Unexpected Behavior between Polystyrene and Untreated and Silane-Treated Glass Beads in Filled Polymeric Composites

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ABSTRACT: Attempting to extend the database of work reported earlier, the practical adhesion between a glass filler, modified by various silane-coupling agents, and a polystyrene matrix is measured and compared with predictions based on a generalized thermodynamic criterion. Measurements leading to adhesion failure are carried out using the single-particle composite method, in which a rectangular polymer specimen containing a single untreated or silane-treated glass bead is subjected to increasing uniaxial tensile stress until interfacial failure, as observed using a microscope, occurs at one of the poles of the sphere. The results show no difference in adhesion strength between an untreated and a silane-treated glass bead, and the interfacial failure mechanism for the polystyrene composites is markedly different from that observed for previously studied systems. Crazes originate at the particle pole at low values of the applied stress and continue to form along the interface with continued strain. A dye test performed on filled composites confirms that the polystyrene is not wetting the untreated glass beads. More studies must be done to determine the origin of the anomalous failure and wetting behavior. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 521–526, 2003

Key words: polystyrene; adhesion; composites; interfaces

INTRODUCTION

Recently, the practical adhesion strength between glass beads, treated with a variety of silane coupling agents,[1,2] and four different thermoplastic amorphous and crystalline polymer matrices have been correlated with predictions based on a general thermodynamic compatibility criterion.[3–5] The criterion chosen was the (negative) molar Gibbs free energy of mixing, $-(\Delta G_{mix})_{0.5}$, for mixing equal molar amounts of the repeat units of the polymer matrix and the organofunctional group of the silane coupling agents. The group contribution method of UNIFAC[6,7] was used to evaluate $-(\Delta G_{mix})_{0.5}$. It can account for size differences and for all physical interactions between the polymer and the silane organofunctional group, viz. dispersion, polar, and acid-base interactions.

In the present work, the objective was to extend the database comparing the UNIFAC-computed mixing parameter with the measured practical adhesion strength using another common thermoplastic amorphous polymer, polystyrene (PS), with a variety of different silane organofunctional groups. The practical adhesion strength was measured using the single-particle composite method,[8] in which a rectangular polymer specimen containing a single silane-treated glass bead is subjected to increasing uniaxial tensile stress until adhesion failure, as observed using a microscope, occurs at one of the poles of the sphere. A successful correlation obtained with this polymer matrix would further substantiate the use of UNIFAC as an effective method for estimating adhesion performance between thermoplastic polymers and silane coupling agents. Instead, significant differences were observed in the failure behavior of the polystyrene composites compared to previous systems, regardless of whether or not the glass beads were silane treated. The objective of the present work thus turned to that of providing an explanation for this discrepancy with expectations. Optical comparisons of the prestressed and failed specimens were made of the polystyrene systems with model systems in which the matrix polymer was polyvinyl butyral to reveal differences in the mode of failure. Of critical importance, a dye test was implemented to assess the degree of wetting of the glass beads by polystyrene in comparison to that by polyvinyl butyral.

MATERIALS AND METHODS

Materials

Smooth spherical glass beads of approximately 650-μm diameter were obtained from MO-SCI Corp.

TABLE I
Names and Structures of Organofunctional Silanes Used in This Work

Organofunctional silane[a]	Structure of organofunctional group
n-Octyltriethoxysilane	—$(CH_2)_7CH_3$
3-Chloropropyltrimethoxysilane	—$(CH_2)_3Cl$
3-Iodopropyltrimethoxysilane	—$(CH_2)_3I$
Phenyltrimethoxysilane	—Ph
Vinyltrimethoxysilane	—$CH\!=\!CH_2$
3-Aminopropyltrimethoxysilane	—$(CH_2)_3NH_2$
N-(2-Aminoethyl)-3-aminopropyl- trimethoxysilane	—$(CH_2)_3NHCH_2NH_2$
Trimethoxysilylpropyldiethylenetriamine	—$(CH_2)_3NH(CH_2)NH(CH_2)_2NH_2$

[a] Commercial organofunctional silanes obtained from United Chemical Technologies, Inc., Bristol, PA.

