

# Interfacial activity of particles at PI/PDMS and PI/PIB interfaces: analysis based on Girifalco–Good theory

Prachi Thareja · Sachin S. Velankar

Received: 3 January 2008 / Revised: 23 April 2008 / Accepted: 5 May 2008 / Published online: 18 June 2008  
© Springer-Verlag 2008

**Abstract** Particles that are partially wetted by oil and water are known to adsorb at oil/water interfaces. By the same mechanism, particles that are partially wetted by two immiscible polymers should adsorb at the interface between those two polymers. However, since chemical differences between immiscible polymers are relatively modest, particle adsorption at polymer/polymer interfaces may be expected to be relatively uncommon. We have conducted experiments with several particle types added to two pairs of model polymers, polyisoprene/polydimethylsiloxane and polyisoprene/polyisobutylene. Contrary to our expectation, in every case, particles readily adsorbed at the polymer/polymer interfaces. We evaluated the Girifalco–Good theory as a means to predict the interfacial activity of the particles. The solid surface energy required by the Girifalco–Good theory was assumed to be equal to the critical surface tension, which was then found by float/sink tests. Our results suggest that this approach is not able to predict the observed interfacial activity of particles at polymer/polymer interfaces.

**Keywords** Interfacial tension · Pickering emulsion · Immiscible polymer blends · Wettability · Colloids

## Introduction

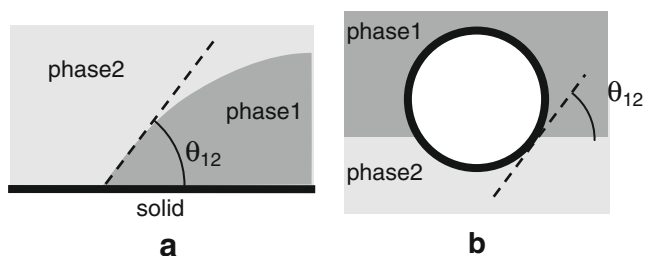
In recent years, there have been several investigations of the effect of solid particles in blends of immiscible homopolymers. Intriguingly, some of these papers have reported that

the particles are often found at the interface between the two immiscible species, raising the possibility of “interfacial composites”—polymer blends that have particles adsorbed at the interface between the polymers. Most such reports concern the interfacial localization of carbon black [1–8] or nanoclays [9–15], but there have also been some reports of other particle types such as alumina [16] or silica with various surface modifications [17–20]. Such interfacial localization of particles has led to suggestions that the particles are playing the same role as a block copolymer compatibilizer.

Block copolymer compatibilizers are usually interfacially active due to their amphiphilicity: Since different blocks of the copolymer have affinity for the two different phases, localization of the block copolymer at the interface is thermodynamically favorable. Certainly, none of the particles used in the research cited above were amphiphilic “Janus” particles but instead may be expected to have uniform surface characteristics. What explains the adsorption of nonamphiphilic particles at interfaces? In small-molecule systems, especially oil/water, interfacial adsorption of nonamphiphilic particles has been attributed to the partial wettability of the particle surfaces. Referring to Fig. 1, the relevant quantity is the contact angle  $\theta_{12}$  made by the phase 1/phase 2 interface at the solid surface: if  $0^\circ < \theta_{12} < 180^\circ$ , the solid surface is partially wetted by both the liquid phases, and particle adsorption at the interface is expected. On the other hand, if the solid particle is fully wetted by either phase, it will not be interfacially active.

The above partial wettability-based explanation for the interfacial activity of particles is well established in oil/water systems and has also been invoked to explain interfacial activity of particles in polymeric systems [20, 21]. Below we will consider the partial wettability picture further, specifically commenting on two differences between oil/water systems and polymer/polymer systems.

P. Thareja · S. S. Velankar (✉)  
Department of Chemical Engineering, University of Pittsburgh,  
Pittsburgh, PA 15261, USA  
e-mail: velankar@pitt.edu



**Fig. 1** **a** Schematic of a phase 1/phase 2 interface making a contact angle at a solid surface. **b** A spherical solid particle with the same interfacial characteristics adsorbs at the phase 1/phase 2 interface

The first difference is that unlike oil and water, polymer molecules are large. Thus, the partial wettability-based picture will become invalid for particles whose size is comparable to the radius of gyration of the two homopolymers, because in that case the particles can swell the polymer chains, and thus act somewhat like a solvent [22]. This paper however only considers particles that are much larger than the polymer molecules, allowing the macromolecular nature of the immiscible phases to be ignored.

The second difference, which is more relevant to this paper, is the degree of chemical incompatibility between two immiscible polymers, as compared to between oil and water. In qualitative terms, a particle that is partially wetted by two immiscible phases may be regarded as having a “chemical nature” that is intermediate between the two phases. The chemical differences between oil and water are large, which may explain why a large variety of particles adsorb at oil/water interfaces [23–25]. In comparison, the chemical differences between any two polymers—even highly immiscible ones—are quite modest, and hence a given particle type is less likely to have a “chemical nature” intermediate between two polymers. This qualitative argument (to be made quantitative later) suggests that particle adsorption at polymer/polymer interfaces will be much less common than at oil/water interfaces. Furthermore, as the chemical nature of the two polymeric phases approaches each other (e.g., as the critical point for phase mixing is approached), particle adsorption is expected to become even less likely.

