Poly(phenylene Oxide) Composites Containing Crosslinked Polystyrene Microspheres. I. Stress–Strain Properties

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Synopsis

The stress–strain properties of poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene composites containing crosslinked polystyrene microspheres have been measured at strain rates of 0.167, 1.67, and 16.7 min^{-1}. It is found that Young's modulus almost has no increase with the filler content. The elongation at break and tensile strength decrease with the volume fraction of the filler, but both tend to flatten out at the volume fraction $v_f > 0.25$ at the strain rate of 1.67 min^{-1}. The two ultimate tensile properties also have maximum values in the relationship with strain rate at the same filler concentration and strain rate conditions. Considering that elongation can be brought about by both matrix and filler, the well-known equation of elongation at break becomes

$$\epsilon_B = \epsilon_B^0\left(1 - cv_f^{1/3}\right)$$

with $c = 1 - (\alpha_f - 1)/\epsilon_B^0$, α_f is the relative elongation at break of the filler. SEM indicates a characteristic brittle fracture of the material. Optical microscopy shows that dewetting takes place at both poles of the microsphere in the drawing direction.

INTRODUCTION

The stress–strain properties of polymer composites containing inorganic particulates have been extensively studied. Theoretical predictions for modulus, elongation at break, tensile strength, and impact strength etc. have been published. Many of them are based on the assumption that a perfect adhesion between filler and matrix exists in the composites. In fact, this request is difficult to meet even with the composites with the surface-treated particulates, because the surface layer may still not be compatible with the matrix.

In this article polymer composites containing crosslinked polystyrene (PS) microspheres have been studied. A compatible polyblend poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/PS was used as the matrix. The crosslinked PS microspheres were used as the filler, which is compatible with the matrix too. A perfect adhesion should exist between them. With crosslinking the spheres have a stable shape in the composites; otherwise, they will dissolve in the matrix into one homogeneous phase. Since both filler and matrix are polymers, a variety of combinations with different T_g and modulus etc. can be chosen. Therefore, studying these polymer-filled polymer composites is expected to be interesting and useful in finding new materials.

EXPERIMENTAL

Materials

PPO and PS are commercial products; the weight average molecular weights are 14,500 (relative to PS in GPC) and 190,000, respectively. Crosslinked PS spheres were prepared from suspension polymerization. The spheres contain 8 wt % of divinylbenzene. Their particle size is 37–90 μm. Toluene and methanol are chemical pure.

Preparation of Sample

Equal weights of PPO and PS were dissolved in toluene to form a homogeneous solution. The concentration was about 10 wt % of polymers. Crosslinked PS microspheres were then added in proportion in the solution with stirring. The suspension was quickly precipitated into an excess of methanol. After being dried in a vacuum oven at 50°C for 2 weeks, the precipitation was pressed at 220°C into sheets of thickness of 0.5–1.0 mm.

Stress–Strain Experiments

The experiments were carried out on an Instron Model 1122 testing machine at 16°C. Sample was cut into standard dumbbell test pieces with 3×0.375 cm neck. Five to ten successful determinations were used to obtain the average value. Crosshead speeds were 5, 50, and 500 mm/min, respectively, which were converted into relative strain rates as $\dot{\epsilon} = 0.167$, 1.67, and 16.7 min^{-1}.

Observation of Microscopy

A Model DX-3A scanning electron microscope (Scientific Instrument Factory, Academia Sinica, China) was used to observe the fracture surfaces of the specimens. The surfaces were coated with thin layers of gold of 200 Å. An optical microscope was also used for the purpose.

RESULTS AND DISCUSSION

Stress–Strain Experiments

No yield point was observed on the stress–strain curves, which shows that the composites of PPO/PS blend and crosslinked PS microspheres are brittle materials. From the initial slope Young's moduli of the composites were calculated at the strain rates of 0.167 and 1.67 min^{-1}. The densities of PPO/PS blend and microspheres were taken as 1.07 and 1.05 g/cm^3, respectively, to calculate the volume fraction.[1] From Figure 1 it can be seen that the modulus tends to slightly and linearly increase with the volume fraction of the filler, the modulus of the crosslinked PS microspheres may be a little higher than the matrix. However, this increase is insignificant. We prefer to take the moduli of the composites as a constant in the following discussion. The modulus at the strain rate of 16.7 min^{-1} was not calculated because of poor accuracy.
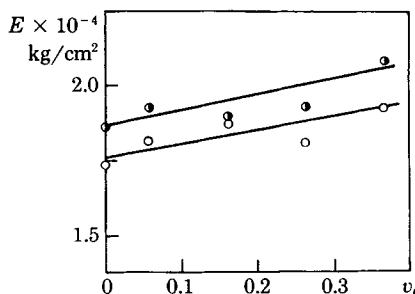
Fig. 1.   Young's modulus of the composite vs. volume fraction of the filler: Strain rate: (O) 0.167 min^{-1}; (◑) 1.67 min^{-1}.
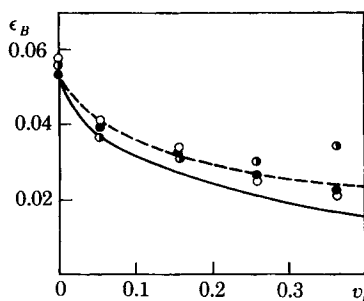

