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Synthesis of composites of silicon rubber and polystyrene using supercritical CO_2 as a swelling agent

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The heterogeneous free-radical polymerization of styrene within supercritical carbon dioxide swollen silicon rubber film has been conducted to prepare the silicon rubber/polystyrene (SR/PS) polymer blends. The PS content in the blends can be controlled by adjusting the soaking time and the concentration of styrene in the supercritical fluid. Scanning electron microscopy (SEM) indicates that the PS phase is uniformly distributed in the blends and the phase size is very small (100 nm to 300 nm), although the two polymers are very different and incompatible. The mechanical properties of the blends and the average molecular weight of the PS polymerized in the matrix were also measured. The results indicate that the average molecular weight of the PS in the blend depends on the PS content or its phase size. The tensile strength of the blends is higher than that of original SR substrate, and there is a maximum in tensile strength *vs.* PS content. The Young's modulus of the blends increases monotonously with PS content in the blends.

Introduction

Polymer blends have received increasing attention in the field of polymer science and industry.[1] The growth in the use of polymer blends is mainly due to their ability to combine the properties of their phases in a unique product. The final properties of polymer blends are directly related to their microstructure and morphology. However, most polymer blends are incompatible, resulting in materials with coarse morphology, weak adhesion among phases, and poor mechanical properties. For many pairs of polymers it is very difficult to prepare their blends because their compatibility is very poor.

Recently, supercritical carbon dioxide (SC CO_2) has attracted much attention in polymer science and technology,[2–5] including polymer synthesis,[6–9] plasticization of polymers,[10–12] foaming of glassy polymers,[13–15] and production of particles.[16–18] SC CO_2 can dissolve many small organic molecules and swell most polymers.[2–4,18] Using SC CO_2 as a swelling agent for the polymer matrix and a solvent for the monomer and initiator, different polymer blends with small domain size have been prepared.[19–21] This method involves infusing or impregnating a CO_2-swollen polymeric host with a mixture of monomer and initiator, and polymerizing the monomer within the host polymer to form the blend. Hayes and McCarthy have prepared a polystyrene/polyethylene blend with very interesting phase morphology that resulted in enhanced mechanical performance when compared to conventional melt-blended systems.[20] A polystyrene/poly(vinyl chloride) blend fabricated using the same method also showed strengthened and toughened properties.[22] Using a similar method, methyl methylacrylate has been grafted onto isotactic polypropylene.[23]

It is well known that silicon rubber (SR) is a polymer with good elasticity, and polystyrene (PS) is a plastic with high modulus. Their blends may bring these properties together, and result in materials with good elasticity and strong modulus. However, SR and PS are incompatible because they are very different in many properties, and thus it is very difficult to blend them with fine domain size using conventional techniques. We did not find any work about the blending of these two polymers in the literature. In this work, we tried to fabricate SR/PS blends, using SC CO_2 as a swelling agent, by the polymerization of styrene within the SR matrix. We focus on: (1) whether or not blends with a fine phase size can be prepared; (2) the effect of monomer concentration in the fluid phase during the soaking process and soaking time on the composition of the blends; (3) how the mechanical properties and morphology change with the composition of the blends; and (4) the effect of the composition of the blends on the molecular weight of the PS polymerized within the SR matrix.

Experimental section

Materials

Silicon rubber films with a thickness of 1 mm were supplied by the Beijing Plastic Factory, which were cross-linked at 165 °C and had about 1.5 cross-linking points for every *ca.* 1000 Si–O bonds. Styrene, produced by the Tianjin Special Chemical Reagent Center (A. R. grade), was used after purification, by washing with 5% sodium hydrate solution twice, and distillation at reduced pressure. Benzoyl peroxide (BPO) was purchased from the Beijing Jinlong Chemical Reagent Company and was used after recrystallization in chloroform. Carbon dioxide with purity of 99.95% was provided by the Beijing Analytical Instrument Factory and was used as received.