Contrary to this expectation, our early experiments on a model polymer blend of polyisoprene (PI) and polydimethylsiloxane (PDMS), showed that a wide variety of particle types adsorb readily at the PI/PDMS interface. Intrigued by this, we then tested a second pair of polymers, PI and

polyisobutylene (PIB), which are chemically even more similar to each other (as gauged by the interfacial tension between them) and still found that most particles types adsorb at the interface. The goal of this paper is to describe these observations and interpret them in terms of the Girifalco–Good theory of the work of adhesion.

This paper is organized as follows. We first show experimentally that particles readily adsorb at polymer/polymer interfaces. We then discuss the theory of interfacial adsorption, followed by experiments to determine the solid/polymer interfacial energy and finally compare the theoretical predictions with our experimental observations.

## Materials and methods

Table 1 lists the three polymers used in this research, along with some of their properties. These polymers were chosen for experimental convenience: They are molten at room temperature, thus allowing all experiments to be performed at room temperature. The surface tensions of the polymers were measured by the pendant drop method at room temperature and are listed in Table 1.

Two blend pairs were made from these three polymers: PI/PDMS and PI/PIB. The interfacial tension between PI and PDMS was measured by the pendant drop method and found to be 2.73 mN/m. The interfacial tension between PI and PIB could not be measured by the pendant drop method because the very small density difference between them causes an unacceptable uncertainty in the result. Accordingly, the PI/PIB interfacial tension was measured by the deformed drop retraction method. Details of the method are available elsewhere [26, 27], but briefly, droplet–matrix blends of 5% PI in PIB were sheared in a home-built shear apparatus so as to deform the drops into ellipsoidal shapes. Upon cessation of the shear, the interfacial tension-driven recovery of the drops to spherical shapes was recorded by video microscopy. Interfacial tension can then be obtained from the kinetics of the shape recovery [26, 27]. The PI/PIB interfacial tension was found to be 0.28 mN/m; this low value is indicative of the chemical similarity of the two polymers.

The various particles used in this research are listed in Table 2, and SEM images are presented in Fig. 2. Most of them are commercial materials and were made available by

**Table 1** Homopolymers and their properties

Polymer	Supplier	MW (g/mol)	Viscosity (Pa s) <sup>a</sup>	Density <sup>b</sup> (kg/m <sup>3</sup> )	Surface tension (mN/m)
PDMS	Rhodia	135,600	100	960	19.2
PIB	Soltex	2400	333	910	32.1
PI	Kuraray America	29,000	131	910	35.9

<sup>a</sup> Terminal complex viscosity at 25 °C measured with an ARES 2000 rheometer

<sup>b</sup> Quoted by manufacturer

**Table 2** Test particles, suppliers, and specified sizes

Particles	Shape, average size <sup>a</sup> (μm)	Supplier
PTFE	Irregular, 8	Dyneon
Silica <sup>b</sup>	Spherical, 2.7	Tokoyama
Titanium dioxide	Irregular, 0.5	Sigma Aldrich
Iron oxyhydroxide	Elongated, 0.6×0.12	Elementis Pigments
Carbonyl iron	Spherical, 3	ISP Technology

<sup>a</sup> All sizes except silica are approximate

<sup>b</sup> Rendered hydrophobic by treating with DCDMS

the manufacturers. The only exception is the monodisperse 2.7-μm-diameter spherical silica particles, which were purchased from Tokuyama Corp. The as-received silica particles had hydrophilic surfaces, which were hydrophobically modified by treating with dichlorodimethylsilane (DCDMS) as described previously [20].

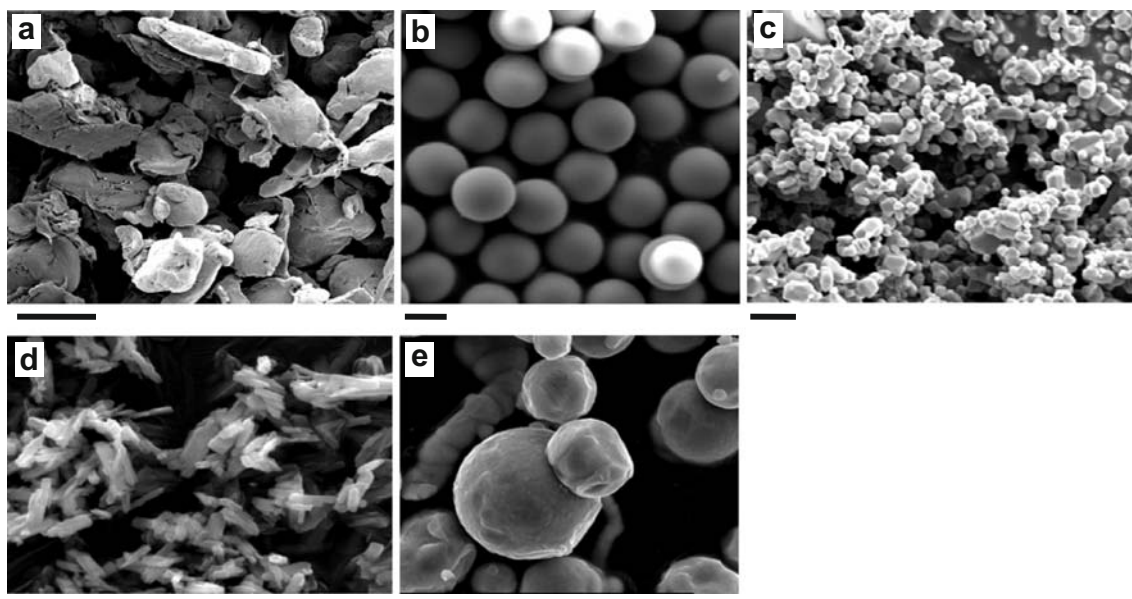
Interfacial activity of particles was tested by blending the particles into blends of the immiscible homopolymers and then examining the blends by optical microscopy. Blends were composed of 5 wt% PI, 0.1 wt% of particles, and the remainder PIB (or PDMS). Blends were prepared by predispersing the appropriate amount of particles into the matrix phase (PIB or PDMS) and then blending in the PI phase as drops. All blending was performed in a Petri dish by hand with a spatula. The particle loading was kept to a low value of 0.1 wt% to minimize visualization problems; higher loading causes intense scattering and/or opacity of the blends. Optical microscopy was conducted on a CKX-41 microscope equipped with ×20 and ×40 magnification objectives, and images were captured with a Basler 302f area scan camera.

