Study on a Water-Swellable Rubber Compatibilized by Amphiphilic Block Polymer Based on Poly(ethylene oxide) and Poly(butyl acrylate)

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ABSTRACT: A water-swellable rubber (WSR), compatibilized by the amphiphilic block copolymer, has been prepared by blending a natural rubber (NR) matrix with crosslinked sodium polyacrylate (CSP), poly(ethylene oxide)-b-poly(butyl acrylate) (PEO-b-PBA), poly(ethylene glycol) (PEG), reinforced filler, and vulcanizing agents. The preparation process was described. The microphase structure of WSR was characterized by a scanning electron microscopy (SEM) photograph. The dependence of the degree of the water-absorbing and the water-swelling, the water-absorbing and water-swelling rates on CSP, PEG, and PEO-b-PBA contents were investigated. The compatibilizing mechanism of PEO-b-PBA on WSR was studied. And the optimum composition range was identified: CSP (30–60 phr), PEG (10–20 phr) PEO-b-PBA (PEO/PBA = 0.36, 5 phr). © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3120–3125, 2002

Key words: rubber; resin; compatibilization; amphiphiles; block copolymers

INTRODUCTION

Water-swellable rubber (WSR) is a new kind of functional elastomer with elastic sealing and water-swelling properties. It can be used widely as caulking, sealing of gaps, and waterproof materials. In recent years, many articles about water-swellable rubber have been reported, but they are mainly confined to patent literature,[1–3] and data on the relation among the component, structure, and property of the rubber are scarce. WSR is normally prepared through multicomponent mechanical blending of a rubber matrix, a super water-absorbent resin, and other hydrophilic ingredients. But due to the hydrophilic polar nature of water- absorbent resin and the hydrophobic nonpolar nature of the rubber matrix, the aggregation and poor dispersion inside the rubber often lead to the instability and degradation of water-swelling ability, mechanical properties, long-term water retention, and so on. And the practical application has been strongly limited. So how to improve the miscibility of water-absorbent resin and rubber comes to be the problem that must be solved in its application.

In general, utilizing a copolymer as compatibilizer to improve a blend's miscibility[4–7] is an effective and usually used method. Directed against the hydrophilicity of absorbent resin and the hydrophobicity of rubber, if an amphiphilic copolymer is used in the blend as compatibilizer, the miscibility of hydrophilic dispersion and hydrophobic continuous phase is expected to be improved greatly, and the loss of super water-absorbent resin from the rubber matrix to be reduced. In such a way, the water-swellable ability and mechanical property may be enhanced. For example, Zhang Zhihao et al.[8] studied the compatibilization of amphiphilic poly(vinyl alcohol)-g-poly(butyl acrylate) (PVA-g-PBA) on blend of chlorohydrin rubber and crosslinked polyacrylate and the results showed that the water-swelling ability could be improved. So far, the study on the compatibilization of amphiphilic block copolymer in a water-swellable rubber has seldom been reported.

We know that poly(ethylene glycol) (PEG) has excellent hydrophilicity. At the same time, poly(butyl acrylate) (PBA), possessing longer soft-side chains, is a kind of hydrophobic polymer and has quite good elasticity. So the combination of hydrophilic PEG and hydrophobic PBA may be served as compatibilizer in the blend of water-absorbent resin and rubber.

In our preceding work, we have synthesized a kind of amphiphilic poly(ethylene oxide)-b-poly(butyl acrylate) (PEO-b-PBA) by redox radical polymerization. In this study, natural rubber (NR) matrix with crosslinked sodium polyacrylate (CSP), with excellent elasticity was selected as matrix. Crosslinked sodium polyacrylate (CSP), possessing high degree of absorption and water absorbing rate as well as stability, was selected as absorbent resin, precipitated silica as reinforced filler, and PEG as assistant absorbent filler. At the same time, PEO-b-PBA was selected as compatibilizer to improve the miscibility of NR and CSP. By the multicomponent blending method, a kind of water-swellable rubber with excellent water absorptivity was prepared. The microphase structure of WSR was characterized by scanning electron microscopy (SEM) photograph. The dependence of the degree of the water-absorbing and the water-swelling, the water-absorbing and water-swelling rate on CSP, PEG, and PEO-b-PBA contents were investigated. The compatibilizing mechanism of PEO-b-PBA on WSR was studied.

