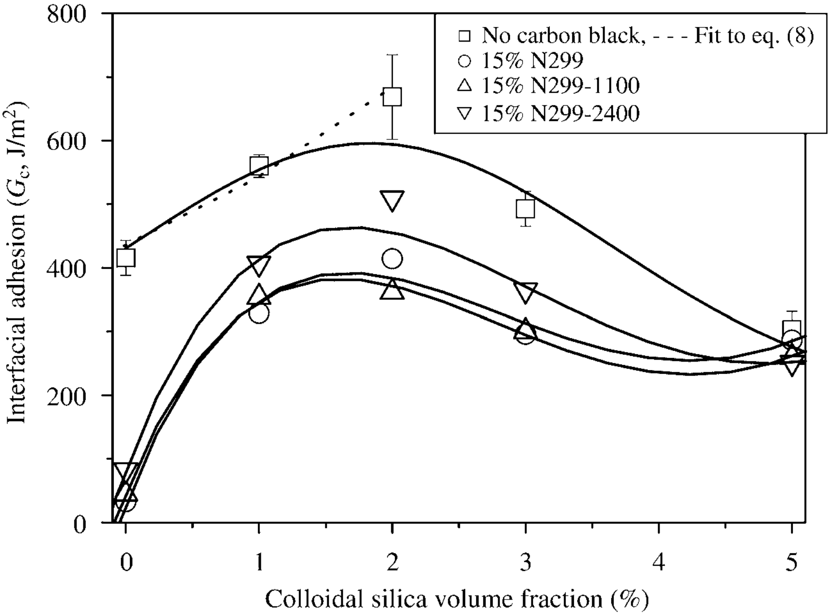


Figure 5. Iterfacial adhesion (fracture toughness, G_c) of PS/PS interface with volume fraction of $\phi = 15\%$ carbon black fillers as a function of the volume fraction of colloidal silica particles. The dashed line is a fit to equation (8) with the parameters listed in Table 2 and the solid lines are drawn to guide the eye.

we plotted G_c as a function of carbon black concentration, the interfacial adhesion increases rather sharply with silica filler concentration and reaches a maximum of 700 J/m^2 at ϕ approx. 2%. The dashed line corresponds to a fit with equation (8), where ω is about 0 and f is about 5. Hence, the chain dynamics across the interface is not affected in our system by the introduction of silica. The rapid dynamics also allows us to sense the effects of reinforcement by the colloidal silica on the modulus and interfacial fracture energy, even after a very short annealing time.

As ϕ increases further we find that G_c decreases to a value of 300 J/m^2 at ϕ approx. 5%, which is roughly 20% less than the bare interface value. At present we do not have an explanation for the decrease. Since the interaction between the surfactant coating of the colloidal silica particles and the PS matrix is weak or slightly unfavorable, we can only postulate that clustering of the particles may be occurring with increased annealing time, as was previously reported by Sharma *et al.* in dewetting studies [19]. Clustering decreases the effective filler concentration, and if the clusters are too large, they may interfere with adhesion by nucleating large structural defects at the interface.

In Fig. 5 we also plot the fracture toughness as a function of concentration when colloidal silica is added to samples already containing 15% carbon black of the three types. In each case dramatic improvement in the fracture toughness is seen even with the addition of 1% silica.