(Rolla, MO). An "untreated" surface was prepared by cleaning as-received beads in a Nochromix solution, rinsing with deionized water, and then drying overnight in air at 525°C. Modified surfaces were prepared by treating cleaned glass spheres with eight different organofunctional silanes, summarized in Table I The silanes are henceforth referred to as octylsilane, chloropropylsilane, iodosilane, phenylsilane, vinylsilane, mono-aminosilane, di-aminosilane, and tri-aminosilane. A silane concentration of 0.5 vol % in pure water was used for all three mono-aminosilane treatments, while silane concentrations of 0.5 and 2.0 vol % in a 95% ethanol–5% water mixture were used for the phenyl and vinyl-functional silane treatments, respectively. Each silane solution was allowed 60 min for hydrolysis, and after the glass beads were added, 90 min were allowed for complete reaction of the silanes with the surface. The glass beads were removed from each solution in a Büchner funnel, washed with pure solvent, and dried for 1 h at 125°C. Vapor treatments were used for the octyl-, chloropropyl-, and iodofunctional silanes, and these were performed by enclosing clean glass beads in an atmosphere saturated with the silanes at approximately 65°C for 6 h. All treatments were assumed to provide complete surface coverage, and were chosen to induce corresponding differences in the adhesion strength.

Three different polystyrene (PS) matrices were used. Polystyrene (henceforth PS I) of 190,000 molecular weight (M_w) and 100°C glass transition temperature (T_g) was obtained from Scientific Polymer Products, Inc. (Ontario, NY), additive-free Styron 663 (henceforth PS II) of 305,000 M_w and 108.3°C softening point (the T_g was not provided) was obtained from Dow Chemical Co. (Midland, MI), and additive-free polystyrene (henceforth PS III) of molecular weight 800–5000 and a T_g range of 80–90°C was obtained from Polysciences, Inc. (Warrington, PA). Polyvinyl butyral (PVB) of 110,000 molecular weight and 51°C glass transition temperature was also obtained from Scientific Polymer Products, Inc. (Ontario, NY).

Composite manufacture

Initially, the as-received polystyrene pellets (PS I and PS II) and flakes (PS III) were finely ground in a Waring® (Torrington, CT) laboratory blender and stored separately. Single-particle composite specimens were then prepared as follows. Forty grams of finely ground PS I or PS II powder were placed into a mold, followed by a careful placement of 10 untreated or silane-treated beads, and then another 40 g of powder on top of the beads. This arrangement was then molded in a Tetrahedron Associates, Inc. (San Diego, CA) MTP-14 Compression Press into disks of 15-cm diameter and 4-mm thickness under the following conditions: the mold was heated and held at a constant temperature of 171.1°C for 15 min as the molding pressure was increased to 3.8 MPa. The mold was allowed to cool and then annealed for 10 min at approximately 10°C above the T_g or softening temperature for PS I or PS II, respectively, before the set-point temperature was reduced to ambient temperature and the mold allowed to cool. The slow cooling was intended to minimize residual stresses in the composite due to differences in thermal expansion coefficients between the matrix polymer and filler. It is suspected that additional stress relaxation takes place as the composite is cooled down below the T_g (or softening point) because the maximum cooling rates obtained with the press are lower than those observed in industrial injection molding conditions, and therefore, the volumetric coefficient of thermal expansion used for polystyrene (the same value was used for both PS I and PS II) was taken as its value below the T_g.

Filled composite specimens were prepared using PS II, PS III, and PVB. In each case, polymer, and cleaned, untreated glass beads were mixed in weight proportions necessary to obtain a composite of 25% filler volume fraction with the same diameter and thickness of the disks above. The molding conditions used for the PS II filled composites were the same as those noted above, whereas for the PS III-filled composites,

the mold was only heated to a constant temperature of 150°C due to the lower T_g of the polymer. The PVB-filled composites were prepared using the same conditions reported in ref. 3. The homogeneity of all the filled composites could be monitored by looking at the surface of the composites.

Single-particle composite mechanical testing

The single-particle composites, each of 9 mm width, 65 mm length, and 4 mm thickness, and each with a single, centered untreated or silane-treated glass bead, were uniaxially tensile tested using a Satec T-1000 mechanical tester (Satec Systems, Inc., Grove City, PA). A Wild Makroskop M420 microscope (Wild Heerbrugg, Ltd., Heerbrugg, Switzerland) with a 4915–2000 Series High Performance Monochrome CCD camera (Cohu, Inc., San Diego, CA) was positioned in a direction normal to the tensile strain of the composite to veiw the particle during testing. A 100-W illuminator was positioned behind the composite to illuminate the particle. Live digital video images captured by the CCD camera could be fed directly to a Macintosh computer containing a frame grabber board and NIH Image software to record the complete tensile test. The experimental setup for testing the single-particle composites is shown in ref. 3.