Fig. 2.   Elongation at break of the composite vs. volume fraction of the filler. Strain rate: (●) 16.7 min^{-1}; others as in Figure 1; (—) calculated from eq. (1); (- - -) from eq. (6).

Figure 2 shows the dependence of elongation at break on filler content. In the literature it is often seen an equation as[2]

$$\epsilon_B = \epsilon_B^0\left(1 - v_f^{1/3}\right) \tag{1}$$

which assumes that a good adhesion exists between matrix and filler and does not consider the deformation of the (inorganic) filler. Equation (1) gives lower values than our experimental results. If $\alpha = l/l_0$ is defined as the draw ratio of the composite, where l_0 and l are the lengths of the test piece before and after drawing, respectively, and if it is assumed that both matrix and filler contribute elongation, it should have

$$\alpha'\left(1 - v_f^{1/3}\right) + \alpha_f v_f^{1/3} = \alpha \tag{2}$$

i.e.,

$$\alpha - 1 = \left(\alpha' - 1\right)\left(1 - v_f^{1/3}\right) + v_f^{1/3}\left(\alpha_f - 1\right) \tag{3}$$

where α' and α_f are the relative elongations of matrix and filler, respectively. Therefore,

$$\epsilon_B = \epsilon_B^0\left(1 - v_f^{1/3}\right) + v_f^{1/3}\left(\alpha_f - 1\right) \tag{4}$$

ϵ_B becomes larger. Let

$$c = 1 - (\alpha_f - 1)/\epsilon_B^0 \tag{5}$$

Equation (4) can be rewritten as

$$\epsilon_B = \epsilon_B^0\left(1 - cv_f^{1/3}\right) \tag{6}$$

A curve according to eq. (6) was plotted in Figure 2, where c was taken as $c = 0.81$, i.e., $\alpha_f = 1.01$. This means that the relative elongation of the filler is not negligible. Equation (6) gives good agreement with the experimental results.

There are many equations for tensile strength of composites such as[3-7]

$$\sigma_B = \sigma_B^0(1 - bv_f) \tag{7}$$

$$\sigma_B = \sigma_B^0\left(1 - bv_f^{2/3}\right) \tag{8}$$

$$\sigma_B = \sigma_B^0 \exp(-rv_f) \tag{9}$$

where b and r are constants. Equation (7) exists no matter how the adhesion between matrix and filler phases is; Equation 8 assumes no adhesion, while eq. (9) needs adhesion between two phases. All these equations indicate a decreasing function of the filler content. However, it is also predicted for the case of good adhesion that the tensile strength of a filled polymer can be greater than that of an unfilled polymer.[2] In Figure 3 are shown the experimental data and the calculated curve of eq. (8) with $b = 1.21$.[5] It can be seen that eq. (8) cannot describe our data. Following Nielsen's assumption,[2] tensile strength is estimated for the rigid polymers, which have linear (Hookean) stress–strain curves, as

$$\sigma_B = E\epsilon_B = E\epsilon_B^0\left(1 - cv_f^{1/3}\right) = \sigma_B^0\left(1 - cv_f^{1/3}\right) \tag{10}$$
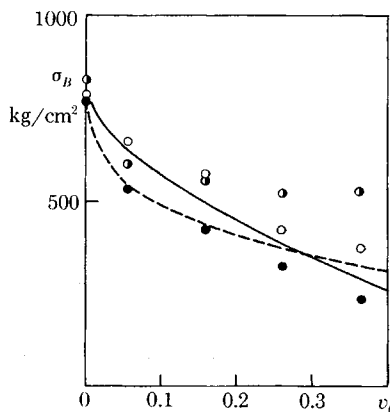

Fig. 3. Tensile strength of the composite vs. volume fraction of the filler: (—) calculated from eq. 8; (- - -) from eq. (10); others as in Figure 2.
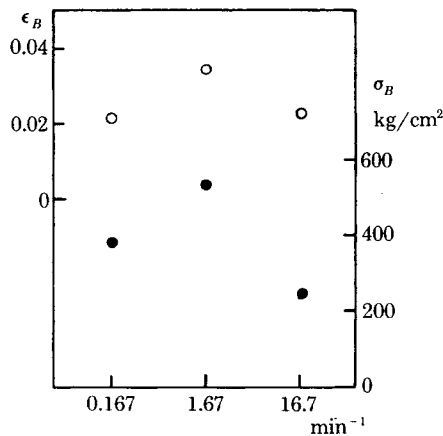
Fig. 4.   Ultimate tensile properties of the composite at $v_f = 0.35$ vs. strain rate: (○) elongation at break; (●) tensile strength.

