Enhanced Interfacial Adhesion between PPO and Glass Beads in Composites by Surface Modification of Glass Beads via In Situ Polymerization and Copolymerization

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Glass beads were modified with vinyl triethoxyl silane (VTES) followed by in situ copolymerization with styrene (St) and by direct modification with St via in situ polymerization. It was seen that the presence of glass beads did not inhibit the polymerization of St, and FT-IR spectra confirmed that the polystyrene (PS) molecules were grafted on the surfaces of glass beads. When the modified glass beads were filled in a poly(phenylene oxide) (PPO) matrix, the PS segments on the surfaces of glass beads clearly improved compatibility and enhanced interfacial adhesion between the PPO matrix and glass beads, which was responsible for the slightly increased glass transition temperature of the PPO component. Surface modifications, especially by in situ copolymerization of VTES and St, increased significantly notch impact strengths and marginal stiffness and tensile strengths of PPO/glass bead composites.

Introduction

Rigid inorganic particles have been used increasingly to enhance stiffness and/or lower the costs of polymer products. However, particle-reinforced polymer composites (PRPCs) exhibit poor mechanical properties, particularly the impact strength because the rigid inorganic particles and polymer matrix are incompatible owing to their fundamentally different structures. How to improve the interface adhesion between inorganic particles and polymer matrix is a key problem in PRPCs.[1−4] Low molecular silane or titanate coupling agents were commonly used to modify the inorganic surfaces. Block or graft copolymers are also used to improve the adhesion of the components.[5−9] Plasma treatment of inorganic particles enables a structural change on their surfaces and increases the compatibility between particles and polymer matrix.[10−12] However, this method is not employed in the plastics industry on a large scale. Inorganic particles were also modified by irradiation grafting of the monomer and then compounded with the polymer matrix.[13−16] Encapsulation of inorganic particles by a polymer layer, so-called core−shell particles, was conducted by applying an emulsion polymerization process, where the in situ polymerization of monomer occurred primarily at the surface of unmodified particles due to the adsorption of the monomer on the surface, followed by polymerization in the adsorbed layer.[17−20]

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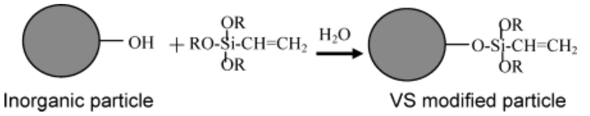
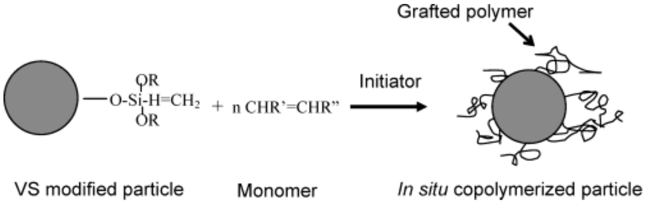
Recently, Xie et al.[21] modified talc surfaces by in situ polymerization of methyl methacrylate (MMA), and the PMMA layer covered on the particles reduced the surface energy of talc as well as promoted its dispersion in the PVC matrix. However, the polymer layer adsorbed on the talc surface was only via physical interaction; hence, the reinforcing and toughening efficiencies of talc on PVC were limited. Bourgeat-Lami et al.[22−27] functionalized the inorganic particles and then treated them by in situ emulsion polymerization. In this study, we proposed an in situ copolymerization technique to modify the surfaces of inorganic particles to improve the compatibility and interfacial adhesion between inorganic particles and polymer matrix. First, the inorganic particles were modified with vinyl siloxane (VS), such as vinyl trialkyloxyl silane. It is well-known that the silanol groups generated by hydrolysis of alkyloxyl groups react with silanol groups on the inorganic particles surface through dehydration and condensation to form Si−O bonds. Therefore, vinyl siloxane (VS) was grafted on the particle surfaces as illustrated below:



Second, these VS-modified particles are further modified with vinyl monomer by in situ copolymerization shown below:



It should be mentioned that with the choice of a monomer in the copolymerization step, its miscibility/compatibility with the polymer matrix should be considered. As such, the modified inorganic particles will show good interfacial interaction with the polymer matrix.