Blend synthesis

About 2 g SR specimen was sealed in a stainless-steel vessel of 30 mL together with BPO/styrene solution (0.3 mol% BPO). The vessel was then placed in a constant-temperature water bath of 35.0 °C. CO_2 was charged into the vessel up to 12.0 MPa, and equilibrated for a suitable period of time. Then, the vessel was drained, charged with N_2, and heated to 120 °C to initiate the polymerization of styrene within the SR substrate for 6 h. The reactor was cooled and opened, and the blend sample was weighed. Nearly all the monomers were polymerized in this process, which was confirmed by the fact that the weight loss of SR/PS blends was negligible after extracting for 10 h by SC CO_2.

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Characterization

The compositions of the composites were examined gravimetrically. Determination of the molecular weight of the polystyrene in the blends involved separating the PS and SR, and gel permeation chromatography (GPC). The blend specimens were Soxhlet-extracted with hot tetrahydrofuran (THF) for 24 h. This solution was rotary evaporated to isolate the PS. The molecular weight of PS was then analyzed using a GPC (PL-GPC210) with THF as the mobile phase.

The morphology of the fractured specimen at the liquid nitrogen temperature was studied using SEM (s-530) in the normal secondary electron imaging (SEI) mode. The surface of the specimen was coated with gold to avoid charging under an electron beam.

The tensile properties of the SR/PS blends were determined on a universal tensile tester (Instron 1122) using a load of 5 kg. The elongation at break and tensile strength were measured at a crosshead speed of 100 mm min^{-1}. The average of five tests was reported. The dynamic mechanical properties of the SR/PS blends were measured by a dynamic mechanical analyzer (PerkinElmer DMA-7). The specimens were 3 mm wide and 10 mm long. The mode of force loading was three-point bending. The testing frequency, heating rate, and scanning temperature range were 1 Hz, 5 °C min^{-1}, and −150 °C to 150 °C, respectively.

Results and discussion

Synthesis of blends

To prepare SR/PS blends with different compositions, the effects of the soaking time and monomer concentration in the fluid phase on the mass uptake of SR substrates were studied, and the results were shown in Figs. 1 and 2. The fluid phase was homogenous under the soaking conditions, a fact known from experiments conducted using an optical cell reported previously.[21]

During the soaking process, the monomer distributes between the SR substrate and the CO_2-rich fluid phase. The monomer infuses into the SR substrate with the aid of SC CO_2 until equilibrium is reached. The equilibrium time should depend on the properties of the fluid phase and the solid substrate. Fig. 1 shows the dependence of PS content in the blends on the soaking time. The original concentration of styrene in the fluid is 0.43 mol L^{-1}. As expected, the PS content in the composites increases rapidly with soaking time initially, and reaches a constant value after about 5 h, indicating that equilibrium can be reached in 5 h. This means that the soaking time must be at least 5 h in order to obtain an SR/PS blend with an equilibrium composition. In this work, the matrix was soaked for at least 7 h to prepare blends with different equilibrium compositions.

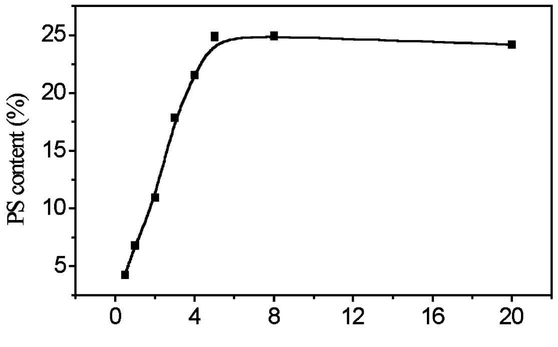


Fig. 1 Dependence of PS content on the soaking time at 308.15 K and 12.0 MPa (styrene concentration in the fluid is 0.43 mol L^{-1}).