Each experiment began with the uniaxial tensile straining of the single-particle composite using a test rate of 0.991 mm/min. At the start of a test, a stopwatch was engaged and the live digital images monitored. The time-to-failure was recorded to allow the load at failure to be obtained from the force-time data collected by the mechanical tester and fed to a computer. The maximum local stress at failure was calculated from the load at failure using the cross-sectional area of the single-particle composite and elasticity theory.

Analysis

Because the interface is strained to failure, the macroscopic applied stress at failure, i.e., the load at failure divided by the cross sectional area, can be used to calculate the maximum local stress, s_{loc}, at the filler particle pole from the superimposed solutions of Goodier[9] and Beck et al.[10] as derived by Harding and Berg:[8]

$$S_{loc} = \left[\frac{(S_{rr})_{R,pole}}{(S_z)_\infty} \right] (S_z)_{\infty,fail} + (S_{rr})_{R,thermal}. \quad (1)$$

where s_{loc} is identified as the "interfacial strength" in Harding and Berg[8] as well as in ref. 3. The ratio in the first term is Goodier's analytical solution of the radial stress component at the particle pole, $(s_{rr})_{R,pole}$, corre-
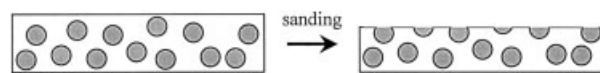
Figure 1 To perform the dye test, a filled composite specimen is sanded down to expose the interfaces between the glass beads and polymer. Note: the size of the particles are exaggerated.

sponding to the applied (constant) macroscopic tensile stress, $(s_z)_\infty$. This is the only stress component pertinent to the calculation because a specimen is subjected only to uniaxial tensile stress until adhesion failure occurs at the particle pole, $(s_z)_{\infty,fail}$. The second term, $(rr_{rr})_{R,thermal}$, derived by Beck et al., represents the contribution of residual thermal stresses (the radial component only) to the local stress. These stresses exist at the interface (prior to tensile testing) and are caused by differences in the coefficients of thermal expansion between the particle and the matrix. At least five samples were tested for each of the silane treatments.

Computations using UNIFAC

The (negative) Gibbs free energy of mixing, $(-\Delta G_{mix})_{0.5}$, was calculated at 100°C from the chemical structure of the polymer repeat unit and the silane organofunctional group using the UNIFAC method included on the process simulator Aspen (Aspen Technology, Inc., Cambridge, MA); 100°C was chosen as the calculation temperature because it corresponds to the glass transition temperature of the polymer, below which it was assumed that the structure of the interphase was "frozen in." The functional groups used for the PS repeat unit were 1 CH, 1 CH_2, 1 AC, and 5 ACH (where A refers to aromatic). The functional groups used for the organofunctional groups of each silane, listed in Table I, can be found in refs. 3–5. Complete free energy vs. composition plots were obtained for all systems to determine if there was any phase splitting (indicated by a concave downward portion in the plots) or asymmetry (indicated by a minimum in $-\Delta G_{mix}$ at a composition other than 0.5). Because no phase splitting was observed, and the degree of asymmetry was minimal for all cases, equal molar contributions of the polymer repeat unit and the silane organofunctional group were used to describe the interaction, $(-\Delta G_{mix})_{0.5}$.