EXPERIMENTAL

Materials

Nature rubber was obtained from Da Tong Rubber Factory, Shanxi Province, China. Crosslinked polyacrylate was synthesized by Wang Guojie[9] (the average particle diameter, 17 μm; the water absorptivity, 1200 g/g). PEO-b-PBA was synthesized by ourselves. PEG (M_w 2000), Zinc oxide, promoter M, stearic acid, precipitated silica, and sulfur were all chemical grade.

Preparation of samples

The samples were first prepared by blending at room temperature, and then vulcanized. The details of preparing process are as follows. NR was first placed on a open two-roll mill and masticated for 2 min. The weighed stearic acid, precipitated silica, CSP, PEO-b-PBA, PEG-2000, promoter M, and sulfur were added one by one, after which the sample was mixed for a further 10 min. The blended materials were put in a 80 $\times$ 60 $\times$ 1 mm^3 mold, preheated for 3 min, and cured for 20 min at 142 $\pm$ 1°C in a press vulcanizer of 16 ton. After that, the mold was taken out and cooled down at room temperature.

Water-swellable properties text

The vulcanized strips of the water-swellable rubber were cut to sheets with dimensions 40 $\times$ 20 $\times$ 1mm, and each was weighed and immersed into ion-exchanged water at room temperature. The samples were got out at specified intervals, gently blotted with tissue paper to remove the excess water on the surface; the weight and the volume of each swollen sample were recorded. This process was repeated at several time intervals and the time of water absorbing and water swelling to maximum value (T_S) indicated the absorbing and swelling rate. The degree of water absorbing by weight (S_w, the unit is g/g) and water swelling by volume (S_v, the unit is mm^3/mm^3) were calculated by the following equations:

$$S_w = \frac{W_1 - W_0}{W_0} \qquad (1)$$

$$S_V = \frac{V_1 - V_0}{V_0} \qquad (2)$$

where W_0, W_1 (the unit is gram) are the weight and V_1, V_0 (the unit is mm^3) are the volumes of the samples before immersing into water and after swelling with water in different time, respectively.

SEM analysis

The microphase structure of water-swellable rubber was observed on a JXA-840 scanning electron microscope (SEM). Samples were cryogenically fractured in liquid nitrogen, and coated the broken surface with gold in a sputter machine prior to the installation in the SEM chamber.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM) observation of the microstructure of WSR

Figure 1 is the SEM photograph showing microphase morphology of blend. As shown in Figure 1(a), before adding to the compatibilizer, the interface between the two-phase and the sunken pit produced after CSP dropped from NR matrix can be clearly seen. This shows that CSP with a hydrophilic polar nature distributes unevenly within the NR matrix of hydrophobic nonpolar nature. The adhesion between the two phase is weak and the interfacial tension is strong. When the WSR was cryogenically fractured in liquid nitrogen, the CSP fell off easily from the NR matrix. The SEM photographs of WSR with a PEO-b-PBA content of 5, 10, and 20 phr are shown in Figure 1(b), 1(c), and 1(d), respectively. It can be seen that PEO-b-PBA distributes in the interface between CSP and NR, no sunken pit was observed, and crack on CSP surface appeared. This is because CSP and NR are linked together by PEO-b-PBA, with PEO blocks attached to CSP and PBA blocks attached to NR. With such a structure, the adhesion between CSP and NR is increased. When cryogenically fractured in liquid nitro-
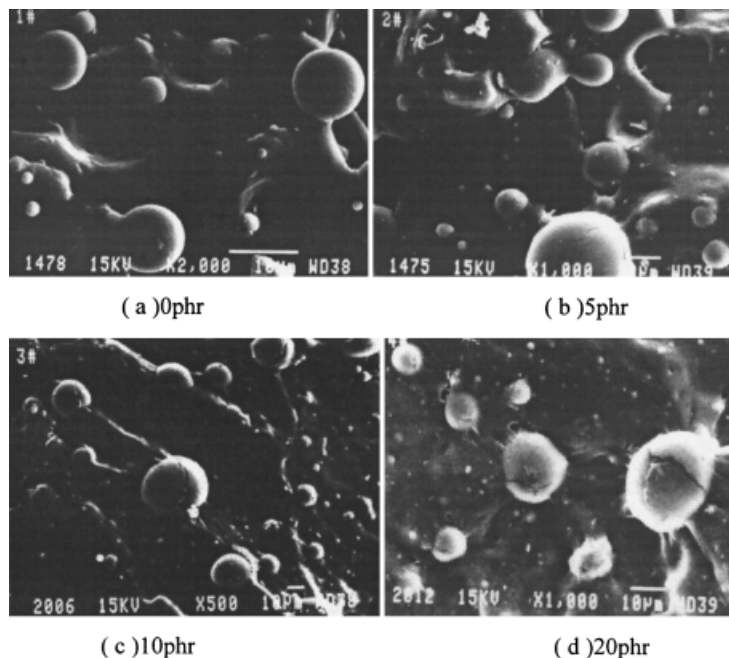
Figure 1 SEM photograph showing microphase morphology of blend. CSP: 40 phr; PEG-2000: 15 phr; PEO-b-PBA: (a) 0 phr, (b) 5 phr, (c) 10 phr, and (d) 20 phr.