Poly(phenylene oxide) (PPO) is an engineering thermoplastic with high tensile strength, excellent heat resistance, and dimensional stability. But its brittleness and poor processability have limited its wider use. Wang et al.[28] toughened PPO with maleic anhydride grafted styrene−ethylene/butadiene−styrene triblock copolymer (SEBS-*g*-MA). Although the notched impact strength was greatly increased with 20 wt % SEBS-*g*-MA, the stiffness and tensile strength were also significantly reduced. In the present work, an attempt to reinforce and toughen PPO with rigid inorganic glass beads (GB) was carried out. To improve the compatibility with PPO, glass beads were modified with vinyl triethoxyl silane (VTES) followed by in situ copolymerization with styrene (St) as well as directly modified with St through in situ polymerization. Then, the modified GB particles were compounded with PPO. The effects of surface modifications of glass beads on interfacial adhesion and reinforcing and toughening effectiveness of PPO/GB composites were investigated.

Experimental Work

Materials. Poly(phenylene oxide) (PPO, N225X) was supplied by GE Company, United States. Two kinds of untreated glass bead particles (GB) with average diameters of about 12 and 30 μm were used and designated hereafter as SGB and LGB, respectively. Vinyl triethoxyl silane (VTES) was purified by distillation under reduced pressure before use. Chemically pure grade styrene was first washed with alkali solution and deionized water and then dried to remove the inhibitor.

Surface Modification of GB. Surface modification of GB with 25 wt % styrene was conducted by in situ polymerization at 70 °C in accordance with the conditions mentioned in ref 21.

In situ copolymerization of GB/VTES/St was performed as follows. GB particles were first treated by VTES aqueous solution for 2 h at ambient temperature. The amount of VTES was 1 wt % based on the GB amount. Vinyl groups were grafted on the GB surfaces by the coupling reaction of VTES with GB by Si−O bonds. Then, the VTES-modified GB and 25 wt % of styrene monomer (based on GB component) were copolymerized. VTES-modified GB, styrene monomer, deionized water, and sodium dodecyl sulfonate (emulsifier) were added to a 1000-mL glass reactor vessel. The mixture was heated and stirred constantly until the reaction temperature was reached. A preheated aqueous solution of ammonium persulfate (initiator) at the reaction temperature was now added to the reactor to initiate the polymerization reaction. After emulsion breakage and centrifugation, the final product was dried at 45 °C in a vacuum. The conversion was determined by

$$\text{conversion (\%)} = \frac{\text{precipitate (g)} - \text{GB (g)}}{\text{monomer used (g)}} \times 100\% \quad (1)$$

The polymerization product was extracted with toluene for 24 h in a Soxhlet apparatus to remove any ungrafted polymer and dried to constant weight in a vacuum. Percentage of grafting on GB surface was calculated by

$$\text{percentage of grafting (\%)} = \frac{\text{polymer grafted (g)}}{\text{GB used (g)}} \times 100\% \quad (2)$$

Fourier transform infrared spectroscopy (FT-IR) was applied to characterize the changes in chemical structure of GB after in situ copolymerization. Thin film specimens were pressed with KBr powder.

Preparation of PPO/GB Composites. PPO was compounded with modified or unmodified GB particles in a Barbender Plasticorder PL2000 twin-screw extruder at a barrel temperature of 225 °C and screw speed of 50 rpm. The screw diameter (*D*) was 19.05 mm, and the length−diameter ratio (*L*/*D*) was 20. The predried extrudates were injection-molded to tensile and impact specimens in a Cosmo injection-molding machine (Welltec Industrial Equipment Ltd., HK). The injection barrel temperature profile was set to 240, 260, and 260 °C.