## Results

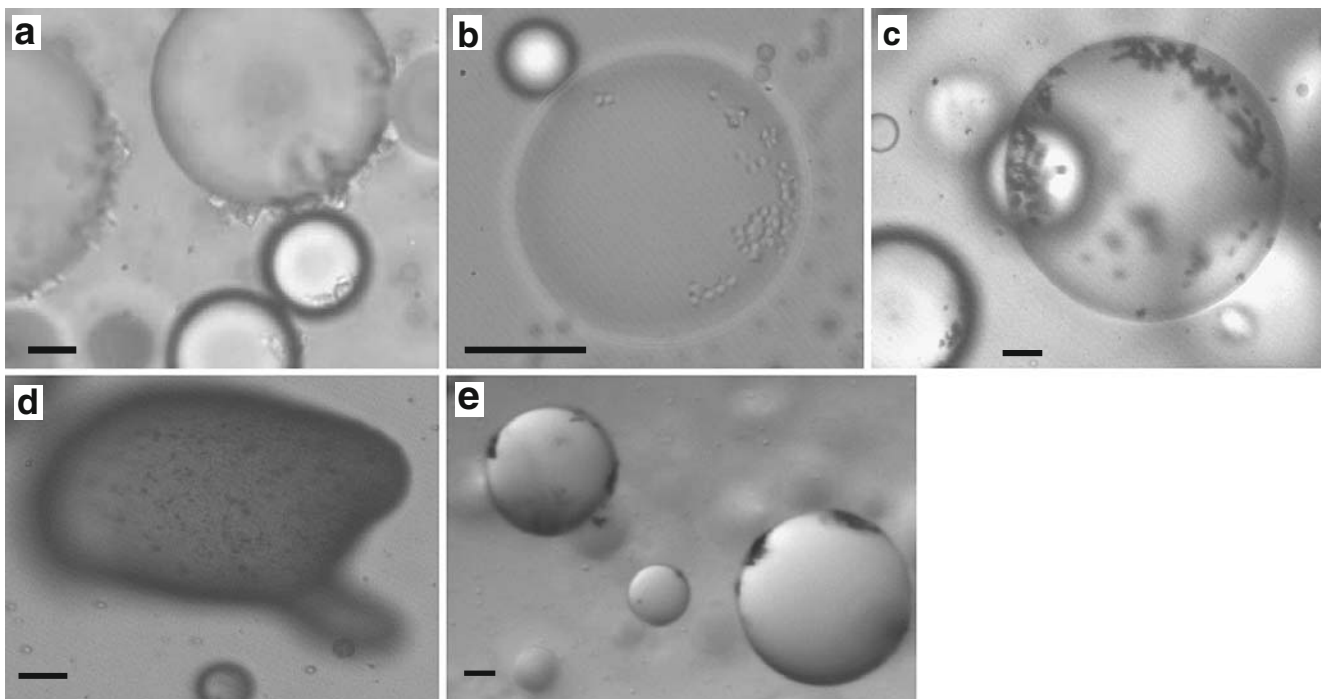
### Interfacial adsorption of particles

Initial tests of interfacial activity of particles were conducted with the PI/PDMS system. In some cases, e.g., PTFE particles added to PI/PDMS blends, interfacial adsorption was obvious even in the as-blended samples. In most cases, however, most particles appeared to be located in the matrix phase in the as-blended samples. Interfacially adsorbed particles became evident (or much more obvious) after allowing samples to sit quiescently for 2–3 days. We believe that under quiescent conditions, the PI drops rise upward due to their lower density, whereas the denser particles settle downward. This internal motion induces collisions between drops and particles, allowing particle adsorption. Figure 3 shows images of the various particle types adsorbed at the PI/PDMS interface. In all cases, interfacial adsorption of particles is unambiguously evident. Figure 3d is especially striking: The PI drop has a prominently nonspherical shape indicating that FeOOH particles jam the interface, and hence interfacial tension cannot force the drop to retract back to a spherical shape. This sample was a mixture of mostly spherical and some nonspherical drops, and such nonspherical drops have been noted previously in oil/water systems, even in an early paper on interfacial adsorption of particles a century ago [25].