For the studied composites, in which the matrix and the filler are both plastics, with good adhesion and similar modulus, a $\sigma_B \sim v_f^{1/3}$ relationship results. As shown in Figure 3, eq. (10) gives good agreement with the experimental results at the high strain rate, when the material obeys Hookean elasticity.

It is interesting to see that decreasing ϵ_B and σ_B flatten out in the properties–filler concentration diagrams at the strain rate of 1.67 min^{-1}, when the volume fraction of PS beads, v_f, is greater than 0.25. The phenomenon was not found for the other two strain rates, which was one decade lower or higher than the indicated strain rate. It is also seen that the above two ultimate tensile properties have maximum values at the same v_f and $\dot{\epsilon}$ conditions in the properties–strain rate diagram, as shown in Figure 4. As mentioned above, it was predicted for the composites with good adhesion that the decreasing tensile strength could flatten out or even go upwards after passing a minimum value with filler concentration increased.[2] But this cannot explain our observations because: (1) Young's modulus of the studied composites is nearly a constant; it cannot be described by Kerner's equation etc. as used in the prediction; (2) only at one particular strain rate the phenomenon is observed. These may be attributable to some relaxation mechanism of the crosslinked PS microspheres. Further study is needed to ascertain and understand the phenomenon.

Microscopic Observation

Scanning electron micrographs were taken for opposite surfaces of a fractured specimen as shown in Figure 5. Most of the microspheres are broken, which indicates a perfect adhesion between the matrix and filler phases. A few crosslinked PS beads are not fractured; they remain in one side. Around spheres there are whitened ridges which indicate that the places once concentrated great stresses. The whole surfaces are rather smooth, this is a character of brittle fracture.