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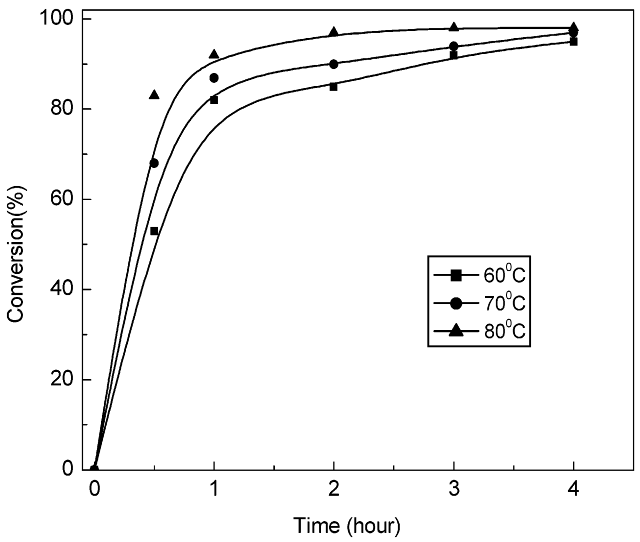

Figure 1. Reaction kinetics curves of in situ polymerization of styrene in the presence of LGB at three different temperatures.

Dynamic Mechanical Analysis and Mechanical Testing. Dynamic mechanical analysis (DMA) was conducted with a TA2980 Instrument dynamic mechanical analyzer at a fixed frequency of 10 Hz and oscillation amplitude of 0.15 mm. The temperature range studied was from 50 to 160 °C with a heating rate of 2 °C/min. Tensile tests were performed on an Instron 4206 machine at room temperature with a crosshead speed of 1 mm/min. Izod impact strength was measured by a Ceast pendulum impact tester. Blunt notches with a tip radius of 0.25 mm were inserted in the impact specimens with a Ceast notching device.

Morphology Observations. The freeze-fractured surfaces at liquid nitrogen temperature were observed using a S-300 scanning electron microscope. All surfaces were coated with a thin layer of gold prior to SEM examination.

Results and Discussion

Reaction Kinetics of In Situ Polymerization of St in the Presence of GB. Figure 1 shows the reaction kinetics of the in situ polymerization of St in the presence of LGB at three different temperatures. The weight ratio of LGB and St is 1:1. The results indicate that temperature significantly affects the polymerization rate of St. The higher the temperature, the earlier the auto-acceleration occurs and the shorter the time to achieve equilibrium conversion. For three temperatures used, the last conversions all approached 95%. It can be concluded that GB particles do not inhibit the polymerization of St.

FT-IR Spectra and Grafting Percentage of PS on the Surface of GB. Figure 2 shows FT-IR spectra of LGB modified with VTES/St by in situ copolymerization after extraction with toluene for 24 h. Peaks can be seen at 3075, 700, and 750 cm^{-1} for C−H stretching vibrations of the monosubstituted benzene ring, at 1490 and 1580 cm^{-1} for multiple-frequency absorptions related to the 700 and 750 cm^{-1} peaks of benzene ring, at 1600 cm^{-1} for vibration of the whole benzene ring, and at 2924 and 2851 cm^{-1} for the C−H stretching vibrations of CH_2 and CH groups. The strong peak at 1080 cm^{-1} is the characteristic absorption of SiO_4^{4-}. These results confirm that PS segments were grafted on the surface of GB particles during in situ copolymerization. The peaks of PS are weak due to the strong bond vibrations of GB particles. On the basis of Soxhlet extractions, the percentages of grafting of PS on LGB and SGB were 6.74 and 8.15%, respectively.