Figure 4 shows images of PI/PIB blends with added particles. Once again, all five particle types adsorbed readily at the PI/PIB interface even though the two phases are much more miscible (i.e. much more chemically-similar) than the PI/PDMS system.



**Fig. 2** SEM images of particles used in this research: **a** PTFE, **b** DCDMS-coated hydrophobic silica, **c** titanium dioxide, **d** iron oxyhydroxide, **e** carbonyl iron. The *scale bar* below **a** represents 10 μm, whereas all other *scale bars* represent 2 μm

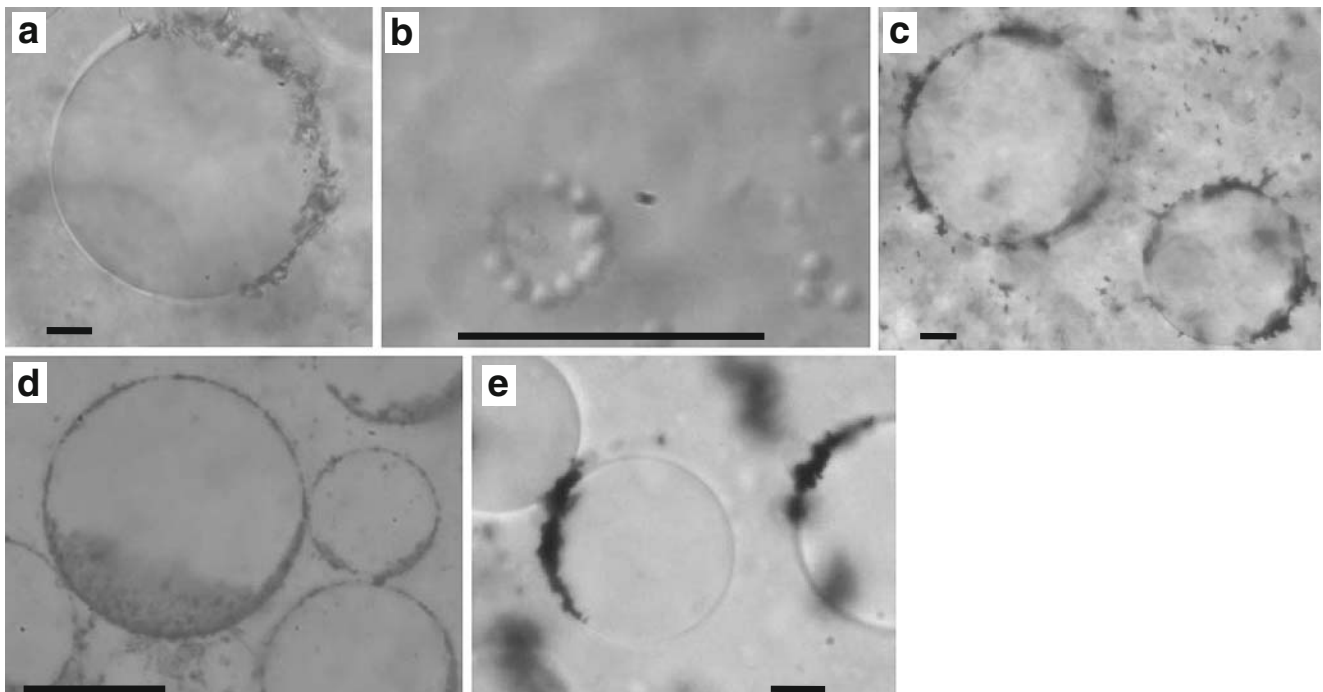


**Fig. 3** Optical microscopy images of various particles adsorbed at the PI/PDMS interface: **a** PTFE, **b** DCDMS-coated hydrophobic silica, **c** titanium dioxide, **d** iron oxyhydroxide, **e** carbonyl iron. In all cases,

the drop phase is PI. Note that in **d**, interfacial crowding of particles causes a strongly nonspherical drop shape. All *scale bars* are 20  $\mu\text{m}$

We note that the images of Fig. 3 have been chosen to show one or two large drops, whereas most drops in the blend were smaller. Furthermore, we reiterate that the low particle loading of 0.1% was chosen only to improve images; we

have also conducted some experiments with higher particle loadings, which show numerous examples of tightly covered drops. However, the image quality at higher particle loadings is usually far poorer. Finally, all the images presented here



**Fig. 4** Optical microscopy images of various particles adsorbed at the PI/PIB interface: **a** PTFE, **b** DCDMS-coated hydrophobic silica, **c** titanium dioxide, **d** iron oxyhydroxide, **e** carbonyl iron. In all cases, the drop phase is PI. All *scale bars* are 20  $\mu\text{m}$

correspond to drops that were inside the bulk of the sample (and not resting against or wetting glass slides).