gen, crack on the CSP surface diffuse tension and CSP does not come off from the NR matrix.

Effect of CSP resin on absorption

Figure 2 shows the dependence of S_w^m and S_v^m (the degree of water absorbing by weight and water swelling by volume, respectively, reaching maximum value) on the amount of CSP. It can be seen that the WSR shows little absorptivity when the amount of CSP is less than 20 phr. With the increase of CSP amount, the WSR shows its excellent ability of absorp-

tion. The S_w^m and S_v^m are equal to 60 and 40, respectively, when the amount of CSP reaches 100 phr.

Figure 3 and Figure 4 show the plot of S_w and S_v vs the soak time, respectively, which indicates that the increase in CSP content expedites the water-swellable process. T_S is reduced with the increase of CSP content. But it can also be seen from Figure 3 that there exists a upper limit of the CSP content for the WSR. When the CSP content is below this limit, S_w and S_v remain approximately constant values after reaching its swollen maximum. When the CSP content exceeds
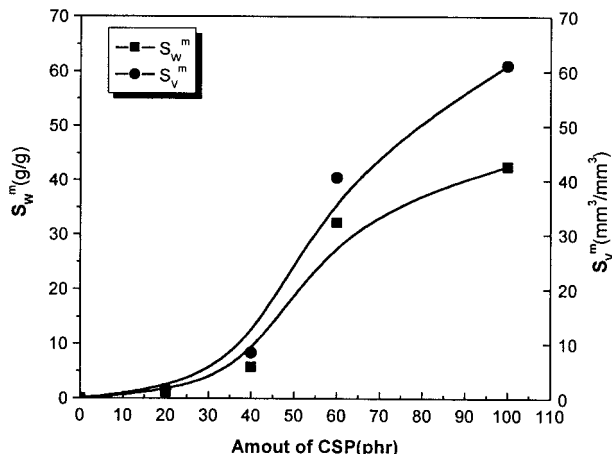

Figure 2 Plots of S_w^m and S_v^m vs amount of CSP. PEG: 10 phr; PEO-b-PBA: 10 phr.
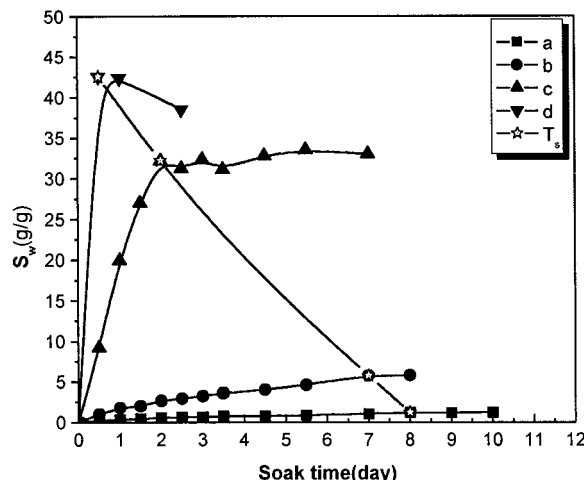