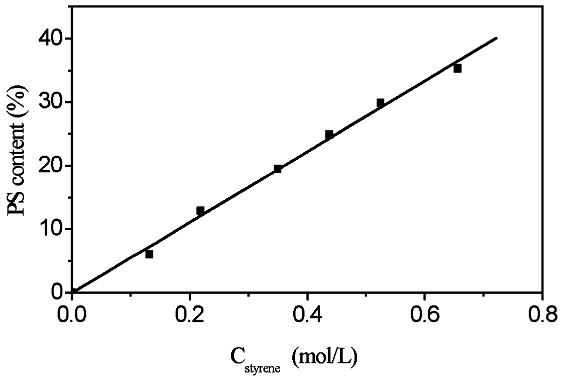


Fig. 2 Effect of styrene concentration in the fluid phase on the PS content in the blends (soaking conditions: at 308.15 K and 12.0 MPa).

Fig. 2 illustrates the effect of styrene concentration in the fluid on the PS content in the blends, which indicates that the amount of PS in the SR/PS blends increases linearly with monomer concentration in the concentration range studied. Therefore, SR/PS blends with different compositions can be obtained by changing the concentration of styrene in the fluid phase during the soaking process.

Morphology

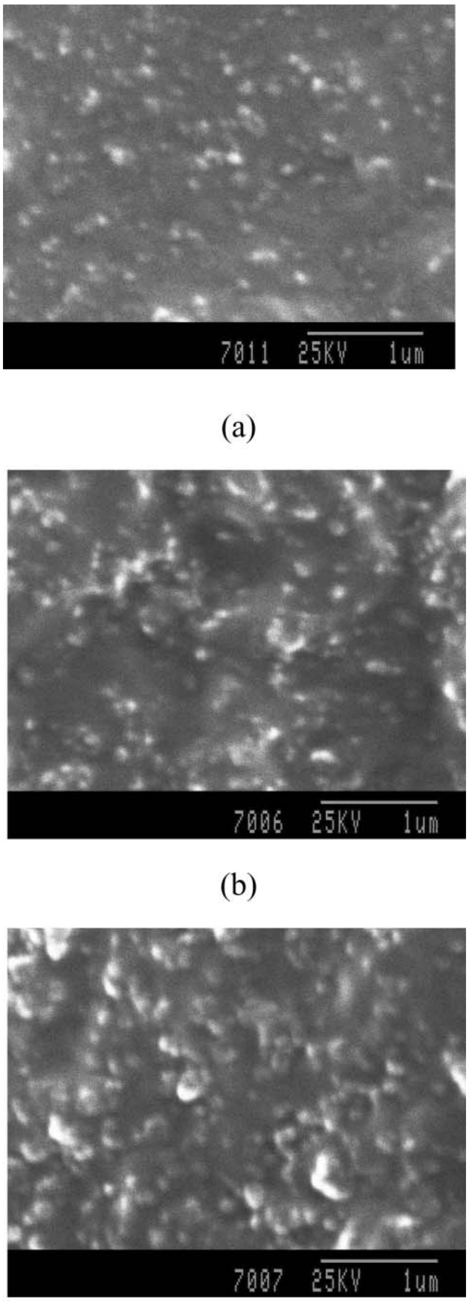
The morphology of a blend is closely related to its properties. Fig. 3 displays SEM micrographs of three samples with PS contents of (a) 6.4, (b) 26.7 and (c) 37.5 wt.%, respectively. It is clear that the domain diameter of the dispersed PS phase is small, generally in the range 100–300 nm, and the PS phase is uniformly dispersed. This can be attributed to the special properties of supercritical fluids (SCFs). SCFs have high diffusivity, low viscosity, and near zero surface tension.[18] Thus, with the aid of SC CO_2, the monomer and the initiator molecules can diffuse into any interchain space in the SR matrix at a faster rate, provided that the size of the space is larger than the molecules. Therefore, the monomer and the initiator are distributed more uniformly in the matrix before polymerization. As a result, the PS phase is dispersed uniformly. As expected, the domain number and the size of the PS phase increase with increasing PS content.