Thus, to summarize the chief experimental result of this paper, a wide variety of particles were found to adsorb readily at PI/PDMS and PI/PIB interfaces. We find the PI/PIB case to be especially remarkable because particles adsorb at the interface in spite of the chemical similarity of the phases. The goal of the rest of this paper is to test whether a simple scheme for estimating interfacial and surface energies can predict the observed interfacial activity.

#### Young's equation

In the Introduction, we discussed partial wettability as the reason for interfacial activity of particles. Quantitatively, the condition for interfacial activity is that  $0^\circ < \theta_{12} < 180^\circ$ . The contact angle can be related to the interfacial energies as per Young's equation:

$$\cos \theta_{12} = \frac{\gamma_{2s} - \gamma_{1s}}{\gamma_{12}} \quad (1)$$

where  $\gamma_{1s}$ ,  $\gamma_{2s}$ , and  $\gamma_{12}$  are the interfacial energies of the phase 1/solid, phase 2/solid, and phase 1/phase 2 interfaces, respectively. Thus, the condition for interfacial activity becomes  $|\cos \theta_{12}| < 1$ , i.e.,  $|\gamma_{2s} - \gamma_{1s}| < \gamma_{12}$ . In contrast, if  $|\cos \theta_{12}| > 1$ , i.e.,  $|\gamma_{2s} - \gamma_{1s}| > \gamma_{12}$ , the particle will be located entirely in the phase, which fully wets the particles (phase 1 if  $\gamma_{1s} < \gamma_{2s}$  and vice versa otherwise).

In the Introduction, we made a qualitative argument that interfacial activity at polymer/polymer interfaces is less likely than at oil/water interfaces; we can now make this argument more quantitative. Immiscible polymers are much more chemically similar to each other than oil and water. As the chemical nature of the two phases approaches each other, the denominator  $\gamma_{12}$  is expected to approach zero faster than the numerator  $|\gamma_{2s} - \gamma_{1s}|$  [28–30]. Thus, with increasing similarity of the phases,  $|\cos \theta_{12}| < 1$  is not likely.

#### Theory: Work of adhesion, solid surface tension, and critical surface tension

While Eq. 1 is theoretically rigorous, it cannot immediately predict interfacial activity. Specifically, while the interfacial tension  $\gamma_{12}$  between the two polymers can be measured experimentally (see “Materials and methods”), the solid/liquid interfacial tensions  $\gamma_{1s}$  and  $\gamma_{2s}$  cannot be determined by a direct experiment. We will therefore use well-established approaches to estimate the *interfacial* tensions between two phases from the *surface* tensions of the two phases. For immiscible phases a and b, the interfacial tension  $\gamma_{ab}$  can be written as:

$$\gamma_{ab} = \gamma_a + \gamma_b - W_{ab}^{\text{adh}} \quad (2)$$

where  $\gamma_a$  and  $\gamma_b$  are the surface tensions (against air) of the two phases and  $W_{ab}^{\text{adh}}$  is the work of adhesion. A large body of literature has been devoted to correlating the work of adhesion with the surface energies of each of the two phases, their chemical nature, and polarity [31–33]. A commonly used equation for the work of adhesion is the Girifalco–Good equation [31, 32]:

$$W_{ab} = 2\phi \sqrt{\gamma_a \gamma_b} \quad (3)$$

where  $\phi$  is an empirical fitting parameter, often taken to be 1;  $\phi=1$  will be assumed in the remainder of this paper. Thus,

$$\gamma_{ab} = \gamma_a + \gamma_b - 2\sqrt{\gamma_a \gamma_b} \quad (4)$$

$\gamma_{1s}$  and  $\gamma_{2s}$  required in Eq. 1 can be obtained from Eq. 4, if the three surface tensions  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_s$  are known. Substituting  $\gamma_{1s}$  and  $\gamma_{2s}$  from Eq. 4 into Eq. 1 yields:

$$\cos \theta_{12} = \frac{\gamma_2 - \gamma_1 - 2\sqrt{\gamma_2 \gamma_s} + \sqrt{\gamma_1 \gamma_s}}{\gamma_{12}} \quad (5)$$

Solving this equation for  $\gamma_s$ :

$$\gamma_s = \left( \frac{\gamma_2 - \gamma_1 - \gamma_{12} \cos \theta_{12}}{2(\sqrt{\gamma_2} - \sqrt{\gamma_1})} \right)^2 \quad (6)$$

Interfacial activity of the particle requires that  $-1 < \cos \theta_{12} < 1$ , i.e.

$$\left( \frac{\gamma_2 - \gamma_1 - \gamma_{12}}{2(\sqrt{\gamma_2} - \sqrt{\gamma_1})} \right)^2 < \gamma_s < \left( \frac{\gamma_2 - \gamma_1 + \gamma_{12}}{2(\sqrt{\gamma_2} - \sqrt{\gamma_1})} \right)^2 \quad (7)$$

In summary, Eq. 7 is the Girifalco–Good theory's prediction for the range of  $\gamma_s$  values that permit interfacial activity of the particles at a phase 1/phase 2 interface. For the PI/PDMS case, we can substitute the surface tensions for  $\gamma_{PI}$  and  $\gamma_{PDMS}$  from Table 1 and  $\gamma_{PI/PDMS}=2.73$  mN/m noted in “Materials and methods” to obtain the condition for interfacial activity in the PI/PDMS system:

$$18.8 < \gamma_s (\text{mN/m}) < 36.4 \quad (8)$$

A similar calculation for the PI/PIB system yields:

$$29.1 < \gamma_s (\text{mN/m}) < 39.2 \quad (9)$$

It is of immediate interest to test whether the surface energies of the interfacially active particles of Figs. 3 and 4 do indeed lie within these ranges; if so, Eq. 7 would have a predictive value.