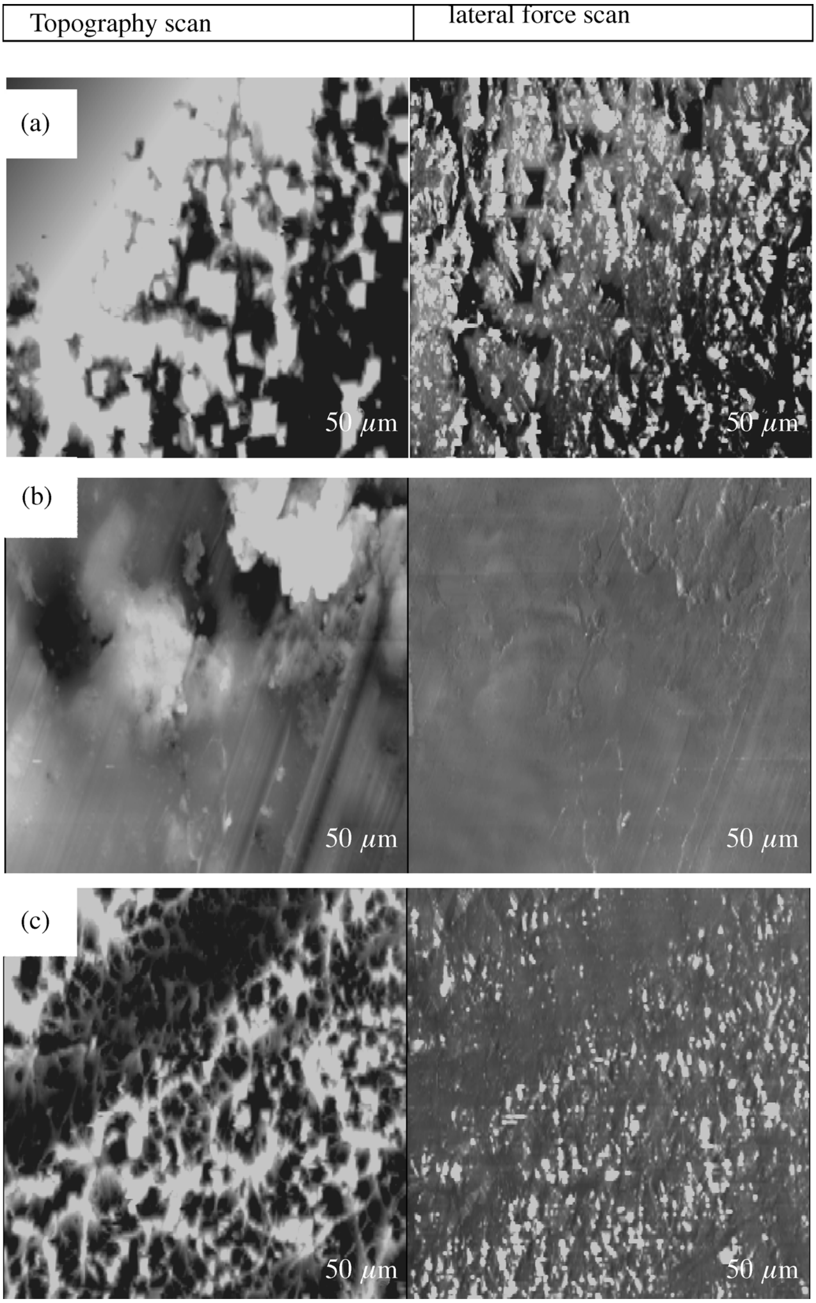


Figure 6. SPM micrographs of the PS/PS interface with (a) no fillers added (b) $\phi = 15\%$ N299 carbon black, (c) $\phi = 15\%$ carbon N299 carbon black with $\phi = 5\%$ colloidal silica fillers. The magnification shown is 50 μm. The left images show topography while the right images show the lateral force scans.

In order to further confirm these results we examined the surfaces of a set of samples, annealed for 2 min, with scanning probe microscopy. The results are given in Fig. 6, where we show both topographical and lateral force scans. From Fig. 6a we see that the topography for the fractured pure PS-PS interface is rough, as would be expected for the large fracture toughness, $G_c = 416$ J/m^2, measured. From the lateral force scan we see that large frictional contrast appears across the ridges. Since this interface fractured mostly via chain scission and crazing, the ridges also correspond to regions of large plastic deformation which occurred just prior to breakage. When polymer chains are stretched to the point of rupture they flow and are no longer glassy. Hence, they become soft and allow the SPM tip to penetrate deeper. This manifests itself as an apparent increase in frictional drag on the tip. When the interface is glassy the SPM tip slips across the interface, since the tip penetration is much smaller. Figure 6b shows the scans that correspond to an interface where 16% carbon black (N299) was added. Here we see that, except for some large dust particles, the interface is very smooth and very little lateral force contrast is seen. This is consistent with the low interfacial adhesion which correlates with the low fracture toughness $G_c = 33$ J/m^2 measured. The mechanism for fracture with low values of G_c is primarily chain pull-out, which does not produce large deformations, giving the surface its smooth appearance.

In Fig. 6c we show the images of the interface when 5% colloidal silica was added to 15% carbon black. Here again we see large topographical features with corresponding friction contrast, indicative of plastic deformations. These features are consistent with the large value of G_c measured, $G_c = 159$ J/m^2, confirming that the addition of colloidal silica cause the interface to fracture via crazing and chain scission.