Mechanical properties

The mechanical properties of the virgin SR and the SR/PS blends with different PS contents were obtained from stress–strain curves, which are shown in Figs. 4–6. Fig. 4 illustrates the dependence of tensile strength on PS content in the SR/PS blends. It can be observed that for all of the SR/PS blends, the tensile strength is higher than that of the original SR substrate. In other words, the PS strengthens the SR in the composition range. The tensile strength of the SR/PS blend with a PS content of 6.4 wt.% is the largest. This is because the PS is more uniformly distributed with smaller size at this concentration, as can be seen from Fig. 3, which improves the adhesion between the SR and PS more effectively. With increasing content of PS, the domain size of the PS increases, resulting in a reduction in the tensile strength of the SR/PS composites.

Fig. 5 demonstrates the effect of PS content in the SR/PS blends on elongation at break. The elongation at break decreases with PS content. This is understandable because SR is a rubber with good elasticity, while PS is more brittle. Their blends possesses properties of these two polymers, *i.e.*, the elasticity of blends decreases with increasing PS content in the blend, which results in a reduction in elongation at break.

Fig. 6 shows a plot of Young's modulus *vs.* PS content in the SR/PS blends. Obviously, the addition of PS into the SR substrate enhanced the Young's modulus. Moreover, the



(a)

(b)

(c)

Fig. 3 SEM graphs of SR/PS blends with different PS contents: (a) 6.4 wt.%, (b) 26.7 wt.%, (c) 37.5 wt.%.

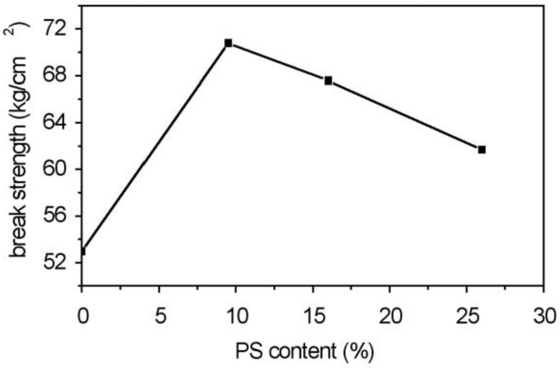


Fig. 4 Dependence of tensile strength on the PS content in the SR/PS blends.

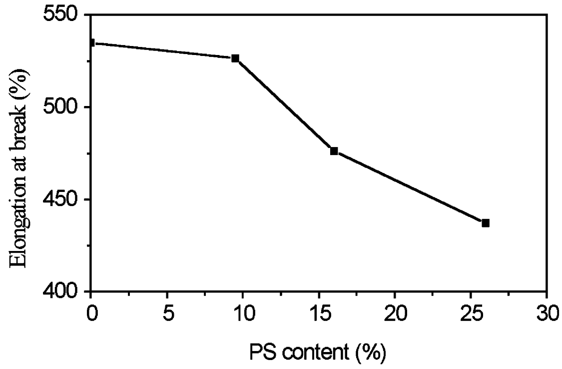


Fig. 5 Effect of PS content in the SR/PS blends on elongation at break.

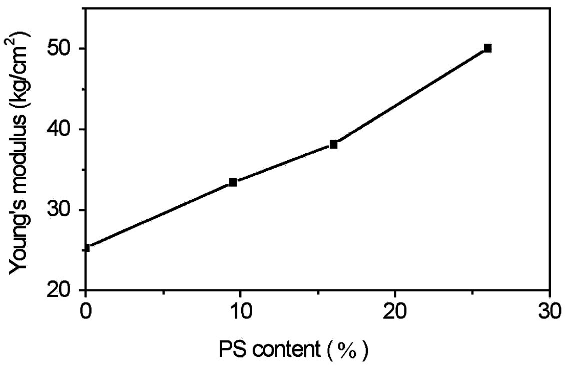


Fig. 6 Dependence of Young's modulus on PS content in the SR/PS blends.

Young's modulus increases with PS content. This is mainly because PS has a relatively high Young's modulus.