How can  $\gamma_s$  be measured experimentally? We use the Zisman's concept of critical surface tension [32, 34, 35].

Consider a liquid/air meniscus in contact with a solid surface. Applying Eq. 1 to this situation:

$$\cos \theta_L = \frac{\gamma_s - \gamma_{sL}}{\gamma_L} \quad (10)$$

where  $\theta_L$  is the contact angle of the liquid/air interface at the solid surface, and  $\gamma_L$  is the surface tension of the liquid. It has been observed that as the surface tension of the liquid decreases,  $\theta_L$  approaches  $0^\circ$  ( $\cos\theta_L$  approaches 1); that is, the liquid has an increasing tendency to wet the surface [32, 34, 35]. The critical surface tension of the solid,  $\gamma_{sc}$ , is defined as the highest surface tension of a liquid that can completely wet the surface; that is, liquids with  $\gamma_L < \gamma_{sc}$  fully wet the surface, whereas those with  $\gamma_L > \gamma_{sc}$  partially wet the surface. By definition, at the critical surface tension,  $\cos\theta_L=1$ , and hence from Eq. 10:

$$\gamma_{sc} = \gamma_s - \gamma_{sL} \quad (11)$$

Applying Eq. 4 to  $\gamma_{sL}$  in Eq. 11, it is easy to show that

$$\gamma_s = \gamma_{sc} \quad (12)$$

thus allowing the solid surface energy to be obtained experimentally. Fox and Zisman's procedure [34] for finding  $\gamma_{sc}$  was devised for solids that were available in the form of a flat solid substrate. In this case, the contact angle of various test fluids on the solid substrate is measured,  $\cos\theta_L$  is plotted as a function of  $\theta_L$  (the so-called Zisman plot), and then the data are extrapolated to  $\cos\theta_L=1$ . However, in the case of solid particles, this procedure cannot be applied since it is not possible to measure  $\theta_L$  values directly. Hence, Marmur et al. [36, 37] have developed an alternate method, called the float/sink test. In this test, the solid particles are scattered on the

surface of a test liquid. If the particles sink, they are regarded as being fully wetted by the fluid, whereas if they float, they are only partially wetted. This test is repeated using several test fluids spanning a range of surface tensions; it is then easy to determine  $\gamma_{sc}$  as the surface tension below which particles sink. This is the method we will follow in the next section to determine  $\gamma_{sc}$ .

Finally, we note that Eq. 3 is not the only means of correlating the work of adhesion to the surface tension. An alternate form is the harmonic equation:

$$W_{ab}^{adh} = \frac{4\gamma_a\gamma_b}{\gamma_a + \gamma_b} \quad (13)$$

which has been shown to work well for interfaces between materials of low polarity such as polymer/polymer interfaces [33, 38]. The corresponding prediction for the interfacial tension is:

$$\gamma_{ab} = \gamma_a + \gamma_b - \frac{4\gamma_a\gamma_b}{\gamma_a + \gamma_b} \quad (14)$$

Using Eq. 14 in Eq. 11 still predicts Eq. 12; that is, the idea that the solid surface energy is equal to its critical surface tension is broadly applicable, and is not dependent on the Girifalco–Good equation for the work of adhesion.

#### Determination of critical surface tension

Float/sink experiments were conducted using the liquids listed in Table 3. Initial experiments using the eight fluids marked with a superscript “1” yielded approximate critical surface tensions for most of the particles used. Additional experiments were then conducted with the fluids marked “2” to establish the critical surface tensions more narrowly.

**Table 3** Results of float/sink tests

Test liquid	Surface tension $\gamma_L$ (mN/m)	PTFE	DCDMS	TiO <sub>2</sub>	FeOOH	Fe
Hexane <sup>1</sup>	18.4	Sink	Sink	Sink	Sink	Sink
Octane <sup>1</sup>	21.6	Sink	Sink	Sink	Sink	Sink
Cyclohexane <sup>1</sup>	25.0	Sink	Sink	Sink	Sink	Sink
Toluene <sup>1</sup>	28.5	Float				
1,2 dichloroethane <sup>1</sup>	33.3	Float	Sink	Sink	Sink	Sink
Benzaldehyde <sup>2</sup>	38.8		Sink			
Nitrobenzene <sup>1</sup>	43.9	Float	Float>Sink	Sink	Sink	Sink>float
Ethylene glycol <sup>2</sup>	46.5			Sink		Sink
Diiodomethane <sup>1</sup>	50.8	Float	Float	Sink>Float	Sink	Sink
Glycerol <sup>2</sup>	63.3			Float	Sink	Float
Water <sup>1</sup>	72.3	Float	Float	Float	Float	Sink>float
Particle surface energy, $\gamma_s$ assigned		25–28.5	38.8–43.9	50.8–63.3	63.3–72.3	Uncertain; 46 for pure iron
Limits as per Eq. 7	PI/PDMS PI/PIB			18.8/36.4 29.1/39.2		

In each case, approximately 10 ml of the liquid was placed in a vial. A small quantity of particles were placed on a weighing pan and spread with a spatula to disrupt any large aggregates. They were then transferred to the vial by inverting the pan on the mouth of the vial and tapping the pan gently. If particles floated, they were observed for at least 10 min. The values of critical surface tension assigned to each particle type are listed in the Table 3. Two values are quoted for each particle type: an upper bound ( $\gamma_L$  at which particles float) and a lower bound ( $\gamma_L$  at which particles sink). Some comments about each particle type are in order.