Dye test

To examine the intimacy of contact between the glass surfaces and the polystyrene, and polyvinyl butyral (for comparison), filled composite specimens were sanded down, exposing the interfaces between the glass and polymer, as shown in Figure 1, so that dye could be put in contact with the interface. One side of
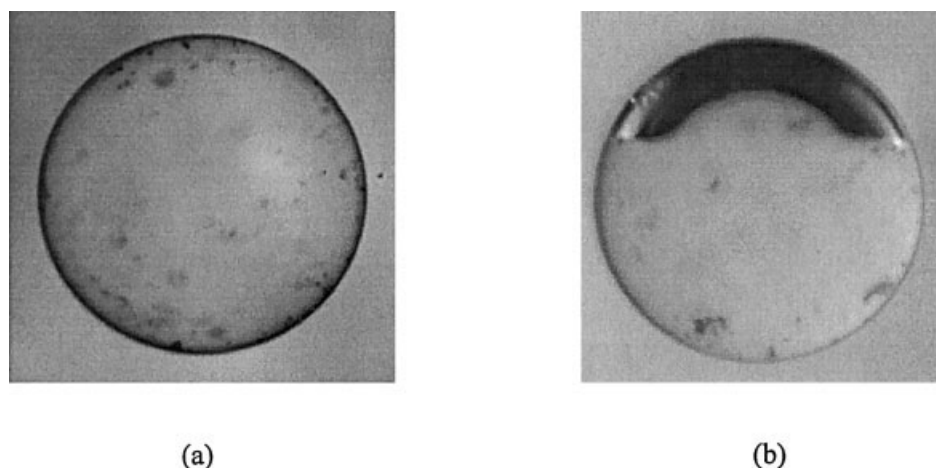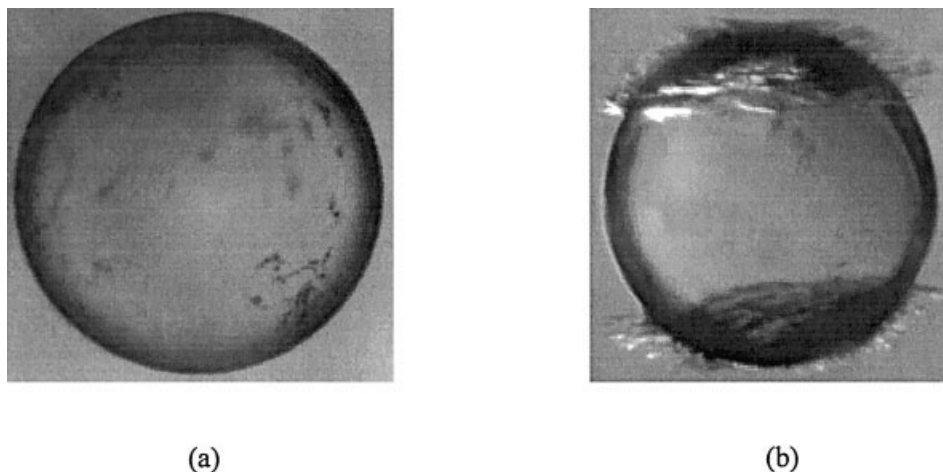
Figure 2 An untreated glass bead imbedded in poly(vinyl butyral), poly(methyl methacrylate), or poly(ethyl methacrylate) (a) before and (b) after mechanical testing. The shadowing around the edge of the particle in (a) is due purely to lighting.

each specimen was ground down (approximately 0.5 mm) and then polished by wet sanding sequentially with 120-, 320-, and 600-grit silicon carbide paper (LECO Corp., St. Joseph, MI) using a Buehler Ecomet III grinder/polisher (Lake Bluff, IL). Although such mechanical sanding might cause a weak interface to fail, optial micrographs revealed no particles to have been detached by the process. The polished specimens were dipped in a methanol bath and then placed in a vacuum for a few minutes to remove any water or air entrapped in the specimens. A cotton swab was then used to apply DYKEM red steel layout fluid (ITW, Olathe, KS) to the polished surface of the specimens. After the dye dried, the excess was removed by polishing first with a 0.3 μm and then a 0.05 μm alumina mixture (Buehler, Lake Bluff, IL). The specimens were then examined using a Zeiss Axiomat Inverted Reflected Light Microscope (Thornwood, NY) to detect any regions where dye had penetrated the interface, indicating noncontact between the phases. Only those particles that had a least half of their volume still imbedded in the polymer where examined.

RESULTS AND DISCUSSION

The premise of the present work is that differences in thermodynamic compatibility between a silane organofunctional group and a polymer material, as characterized by differences in the (negative) Gibbs free energy of mixing of equimolar amounts of the silane organofunctional group and the polymer repeat unit calculated by the UNIFAC method, should correlate with the adhesion strength measurements obtained from the single-particle composite tests as was shown for three previous systems.[3,4] The results, however, were not as expected. Figure 2(a) shows a cleaned, untreated glass bead imbedded in polyvinyl butyral before mechanical testing. Similar images were ob-