Dynamic mechanical analysis

The glass transition temperature T_g of the SR/PS blend is reflected by the tanδ maximum of the α-relaxation. Fig. 7 shows the tanδ curves of the three SR/PS samples with different PS contents. It can be seen that each curve has two main peaks. One is at about −50 °C, representing the T_g of SR. The other occurs at about 120 °C, which results from the PS phase. Fig. 7 also indicates that the T_g of PS decreases slightly with increasing PS content.

Fig. 8 shows the storage modulus of the SR/PS blends. Addition of PS increases the modulus at higher temperatures, and the effect increases with increasing PS content, which is caused by the high modulus of PS.

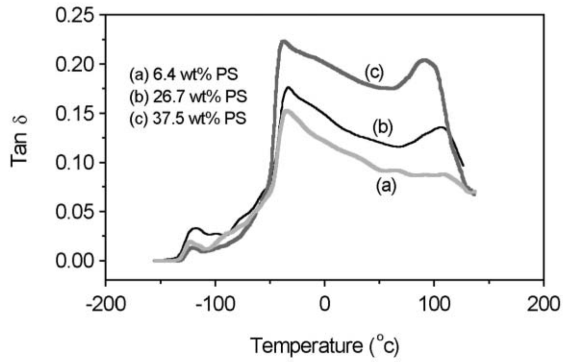


Fig. 7 Tanδ curves of the three SR/PS samples.

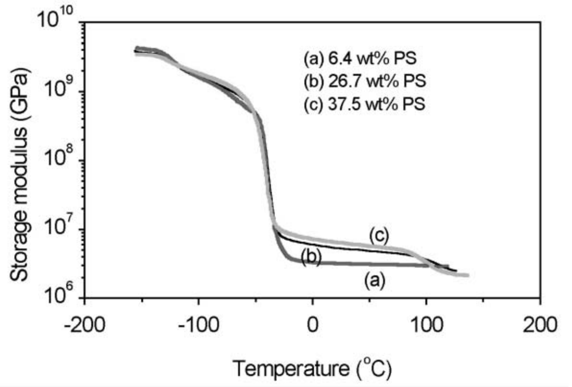


Fig. 8 The storage modulus of the three SR/PS blends.

Table 1 The molecular weight and polydispersity of PS polymerized in SR substrates

Sample	PS content (wt.%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	Polydispersity (M_w/M_n)
1	6.4	1.99	8.98	4.5
2	10.5	2.10	12.85	6.1
3	19.2	2.42	14.49	6.0
4	27.6	2.64	16.94	6.4
5	37.5	3.24	19.75	6.1

Molecular weight of PS in the blends

The molecular weight of the PS polymerized within the SR substrate was also studied. By extraction with refluxing THF, the extractable PS in the blends was separated from the SR, and the molecular weight of the extracted PS was determined by GPC. The results of five samples with different PS contents are listed in Table 1. It is clear that the molecular weight increases with the content of the PS in the blends. This is easy to understand because the size of the PS phase should increase with increasing PS content, as shown in Fig. 3. The polymers should be larger as the phase size is larger. Table 1 also shows that the polydispersity of PS in the blend with 6.4 wt.% PS is smaller than those of the blends with higher PS concentration. This can be explained in the following.

The PS in the blends is synthesized from styrene in the SR matrix. The sizes of the PS domains in the blends are different. However, the difference of the sizes in the blend with 6.4 wt.% PS is relatively small, as is shown in Fig. 3. In other words, the monomers have more similar environments during the polymerization process. As a result, the polydispersity of the polymer is relatively small. By contrast, the size distribution of the PS domains in the blends is wider as the PS content is larger, and thus the molecular weight distribution of the polymer is wider. This explanation is consistent with that for the maximum in the tensile strength *vs.* PS content curve in Fig. 4.

Conclusion

SR/PS blends can be prepared by thermal polymerization of styrene within a CO_2-swollen SR matrix. The PS dispersed homogeneously in the SR substrates and its domain sizes were generally less than 300 nm. The special microstructures and morphology of the SR/PS blends result in enhanced mechanical performances.

Acknowledgements

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