Figure 3 Plots of S_w vs soak time. PEG: 10 phr; PEO-b-PBA: 10 phr; CSP: (a) 20 phr, (b) 40 phr, (c) 60 phr, and (d) 100 phr.
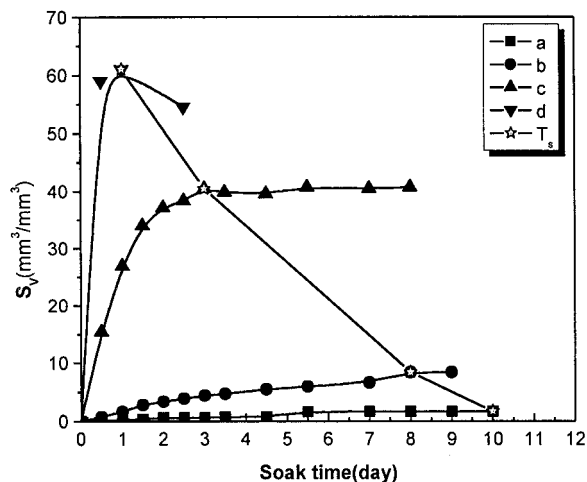
Figure 4 Plots of S_v vs soak time. PEG: 10 phr; PEO-b-PBA: 10 phr; CSP: (a) 20 phr, (b) 40 phr, (c) 60 phr, and (d) 100 phr.

Figure 6 Plots of S_w vs soak time. CSP: 40 phr; PEO-b-PBA; 10 phr; PEG: (a) 0 phr, (b) 10 phr, (c) 15 phr, and (d) 40 phr.

this limit, the WSR will swell to such an extent that the restriction force for CSP resin is small enough to allow the CSP resin escape from the rubber network and diffuse into water, which results in the degradation of S_w and S_v.

Effect of PEG on absorption

As can be seen in Figure 5, the addition of PEG greatly increased S_w^m and S_v^m. T_S is decreased pronouncedly (Fig. 6 and Fig. 7). This is because e though CSP has an excellent ability of absorption, it is found that CSP is confined within the crosslinked network of NR after blended and vulcanized, and could not contact directly with water. The water molecules could be absorbed only through capillary adsorption, surface adsorption, and diffusion process. But the confined force of the network exerting on PEG is relatively weak and PEG can easily diffuse into water when WSR is im-
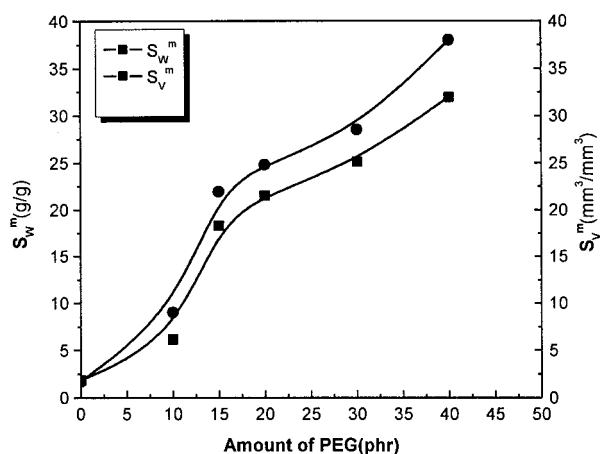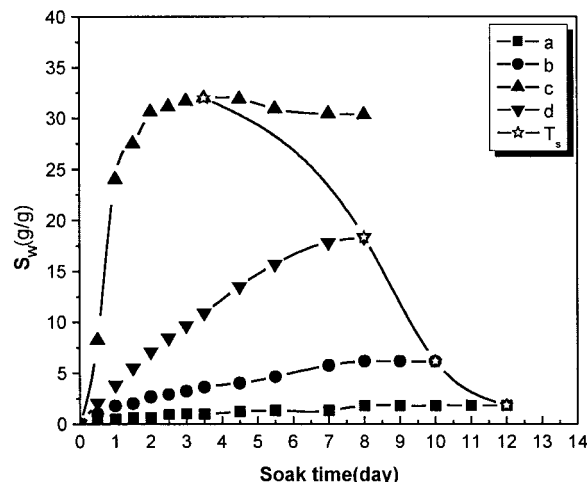
mersed into water. The path way for water molecules is then formed and the outside water molecules can readily diffuse into WSR. But it can also be seen that excess PEG will lead to the decrease of S_w and S_v after reaching maximum value [Figs. 6(d) and 7(d)], which can be explained by the more easy escape of CSP from WSR through the excess pathway.