tained for poly(methyl methacrylate) and poly(ethyl methacrylate) matrix polymers. The shadowing around the edge of the particle is due purely to lighting. During mechanical testing, interfacial failure is instantaneous and results in a dewetting cap that scatters light as shown in Figure 2(b). This type of failure behavior was not observed for the single-particle composites formed with PS I. Figure 3(a) shows a cleaned, untreated glass bead imbedded in the PS I before mechanical testing. The shadowing around the edge of the particle is more prominent than in Figure 2(a). Some of it may be attributed to lighting differences, but it is unlikely to be the complete explanation. In addition, specimens subjected to mechanical testing did not show the same type of interfacial failure behavior. Instead of producing a clean "failure cap," debonding was craze-induced, i.e., a dewetting cap emerged only as crazes formed along the interface, even at low values of the applied stress, as shown in Figure 3(b). The crazes intiated at the particle pole and then continued along the interface of the particle. This suggests that the polystyrene may be forming a weak boundary layer in the matrix, which gives crazing under low stress, leading to a zippering-type of adhesion failure. The location of the initial crazes, i.e., at the particle pole, are indicative of good adhesion, whereas with poor adhesion, crazes usually form at about 60° from the pole.[11] Observations of the fracture surfaces with optical microscopy, however, confirmed that the polymer was failing at the interface, direct evidence of poor adhesion. It should be mentioned that the applied stress required for failure is only slightly greater than that necessary to overcome the thermal residual stresses, which are compressive (negative) in this case. An attempt was also made to increase the magnitude of the thermal residual stresses, because they would act as an adhesion promoter, by annealing the com-

Figure 3 An untreated glass bead imbedded in polystyrene (a) before and (b) after mechanical testing.

posites at a higher temperature and then cooling as rapidly as possible, but with no effect.

Nonetheless, it was suspected that the additional shadowing and different failure behavior may be the result of a weak boundary layer between the polystyrene and untreated glass, especially because the poor compatibility of polystyrene and untreated glass is well documented in the literature.[12–14] In all cases, however, including one of the aforementioned studies, the weak adhesion was overcome by treating the glass surface with organofunctional silanes that are compatible with polystyrene.[12,15,16] In accordance with the objective of this study, the untreated glass beads were then treated with a variety of silane coupling agents, and the adhesion strength was measured. Figure 4 shows the results of correlating
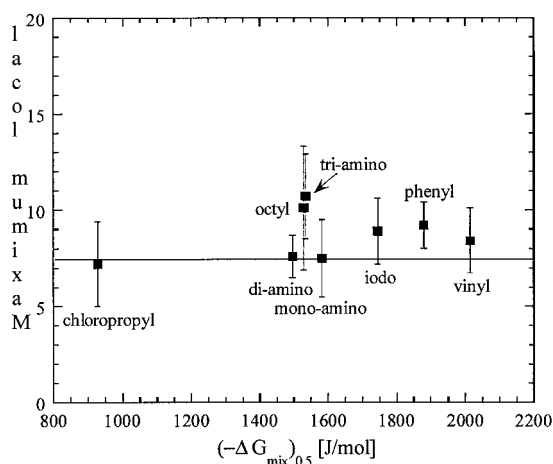

Figure 4 Relationship between the measured adhesion strength and the (negative) Gibbs free energy of mixing, $(-\Delta G_{mix})_{0.5}$, for all systems investigated against polystyrene (PS). Error bars correspond to the 95% mean confidence interval. The solid line crossing the plot corresponds to the measured maximum local stress for the PS I/untreated glass system.

$(-\Delta G_{mix})_{0.5}$ with the adhesion strength measurements, where the error bars correspond to the 95% mean confidence interval. Although there is a large variation in the computed $(-\Delta G_{mix})_{0.5}$ values, there is essentially no change observed in the maximum local stress values. The solid line crossing the plot corresponds to the measured maximum local stress for the PS I/untreated glass system. In all cases, the failure mechanism was the formation of crazes that initiated at the particle pole and then continued down along the particle interface with increasing applied stress, as shown in Figure 3(b). Only the PS I was studied initially, but after noticing that this particular polystyrene can contain up to 6% mineral oil (which could be leading to the weak boundary layer against both untreated and silane-treated glass beads), an additive-free polystyrene was obtained, i.e., PS II. However, single-particle composites formed between this polymer and untreated and phenyl- and vinyl-functional silane-treated particles (these two silanes show the largest $(-\Delta G_{mix})_{0.5}$ with polystyrene) showed the same type of shadowing before mechanical testing, the same failure behavior during testing, and provided the same values for the maximum local stress (values that are the same as those obtained with PS I).

A second possibility for the formation of a weak boundary layer was thought to be the presence of undissolved air at the particle–matrix boundary. Indeed, at a treatment pressure of 2.5 MPa, small air bubble were visible in the matrix. These bubble disappeared, however, when the treatment pressure was raised to 3.5 MPa and beyond, but the same shadowing around the particle surface was observed.