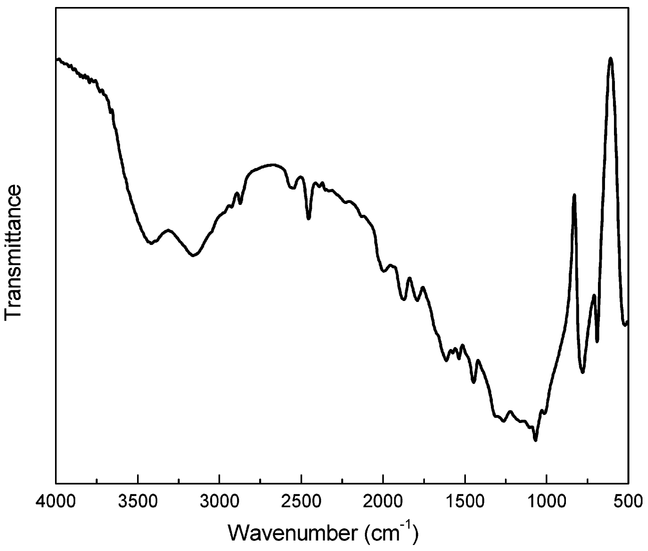

Figure 2. FT-IR spectra of LGB particles modified by in situ copolymerization of VTES/St after extraction with toluene solvent.

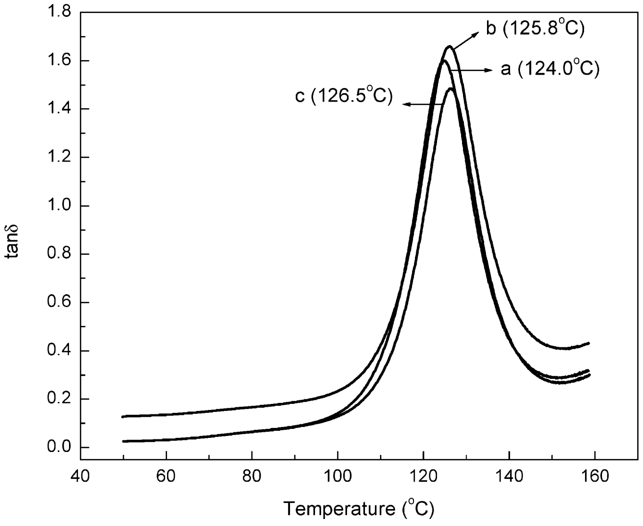

Figure 3. Plots of tan δ versus temperature for PPO/LGB composites. Tan δ values are given adjacent to the peak temperatures. (a) Unmodified LGB particles; (b) LGB particles modified by in situ polymerization of styrene; (c) LGB particles modified by in situ copolymerization of VTES/St.

Interfacial Interaction. Plots of dynamic loss (tan δ) as a function of temperature for the PPO/LGB composites are given in Figure 3. PPO/unmodified LGB composite shows a peak at 124.0 °C, which is associated with the glass transition of PPO. When LGB particles were only treated by in situ polymerization of styrene, the glass transition peak of PPO is increased to 125.8 °C. Further, when LGB particles were treated by in situ copolymerization of VTES/St, the PPO glass transition peak assumes a higher temperature of 126.5 °C. As PS is miscible with PPO thermodynamically,[29−31] the modi-

