

Preparation of a Self-Compatibility Alloy via a Seed-Graft Concentrated-Emulsion Pathway

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ABSTRACT: A novel polymerization procedure, the concentrated-emulsion graft polymerization of styrene monomer with poly(butyl acrylate) seed, was proposed for the production of a self-compatibility macromolecule alloy. The effects of the butyl acrylate content, sodium dodecyl sulfate concentration, and polymerization temperature on the graft ratio were investigated. Scanning electron microscopy, transmission electron microscopy, and impact strength were used to characterize the microstructure and mechanical performance of the self-compatibility macromolecule alloy. The results showed that increasing the butyl acrylate content, reducing the sodium dodecyl sulfate concentration, and improving the polymerization temperature all favored an increased graft ratio, which resulted in increased impact strength of the self-compatibility macromolecule alloy. Therefore, the concentrated-emulsion polymerization method is particularly suitable for seed-graft polymerization. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2915–2920, 2002; DOI 10.1002/app.10288

Key words: concentrated emulsion; graft; self-compatibility; polystyrene; poly(butyl acrylate); alloys; blends

INTRODUCTION

Nowadays, different techniques are used to improve the compatibility of multiphase polymer blends.^{1–3} For the processing of polymer blends, primary methods include the addition of compatibilizers, group reaction, and reaction extrusion.^{4–8} Of course, processing methods play an important role in morphology and physical properties, and each method has its own advantages. Few attempts, however, have been made to simplify processing. In contrast to a conventional emulsion, a concentrated emulsion (with globules of uniform size) has a volume fraction of the dispersed phase that is larger than 0.74 (this repre-

sents the most compact arrangement of spheres of equal size) and can be as large as 0.99.^{9–14} In a previous article,¹⁵ a novel procedure for the self-compatibilization of polymer blends prepared via functionalized concentrated-emulsion polymerizations was proposed. Two functionalized concentrated emulsions in water were prepared, one from a weakly polymerized mixture of styrene (St) and a small amount of acrylic acid and the other from a mixture of butyl acrylate (BA) and a small amount of glycidyl methacrylate. After the concentrated emulsions were partially polymerized, they were mixed and subjected to complete polymerization. During the mixing and subsequent polymerization, reactions between the carboxyl groups of the acrylic acid and the glycidyl groups of the glycidyl methacrylate occurred, and some kinds of graft and/or block copolymers were generated, which constituted the compatibilizers

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of the system. In this work, a novel procedure, a seed-graft concentrated-emulsion pathway, is proposed. A traditional emulsion of BA monomer is prepared first. After the emulsion is polymerized completely, St monomer is added dropwise to the flask to prepare the concentrated emulsion. During the polymerization, a graft reaction between St monomer and poly(butyl acrylate) (PBA) seed occurs, and small amounts of graft copolymers are generated, which constitute the compatibilizers between polystyrene (PS) and PBA. As a result, the polymerization of St monomer and the graft copolymerization of PS and PBA occur at the same time.

EXPERIMENTAL

Materials

St (analytical reagent; Shanghai Reagent Manufacturer, Shanghai, China) and BA (analytical reagent; Beijing Yili Fine Chemicals Co., Ltd., Beijing, China) were filtered through an inhibitor removal column before use. 2,2'-Azobisisobutyronitrile (AIBN; analytical reagent) was obtained from Beijing Reagent Manufacturer No. 3 (Beijing, China), and benzoyl peroxide (BPO; chemically pure) was acquired from the Beijing Kehua Special Reagent United Development Center (Beijing, China). The other compounds, sodium dodecyl sulfate (SDS; 70%; Beijing Qiuxian Chemical Manufacturer, Beijing, China), tetrahydrofuran (analytical reagent; Tianjin Reagent Manufacturer No. 6, Tianjin, China), 1,4-dioxane (analytical reagent; Beijing Chemical Reagent Co., Beijing, China), acetone (analytical reagent; Beijing Chemical Reagent), and methanol (analytical reagent; Beijing Yili Fine Chemicals), were used as received.

Preparation of the PBA Seed

First, an aqueous solution of SDS (in various concentrations) was placed in a 100-mL flask provided with a magnetic stirrer. The flask was sealed with a rubber septum. BA monomer containing AIBN was added dropwise with a syringe to the flask with vigorous stirring. Subsequently, the flask was moved into a constant-temperature bath for the initiation of the reaction.

Concentrated-Emulsion Polymerization

After the PBA seed was produced, St monomer containing BPO as an initiator was added drop-

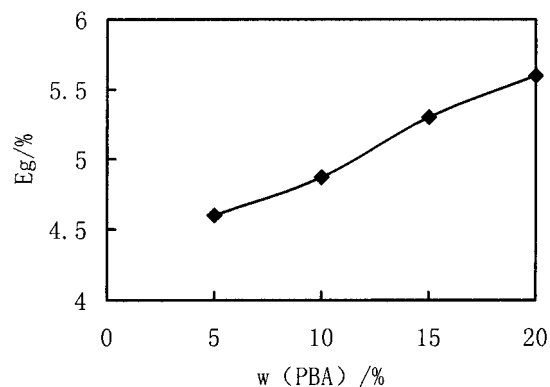


Figure 1 Effect of the BA content on the graft ratio.

wise to the flask with vigorous stirring until the volume fraction of the aqueous solution became a selected value (usually 0.2). The entire addition process lasted 5 min. A concentrated emulsion was thus generated. Subsequently, the flask was moved into a constant-temperature bath for the initiation of the reaction. During the polymerization, graft copolymers were produced because of the chain transfer. The product was washed and dried.