These results are consistent with the results of Zhang *et al.* [2] where they found that the addition of a small amount of silica to samples already containing carbon black resulted in restoring the broad interface between the polyolefin rubbers. They postulated that the effects observed for the mixed filler system were due to entropic segregation of unbound polymer from the physically cross-linked regions rich in carbon black. Hence, they predicted that this effect should be universal to any system with mixtures of strongly and weakly interacting filler particles.

There are many applications where mixtures of carbon black and silica are not desirable since the insulating silica particles degrade the electrical conductivity of the composite. We, therefore, attempted to mix small amounts of the weakly interacting heat-treated N299-2400 carbon particles with the strongly interacting N299 particles at the PS/PS interface. The interfacial adhesion for a sample containing 17% N299 is plotted as a function of N299-2400 volume fraction in Fig. 7. From Fig. 7 we can see that a peak in the fracture toughness, similar to that observed for silica filler, occurs at $\phi = 2\%$.

The magnitude of the peak is somewhat lower, but this may just reflect the fact that the polymer interactions with the heat treated carbon black are higher than those with colloidal silica.

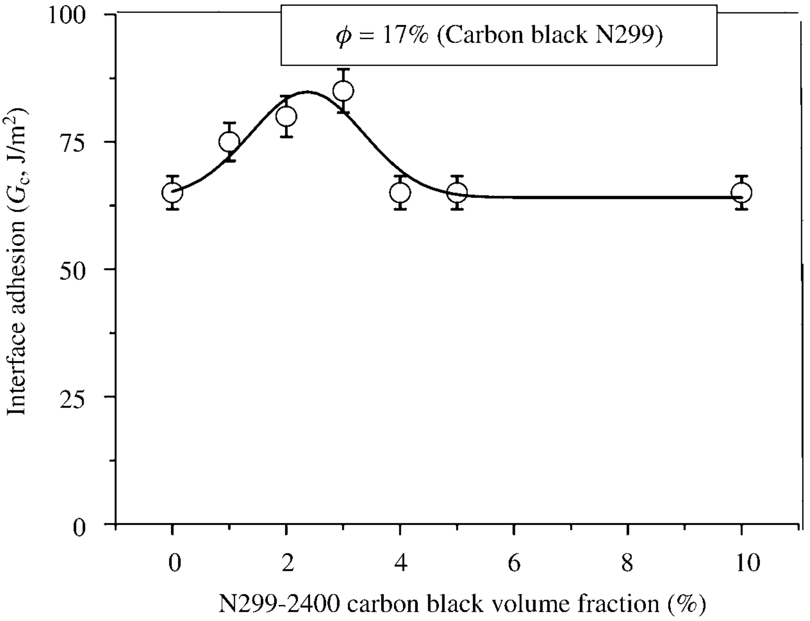


Figure 7. Interfacial adhesion (fracture toughness, G_c) of PS/PS with $\phi = 17\%$ N299 carbon black as a function of the volume fraction of N299-2400 carbon black. The solid line is just to guide the eye.

4. CONCLUSIONS

In conclusion, we have shown that the addition of small amounts of carbon black can drastically reduce the interfacial fracture toughness between polymers. This is interpreted as being due to strong interactions between the filler particles and the polymer chains which hinder interfacial dynamics. The effect is less severe when carbon black particles, which have been heated in argon to 2400°C, are used. These particles are 97% crystalline and hence have far fewer sites for adsorbing polymer chains.

The interfacial adhesion (fracture toughness) was found to increase with time as $t^{1/2}$, regardless of filler concentration, indicating that interface formation was diffusion limited.

A distinct minimum (at ϕ approximately 5%), in the interfacial adhesion (fracture toughness) of interfaces annealed for times longer than 5 min was found. This feature could be explained as a balance between the increase in modulus and the decrease in polymer chain dynamics as a function of carbon black concentration.

The addition of weakly interacting fillers such as colloidal silica, or N299-2400 crystalline carbon black, reinforces the interface for concentrations $\phi < 5\%$. A 20% decrease in G_c was observed for ϕ approx. 16%, which was ascribed to clustering.

Mixtures of small quantities of inert fillers with interfacially active ones can correct the adverse effects on adhesion. This observation has practical importance since one can now obtain optimum adhesion without compromising the mechanical integrity provided by the reactive filler.

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