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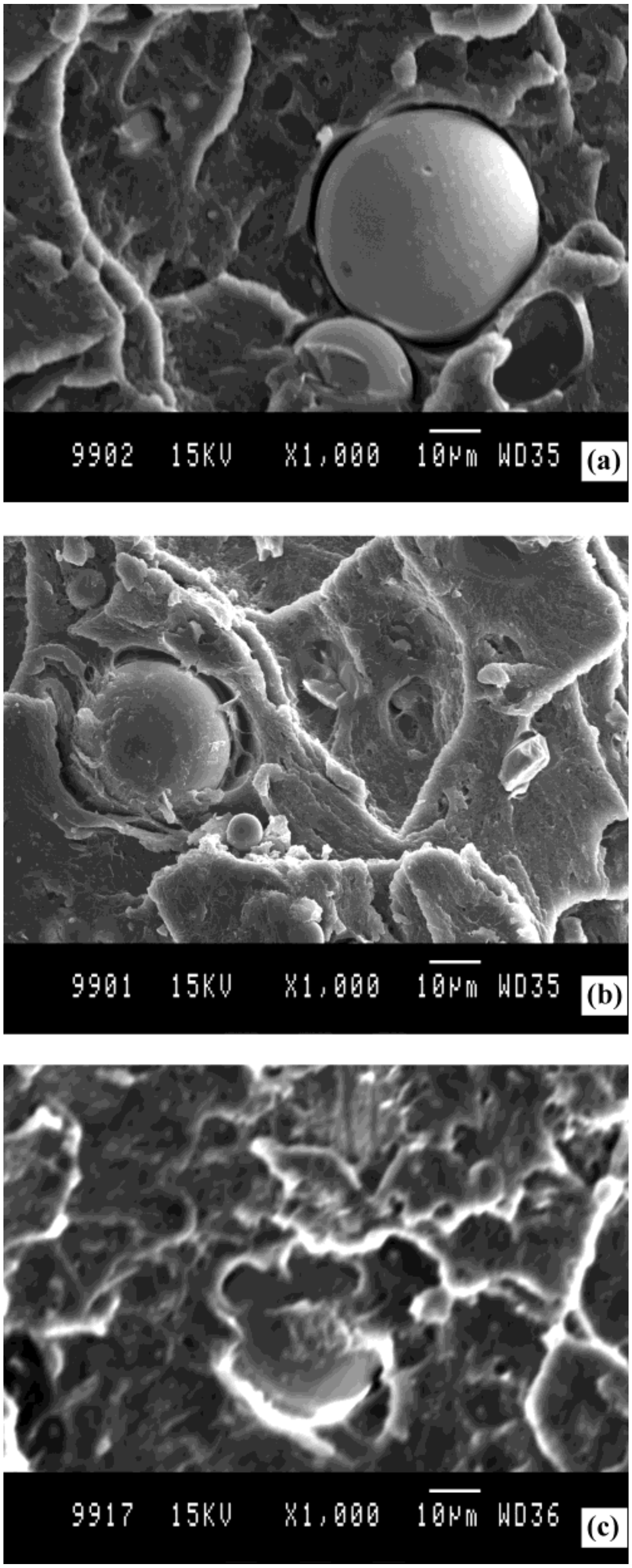

Figure 4. SEM photographs of freeze-fractured surface of PPO/LGB (85/15) composites. (a) Unmodified LGB particles; (b) LGB particles modified by in situ polymerization of styrene; (c) LGB particles modified by in situ copolymerization of VTES/St.

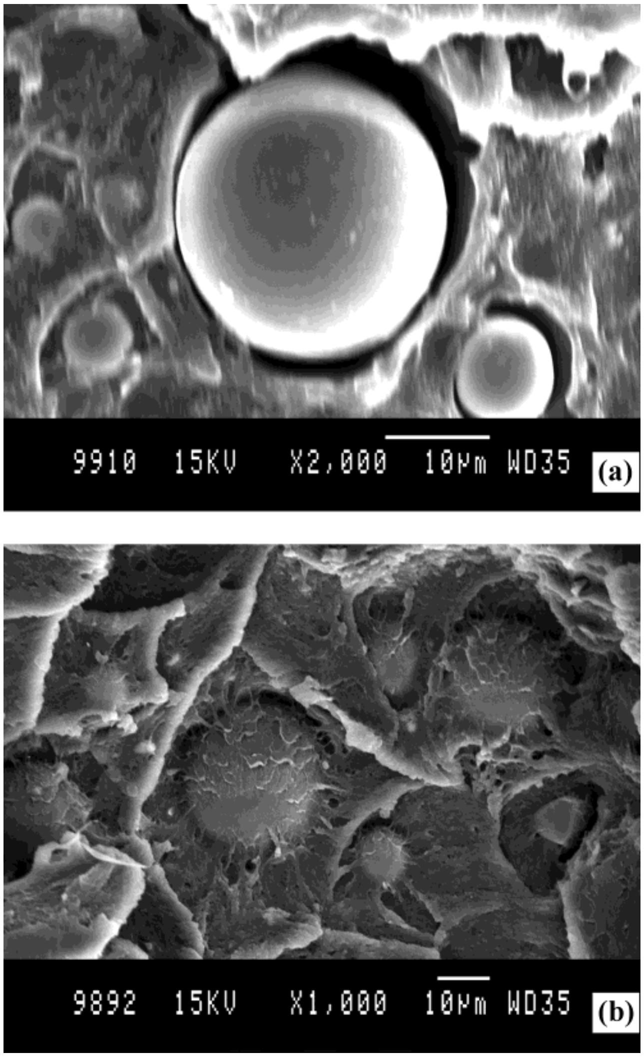

Figure 5. SEM micrographs of freeze-fractured surface of PPO/SGB (85/15) composites. (a) Unmodified SGB particles; (b) SGB particles modified by in situ copolymerization of VTES/St.