The critical surface tension of PTFE particles was found to be between 25 and 28.5 mN/M. This is significantly higher than the value of  $\sim 20$  mN/m noted previously [32]; however, the manufacturing process for these particles involves thermal degradation, which may have raised their surface energy.

In the case of DCDMS-treated particles in nitrobenzene, most of the particles floated, and only a small fraction sank. Hence, the corresponding surface tension of 43.9 mN/m is regarded as the upper bound. In contrast, most of the TiO<sub>2</sub> particles sank in diiodomethane, and hence 50.8 mN/m is regarded as the lower bound for TiO<sub>2</sub>.

The float/sink test gave ambiguous results for the iron particles; these particles floated in glycerol but sank in water. This contradicts the idea implicit in the concept of critical surface tension that particles sink only when  $\gamma_L$  is reduced. The critical surface energy for pure iron [39] of 46 mN/m suggests that they should have floated in ethylene glycol. In summary, we are unable to obtain a reliable value for  $\gamma_s$  for the iron particles using the float/sink method.

Finally, we note that gravitational effects are expected to be weak in the float/sink experiment. The relevant dimensionless quantity,  $\frac{R^2 \Delta \rho g}{\gamma_L}$  (where  $R$  is particle size,  $\Delta \rho$  is the density difference between the particle and liquid, and  $g$  is gravity) is on the order of  $10^{-5}$  for iron particles and much smaller for all the others. This small value indicates that gravitational forces are much weaker than interfacial forces.

### Comparison with experiment

Equations 8 and 9 had noted the Girifalco–Good prediction of the range of surface energies within which particles are expected to be interfacially active in the PI/PDMS and PI/PIB system. These same ranges are listed in the last two rows of Table 3. It is immediately apparent that the PTFE particles are the only ones whose surface energy lies unambiguously within the bounds predicted by the Girifalco–Good theory. The surface energies of TiO<sub>2</sub> and FeOOH and possibly Fe are much larger than the upper bounds, and hence these particles are predicted not to be interfacially active. Experimentally, however, Figs. 3 and 4 show interfacial activity of all particle types. Thus, we

conclude that the Girifalco–Good theory with  $\phi=1$ , combined with the Zisman concept of critical surface tension, is inadequate to predict the interfacial activity of the particles.

Some comments about errors are in order. All the interfacial and surface tensions measured by the pendant drop method are expected to be highly accurate, to well within 5% [40]. The interfacial tension between PI and PIB measured by deformed drop retraction method may have a more significant error (estimated to be about 15% based on repeated measurements). However, the range of  $\gamma_s$  for interfacial activity (Eq. 7) is not highly sensitive to  $\gamma_{12}$ , and even a 20% error in measuring  $\gamma_{12}$  does not change the conclusion at the end of the previous paragraph.

We have also considered whether an alternative equation for the work of adhesion, the harmonic mean equation (Eq. 13) can predict the observed interfacial activity. Following the same procedure as used to derive Eq. 7, we derived the range of surface energies within which the harmonic mean equation predicts interfacial activity. These limits are  $22.6 < \gamma_s(\text{mN/m}) < 31.5$  for interfacial activity at the PI/PDMS interface and  $31.5 < \gamma_s(\text{mN/m}) < 36.5$  for PI/PIB interfaces. Once again, the experimentally determined surface energies of most of the particles lie above these ranges; that is, the harmonic mean equation cannot predict the interfacial activity.

Both the Girifalco–Good equation and the harmonic mean equation are simplistic approaches for obtaining the interfacial tension from the surface tensions; however, these equations have the advantage of involving quantities that are readily accessible experimentally. The more sophisticated Fowkes theory of the work of adhesion may be able to make more accurate predictions of interfacial activity; however, it is not clear how the information required to apply this theory may be obtained experimentally.

### Summary and conclusions

The primary conclusion of this article is that a wide variety of particle types adsorb at the interface between immiscible homopolymers, even when the homopolymers are chemically quite similar to each other (as gauged by the low interfacial tension between them). Research on “interfacial composites”—polymer blends in which solid particles are adsorbed at the interface—is a newly active area of research, and our results suggest that a wide variety of particles may be candidates for use in interfacial composites.

Secondarily, we have tested the value of the Girifalco–Good theory as a means to predict the interfacial activity. The solid surface energy required by the Girifalco–Good theory was assumed to be equal to the critical surface tension of the particles. The critical surface tension was then found by float/sink tests with several test fluids. Our

results suggest that the Girifalco–Good theory is not able to predict interfacial activity of particles. While we still believe that partial wettability of particles by both phases is responsible for their interfacial adsorption, some more elaborate theoretical approach is necessary to capture the relevant surface energies.