Effect of PEO-b-PBA on absorption

Figure 8 shows the dependence of S_w^m and S_v^m on PEO-b-PBA amount. Fluctuation of S_w^m and S_v^m can be seen. When loading PEO-b-PBA is lower, S_w^m and S_v^m raise with the increase of PEO-b-PBA content.

Because PEO segment can form hydrogen bond with water and combine water, PEO-b-PBA itself can absorb water. In order to investigate the effect of PEO-b-PBA on absorption of WSR, the following equation
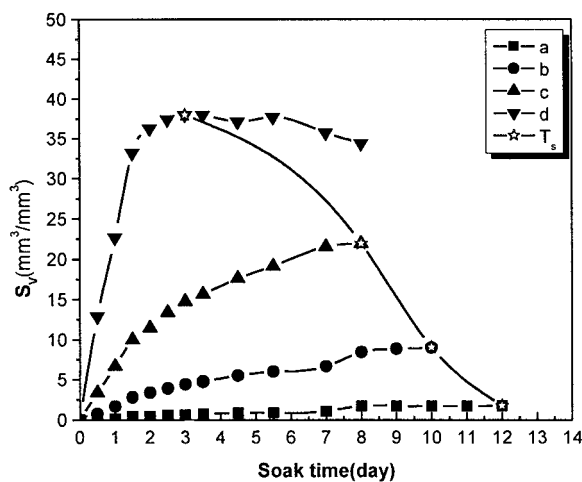

Figure 5 Plots of S_w^m and S_v^m vs amount of PEG. CSP: 40 phr; PEO-b-PBA: 10 phr.

Figure 7 Plots of S_v vs soak time. CSP: 40 phr; PEO-b-PBA: 10 phr; PEG: (a) 0 phr, (b) phr, (c) 15 phr, and (d) 40 phr.
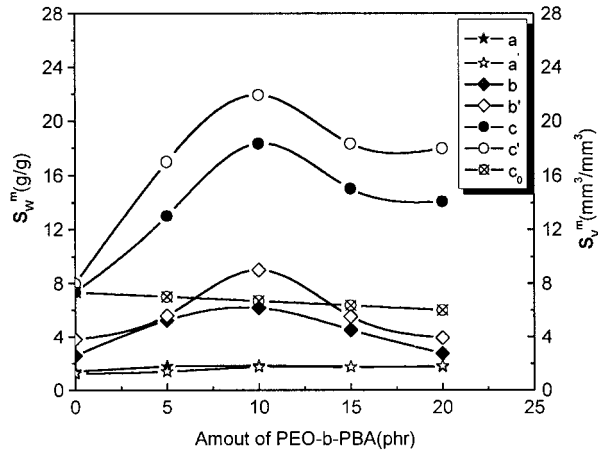
Figure 8 Plots of S_w^m and S_v^m vs amount of PEO-b-PBA. CSP: 40 phr; PEG: (a,a') 0 phr; (b,b') 10 phr; (c,c',c_0) 15 phr (c_0 by calculation). (a,b,c,c_0) S_w^m curves; (a',b'c') S_v^m curves.

is used to calculate the degree of water absorbing by weight of WSR according to the linear combination principle.

$$S_w = X_1 S_{w_1} + X_2 S_{w_2} \tag{3}$$

Here, S_w is the degree of water absorbing by weight of WSR after the addition of PEO-b-PBA; Sw_1 is the degree of water absorbing by weight of PEO-b-PBA; Sw_2 is the degree of water absorbing by weight of WSR before the addition of PEO-b-PBA; X_1 is the weight fraction of PEO-b-PBA and X_2 is the weight fraction of other component.