fied GB particles have excellent compatibility with PPO through physical entanglement of PS at the interface. The enhanced interfacial adhesion constrains motion of PPO molecular chain segments, thereby resulting in an increase of PPO glass transition temperature, albeit marginally by 2−3 °C.

To confirm the interfacial adhesion between PPO and GB particles, Figures 4 and 5 present SEM photographs of freeze-fractured surfaces of PPO/LGB and PPO/SGB composites. It is seen that the surface of the unmodified GB is very clean and a clear gap exists with PPO, indicating poor interfacial adhesion [Figures 4a and 5a]. However, after the GB particles are modified with styrene by in situ polymerization, the PS covered on the GB surface enhances the compatibility and improves the interfacial adhesion between GB and PPO matrix [Figure 4b]. Especially, when the GB particles are modified with VTES/St by in situ copolymerization, the interfacial adhesion is even better [Figures 4c and 5b]. Further, it appears that smaller glass beads give better interfacial adhesion [Figure 5b]. These results confirm that the enhanced interfacial adhesion is caused by the physical entanglement of PS segments grafted on a GB surface with PPO.

Mechanical Properties. To assess the influence of interfacial adhesion on mechanical properties, Table 1 lists Young's modulus, tensile strength, and notched impact strength of PPO composites filled with 15 wt %

Table 1. Mechanical Properties of PPO/LGB (85/15) Composites

samples	Young's modulus (GPa)	tensile strength (MPa)	impact strength (kJ/m^2)
PPO/unmodified LGB	2.10 ± 0.07	46.9 ± 0.3	5.9 ± 0.3
PPO/LGB modified with styrene	2.14 ± 0.04	48.4 ± 0.3	7.3 ± 0.2
PPO/LGB modified with VTES/St	2.20 ± 0.04	49.3 ± 0.2	8.4 ± 0.3

Table 2. Parameters Characterizing Interaction for Different PPO/GB Composites

samples	GB surface modification	$B_{\sigma y}$
PPO/LGB (85/15)	no modification	2.71
	in situ polymerization of styrene	3.03
	in situ copolymerization of VTES/St	3.22
PPO/SGB (85/15)	no modification	3.20
	in situ copolymerization of VTES/St	3.72

of unmodified and modified LGB particles. Evidently, surface modifications only improve Young's modulus and tensile strength of the PPO/LGB composites marginally by about 3−5%. It is known that the tensile strength of polymer composites is affected by the interfacial adhesion. Turcsanyi et al.[32] gave a quantitative relation between tensile strength and interfacial interaction as

$$\sigma_y = \sigma_{ym}\frac{1-\phi_f}{1+2.5\phi_f}\exp(B_{\sigma y}\phi_f) \tag{3}$$

where σ_y and σ_{ym} are yield stresses of the composite and polymer matrix, respectively. φ_f is the volume fraction of particles and $B_{\sigma y}$ is a parameter that characterizes the interfacial interaction. Generally, larger $B_{\sigma y}$ values correspond to stronger interfacial interaction. Later, Pukanszky[33] modified eq 3 by taking into account the change of specimen cross section during tensile tests and suggested that

$$\sigma_T = \sigma_{Tm}\lambda^n\frac{1-\phi_f}{1+2.5\phi_f}\exp(B_{\sigma y}\phi_f) \tag{4}$$

where σ_T is the true tensile strength of the composite, $\sigma_T = \lambda\sigma_y$. σ_{Tm} is the true tensile strength of the matrix. λ is relative elongation, $\lambda = L/L_0$, and it accounts for strain-hardening of the matrix polymer characterized by the exponent n.