Therefore, rather than assuming a weak boundary layer was forming owing either to the presence of an additive or of undissolved air, it was suspected that the polystyrene was incompletely wetting the glass beads. To confirm this suspicion, a dye test was per-
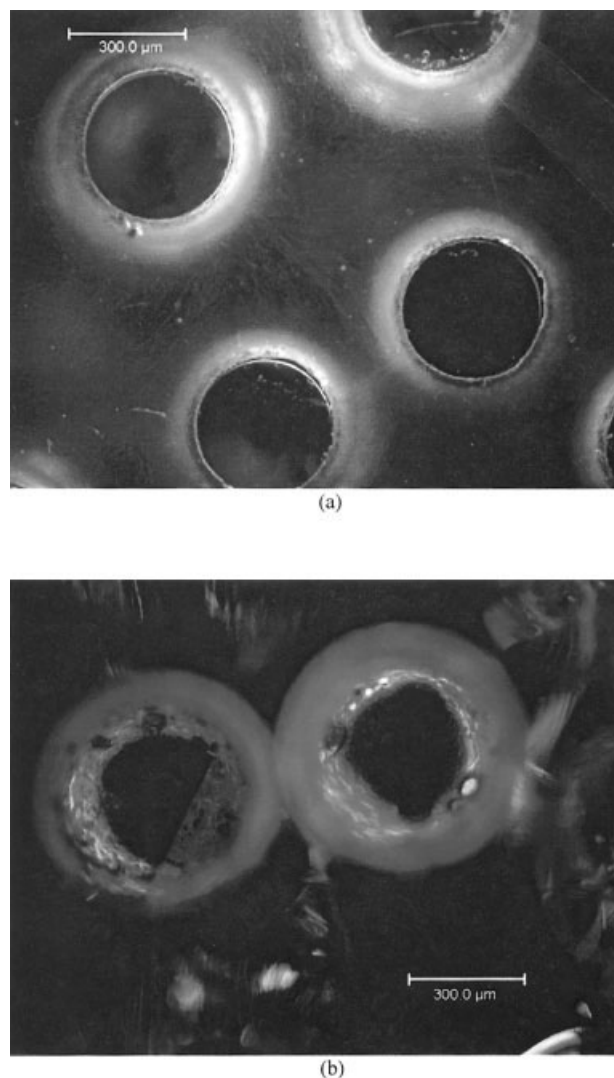
Figure 5   (a) Untreated glass beads in a PVB filled composite after the specimen was subjected to the dye test. There is no red dye visible anywhere in the image indicating perfect wetting contact. (b) Untreated glass beads in a PS II filled composite after the specimen was subjected to the dye test. The red dye nearly surrounds the particles, indicating that the polystyrene is not wetting the particles. Only small islands of contact are evident. This same behavior was observed for filled composites prepared with PS III. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

formed on some filled composite specimens. The results of the test are shown in Figure 5. Figure 5(a) shows untreated glass beads in a polyvinyl butyral matrix after it was subjected to the dye test. There is no red dye in the image, indicating perfect contact between the polymer and untreated glass. On the other hand, Figure 5(b) shows some untreated glass beads in a PS II matrix, and the red dye is completely surrounding the particles, except for a few small areas of contact. It is obvious that the polystyrene is not wetting the beads. What we then seek is a reason for the poor wetting.

It was thought that the poor wetting behavior may be a rheological effect, especially because both PS I and PS II are high molecular weight polystyrenes, and thus at the processing temperatures used, the polymer may be too viscous to wet the particles. Therefore, a polystyrene (PS III) was obtained that had a molecular weight of only 800–5000, and some filled composites were prepared. However, the same type of wetting behavior observed with PS II, shown in Figure 5(b), was also observed with these composites. More studies are required to determine the origin of this unexpected wetting behavior.

CONCLUSIONS

The results indicate that there is poor adhesion between polystyrene and glass, and that it cannot be improved with the use of silane coupling agents. Adhesion strength measurements show that for all systems studied, failure is craze-induced, which initiates at the particle pole and continues down the interface, even at low values of the applied stress. For a system featuring an incompressible filler and either nonwet interface or very poor adhesion, the composite yield stress is determined solely by the yield properties of the polymer matrix. A dye test performed on filled composite specimens detected poor wetting between the glass beads and polystyrene. A study using a lower molecular weight polystyrene established that rheology was not the cause of the incomplete wetting. More studies are required to sort out this wetting behavior.

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