According to eq. (3), the S_W of WSR decreased a little with the increase of the amount of PEO-b-PBA instead [Fig. 8(c_0)] and the trend is very little. This indicates that compared to CSP, the contribution of the absorption of PEO-b-PBA itself to the blend's absorp-
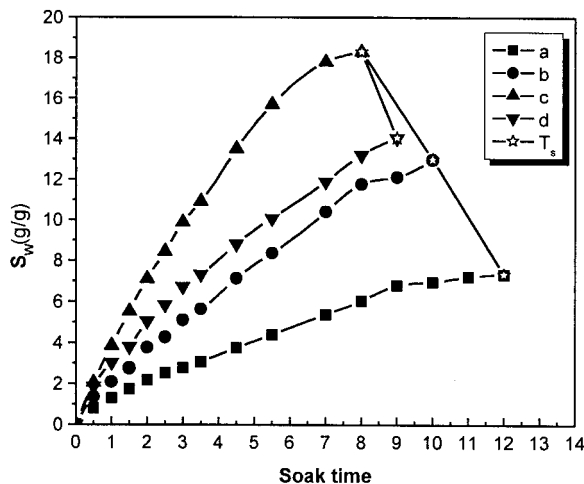

Figure 9 Plots of S_w vs soak time. CSP: 40 phr; PEG: 15 phr; PEO-b-PBA: (a) 0 phr, (b) 5 phr, (c) 10 phr, and (d) 20 phr.
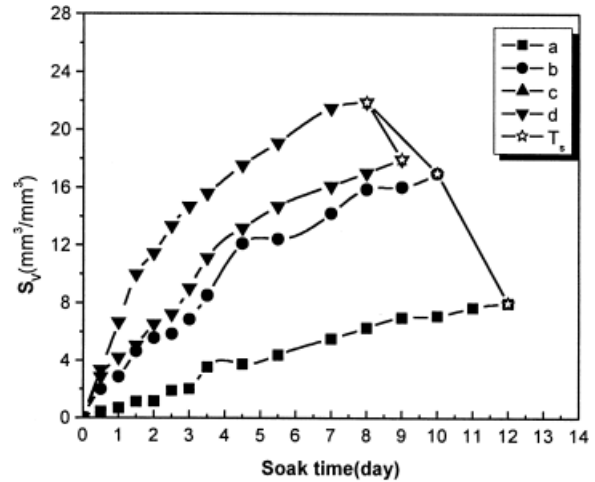

Figure 10 Plots of S_V vs soak time. CSP: 40 phr; PEG: 15 phr; PEO-b-PBA: (a) 0 phr, (b) 5 phr, (c) 10 phr, and (d) 20 phr.

tion is very little. It also can be seen in Figure 8 that the effect of PEO-b-PBA content on absorption is not clear [Fig. 8(a,a')] when PEG is not added and the effect of PEO-b-PBA is pronounced [Fig. 8(b,b',c,c')] with the increasing of PEG content. From the above results, it can be explain that PEO-b-PBA plays a dual role in improving compatibility of WSR. On the one hand, it can improve the compatibility between NR and CSP. On the other hand, it can also improves the compatibility between PEG and NR matrix. The pathway formed by the leaking of PEG to the water becomes more evenly distributed and the water absorptivity of WSR is improved.

From Figure 8, it can also be seen that raising the amount of PEO-b-PBA from 10 to 20 phr makes S_w^m and S_v^m decrease instead, which may be as a result of further raising the PEO-b-PBA loading changing the microphase morphology of multicomponent blend system.

The effect of PEO-b-PBA content on water-absorbing and water-swelling rate is also investigated as can be seen in Figure 9 and Figure 10. In certain range, the swelling rate raised with the increase of PEO-b-PBA content. But the influence is not marked and during a very long period, S_w and S_v remain approximately constant value after reaching the absorbing maximum value. This means that the water-swellable stability is increased. This may be attributed to the improved compatibility between PEG and NR as well as between CSP and NR, resulting in a slower diffusion of PEG and CSP into the water.

CONCLUSION

1. As shown in the SEM photograph, PEO-b-PBA distributes in the interface between CSP

and NR. CSP and NR are linked together by PEO-b-PBA, with PEO blocks attached to CSP and PBA blocks attached to NR. With such a structure, the adhesion between CSP and NR is increased. When cryogenically fractured in liquid nitrogen, crack on CSP surface diffuse tension and CSP does not come off from NR matrix.

2. The CSP resin plays the leading role in absorption. The more the amounts of CSP resin, the higher the expansion ratio of the rubber. The addition of proper amount of PEG-2000 acts as the pathway of water and can strongly enhance the water swellability.

3. The compatibilizer plays a dual role of improving compatibility in system. It can improve the miscibility of CSP resin and NR matrix as well as that of PEG and NR matrix. The compatibilizing effect can be affected by the amount of PEO-b-PBA.

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