Assuming the effect of surface modifications on GB density is negligible, 15 wt % of GB in PPO composites corresponds to a volume fraction φ_f of 0.097. Their elongations at break are all low so that $\lambda \approx 1$; thereby, $B_{\sigma y}$ for PPO/LGB composites can be calculated using eq 4 with given values of σ_T and σ_{Tm} (49.6 MPa) and are listed in Table 2. The $B_{\sigma y}$ parameter is 2.71 for the PPO/unmodified LGB composite. When LGB particles were modified by in situ polymerization of styrene, $B_{\sigma y}$ is increased to 3.03. For the PPO composite filled with GB modified by in situ copolymerization of VTES/St, $B_{\sigma y}$ is further increased to 3.22. Even though the tensile strength improvements by surface treatments of GB were relatively small, as shown in Table 1, $B_{\sigma y}$ appears to be a sensitive parameter that differentiates the effectiveness of the interface adhesion strength. Thus, $B_{\sigma y}$ in Table 2 confirms that PS segments grafting on the GB surface effectively improve the interfacial interaction of GB particles with PPO and that in situ copolymerization of VTES/St is more effective in enhancing interfacial adhesion than in situ polymerization of styrene.

Like the PPO/LGB system, surface modification by in situ copolymerization of VTES/St improves Young's modulus and tensile strength of the PPO/SGB composites by only a small amount of 4−5% (see Table 3). This slight improvement is also reflected by the calculated $B_{\sigma y}$ values using eq 4 and given in Table 2. It is noted that $B_{\sigma y}$ is 3.20 for PPO/unmodified SGB composite and 2.71 for PPO/unmodified LGB composite. This difference may be a manifestation that, for a given φ_f, smaller SGB particles have larger interfacial areas with the PPO matrix than larger LGB particles and hence better adhesion. When the SGB particles were modified by in situ copolymerization of VTES/St, $B_{\sigma y}$ increases to 3.72, implying enhanced interfacial interaction.

Interestingly, notch impact strength of PPO/GB composites was substantially improved by surface modification of rigid GB particles. The impact strength of PPO/(unmodified) LGB composite is 5.9 kJ/m^2. When glass beads were treated by in situ polymerization of styrene and in situ copolymerization of VTES/St, the impact strengths of these composites were 7.3 and 8.4 kJ/m^2, respectively, as shown in Table 1. The same trend of results is observed for the PPO/SGB composites: 6.7 kJ/m^2 for unmodified SGB against 12.1 kJ/m^2 for SGB treated by VTES/St (see Table 3). Obviously, PS segments on GB surfaces improve compatibility and interfacial adhesion between GB and PPO matrix. Improved compatibility enables uniform dispersion of GB particles and dissipation of impact energy. Thus, addition of rigid glass beads to PPO imparts excellent toughness with marginal improvements in both stiffness and strength. This is far more effective than adding rubber to PPO because the toughness improvement is at the expense of significant losses in both stiffness and tensile strength. Also, comparisons of the notch impact strength results in Tables 1 and 3 show that SGB particles provide better toughening efficiency than LGB particles.

Conclusions

The presence of GB particles did not inhibit the polymerization of styrene. FT-IR spectra showed that polystyrene molecules were grafted on GB surfaces during in situ copolymerization of VTES/St. Surface modifications of GB particles, especially with VTES/St, increased the glass transition temperature of the PPO component by a few degrees Celsius, which was attributed to the enhanced interfacial adhesion as con-

Table 3. Mechanical Properties of PPO/SGB (85/15) Composites

samples	Young's modulus (GPa)	tensile strength (MPa)	impact strength (kJ/m^2)
PPO/unmodified SGB	2.11 ± 0.10	49.2 ± 0.6	6.7 ± 0.1
PPO/SGB modified with VTES/St	2.22 ± 0.05	51.7 ± 0.3	12.1 ± 0.9

firmed by SEM observations. In addition, it was found that the notch impact strength was substantially increased, though improvements in tensile strength and Young's modulus were more modest. Finally, smaller GB particles showed better toughening efficiency than larger GB particles.

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