100 μ
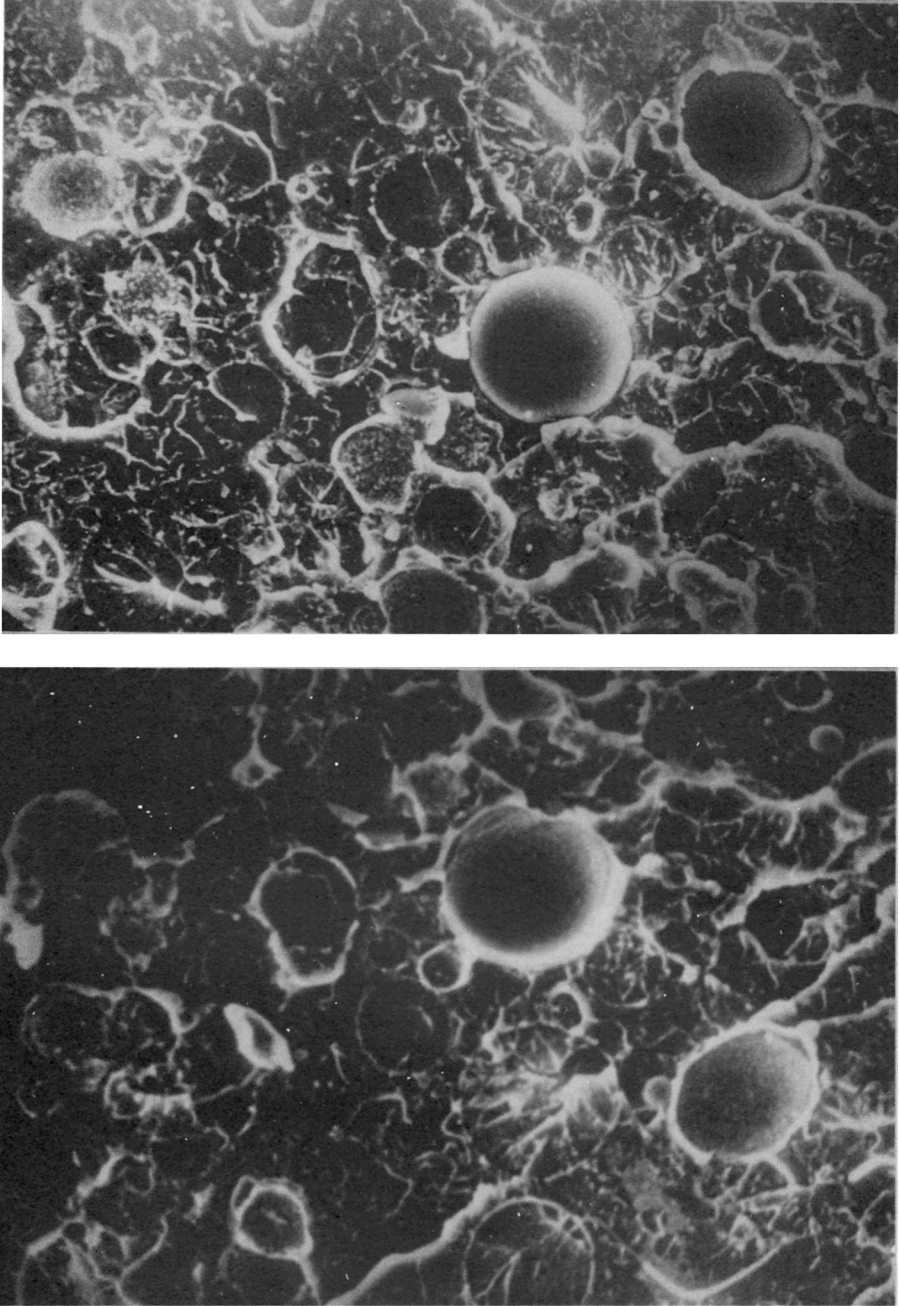
Fig. 5.   Scanning electron micrographs of opposite surfaces of a fractured specimen.
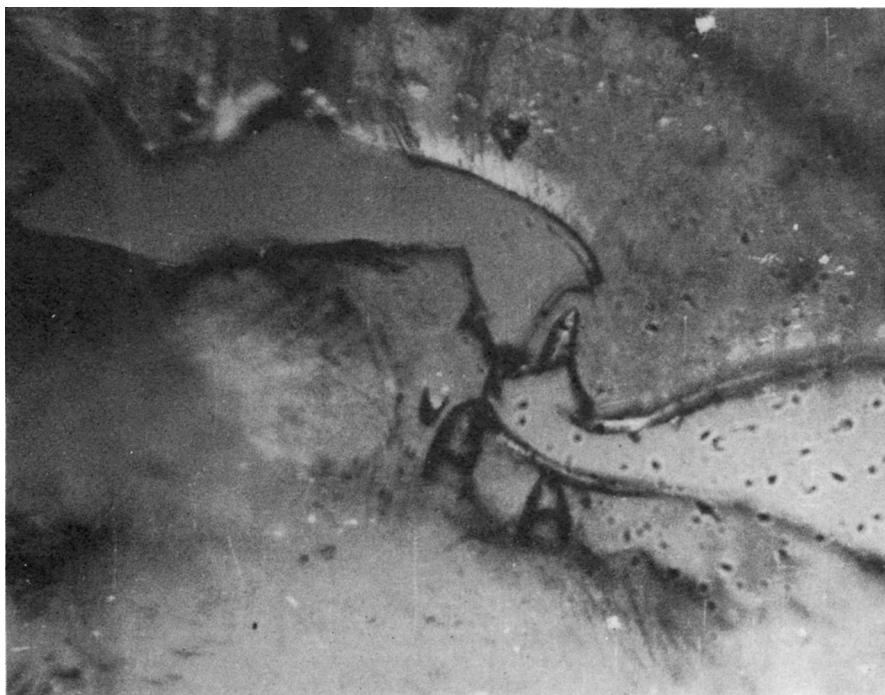
100 μ

Fig. 6.   Optical micrograph of a strip of fractured film of the composite.

Figure 6 is an optical micrograph of a fractured film at the crosshead speed of 3 mm/min. The two halves remaining cannot fit completely. Some parts shrink back after fracture. Dewetting takes place at the two poles of the sphere in the drawing direction. This is in agreement with the observations in the literature concerning perfect adhesion between two phases in composite.[8]

CONCLUSIONS

The tensile properties of PPO/PS composites containing crosslinked PS microspheres have been measured at the strain rates of 0.167, 1.67, and 16.7 min^{-1}. The crosslinked PS microspheres have the same effects as the inorganic particulates: the tensile strength and elongation at break are all decreasing functions of the filler content. The two ultimate tensile properties tend to flatten out with the volume fraction v_f increases and have maximum values in the relationship with strain rate at $v_f > 0.25$ at the strain rate of 1.67 min^{-1}. Considering the deformation of the filler, the well-known equation of elongation at break becomes

$$\epsilon_B = \epsilon_B^0\left(1 - cv_f^{1/3}\right)$$

with $c = 1 - (\alpha_f - 1)/\epsilon_B^0$; α_f is the relative elongation at break of the filler.

SEM shows a brittle fracture of the composite. Most of the spheres are broken at the fracture surfaces. Optical micrograph shows that dewetting takes place at both poles of the spheres.

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