**Acknowledgment** We are grateful to Elementis, Dyneon, and Prof. Phule (University of Pittsburgh) for making the particles available for this research. We thank Rhodia Silicones, Soltex Chemicals, and Kuraray America for providing the PDMS, PIB, and PI homopolymers, respectively. We thank Prof. Barnard, University of Pittsburgh, for the use of his pendant drop apparatus for measuring surface tensions, and Hsin-Ling Cheng and Melissa Angeles, University of Pittsburgh, for obtaining SEM images. This research was supported by a CAREER grant CBET-0448845 from the National Science Foundation, USA.

## References

- Zaikin AE, Mindubaev RY, Arkhireev VP (1999) *Colloid J* 61:459
- Zaikin AE, Zharinova EA, Bikmullin RS (2007) *Polym Sci Ser A* 49:328
- Zaikin AE, Karimov RR, Arkhireev VP (2001) *Colloid J* 63:57
- Soares BG, Gubbels F, Jerome R, Teyssie P, Vanlathem E, Deltour R (1995) *Polym Bull* 35:223
- Soares BG, Gubbels F, Jerome R, Vanlathem E, Deltour R (1997) *Rubber Chem Technol* 70:60
- Gubbels F, Jerome R, Teyssie P, Vanlathem E, Deltour R, Calderone A, Parente V, Bredas JL (1994) *Macromolecules* 27:1972
- Asai S, Sakata K, Sumita M, Miyasaka K (1992) *Polym J (Tokyo, Japan)* 24:415
- Sumita M, Sakata K, Asai S, Miyasaka K, Nakagawa H (1991) *Polym Bull* 25:266
- Ray SS, Pouliot S, Bousmina M, Utracki LA (2004) *Polymer* 45:8403
- Hong JS, Namkung H, Ahn KH, Lee SJ, Kim C (2006) *Polymer* 47:3967
- Ray SS, Okamoto M (2003) *Prog Polym Sci* 28:1539
- Hong JS, Kim YK, Ahn KH, Lee SJ, Kim C (2007) *Rheol Acta* 46:469
- Si M, Araki T, Ade H, Kilcoyne ALD, Fisher R, Sokolov JC, Rafailovich MH (2006) *Macromolecules* 39:4793
- Gelfer MY, Song HH, Liu LZ, Hsiao BS, Chu B, Rafailovich M, Si MY, Zaitsev V (2003) *J Polym Sci Polym Phys* 41:44
- Fang Z, Harrats C, Moussaif N, Groeninckx G (2007) *J Appl Polym Sci* 106:3125
- Evgeni Z, Roza T, Narkis M, Arnon S (2006) *Polym Compos* 27:425
- Elias L, Fenouillot F, Majeste JC, Cassagnau P (2007) *Polymer* 48:6029
- Chung HJ, Taubert A, Deshmukh RD, Composto RJ (2004) *Europhys Lett* 68:219
- Huang YJ, Jiang SJ, Li GX, Chen DH (2005) *Acta Mater* 53:5117
- Thareja P, Velankar SS (2007) *Rheol Acta* 46:405
- Chung H, Ohno K, Fukuda T, Composto RJ (2005) *Nano Lett* 5:1878
- Ginzburg VV (2005) *Macromolecules* 38:2362
- Binks BP (2002) *Curr Opin Colloid Interface Sci* 7:21
- Tambe DE, Sharma MM (1993) *J Coll Int Sci* 157:244
- Pickering SU (1907) *J Chem Soc Abstracts* 91, 92:2001
- Luciani A, Champagne MF, Utracki LA (1997) *J Polym Sci Part B Polym Phys* 35:1393
- Xing PX, Bousmina M, Rodrigue D, Kamal MR (2000) *Macromolecules* 33:8020
- Cahn JW (1977) *J Chem Phys* 66:3667
- Bonn D, Ross D (2001) *Rep Prog Phys* 64:1085
- Budkowski A (1999) *Interfacial phenomena in thin films*. In: Budkowski A, Hamley IW, Koike TT (eds) *Phase coexistence and segregation, interfaces/crystallization/viscoelasticity*. Springer, Berlin, p 1
- Adamson AW, Gast AP (1997) *Physical chemistry of surfaces*, 6th edn. Wiley, New York
- Ross S, Morrison ID (1988) *Colloidal systems and interfaces*. Wiley, New York
- Wu S (1982) *Polymer interface and adhesion*. Marcel Dekker, New York
- Fox HW, Zisman WA (1950) *J Coll Sci* 5:514
- Zisman WA (1964) *Adv Chem Ser* 43:1
- Marmur A, Chen W, Zografi G (1986) *J Coll Int Sci* 113:114
- Brandriss S, Margel S (1993) *Langmuir* 9:1232
- Wu S (1974) *J Macromol Sci Rev Macromol Chem* 10:1
- Arkles B (1977) *Chemtech* 7:766
- Lin SY, Chen LJ, Xyu JW, Wang WJ (1995) *Langmuir* 11:4159