Graft Copolymer Content Measurements^{2,3}

A preweighed powder was immersed in acetone at room temperature through the addition of a small amount of BPO for crosslinking. After the crosslinking was finished, an acetone solution containing graft polymers was cast to form a film, which was cut into narrow sheets after the solvent evaporated. With 1,4-dioxane as the extracting agent, the PS homopolymer in the samples was extracted at room temperature. Subsequently, methanol was added to the 1,4-dioxane extract for precipitation fractionation. The precipitation product was washed and dried, and the weight was the content of the PS homopolymer, the graft reaction of which did not occur. The graft ratio (E_g) was calculated as follows:

$$E_g = \frac{(w_1 - w_2)}{w_1} \times 100\%$$

where w_1 is the weight of PS and w_2 is the weight of the precipitation product.

Electron Microscopy

The samples were dyed with osmic anhydride after subzero microtoming. The microstructure was

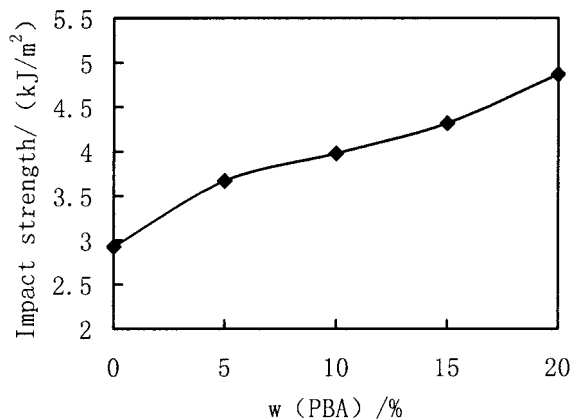


Figure 2 Effect of the BA content on the impact strength. The amount of the emulsifier for the preparation of the PBA seed was 0.6 g/g of H₂O.

examined with a Hitachi H-800-1 transmission electron microscope (Japan). The morphologies of the fractured surfaces of the alloys were investigated with a Cambridge S250 scanning electron microscope (UK).

Impact Testing

Powders of the graft copolymers were thermo-pressed at 140°C and 8 MPa for 3–5 min to the size described by ASTM Standard D 256. The

impact testing was conducted at room temperature (23°C) with a Charpy Xoj-4 (Wu Zhong Testing Instrument Co., China) impact-testing instrument.

RESULTS AND DISCUSSION

Effect of the BA Content on the Graft Ratio and Impact Strength

The curve of the PBA content versus the graft ratio is presented in Figure 1. The graft ratio was about 4.6 and 5.6% for 5 and 20% PBA, respectively, and a larger amount of BA produced a higher graft ratio. This indicates that a higher amount of BA produced a larger surface area of PBA seeds, which increased the opportunity for a graft reaction between PBA seeds and St monomers.

With PBA as the dispersed phase and PS as the continuous phase, better compatibility between the two phases resulted in a higher compact strength. Therefore, the effect of compatibilization can be characterized by the impact strength of a sample, which constitutes a measure of its toughness. The relationship between the impact strength and the amount of BA is presented in Figure 2, which shows that the greater the amount of BA was, the higher the impact strength

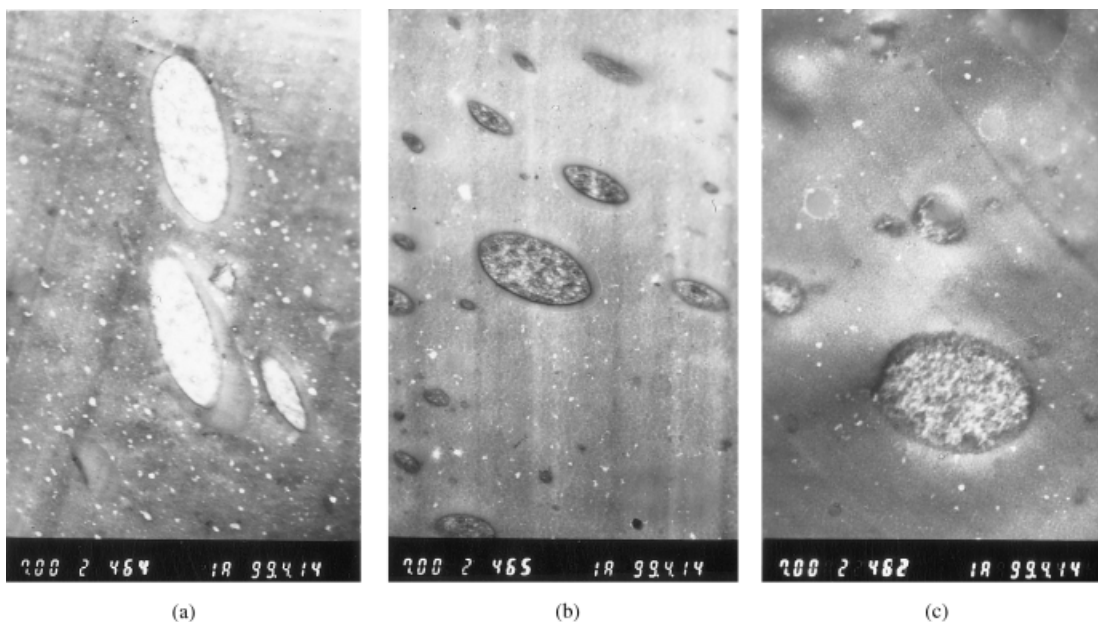


Figure 3 TEM micrographs of PS-PBA alloys obtained by the polymerizations of concentrated emulsions containing different amounts of BA. The amounts of PBA were (a) 5.0, (b) 10.0, and (c) 15.0 wt %.

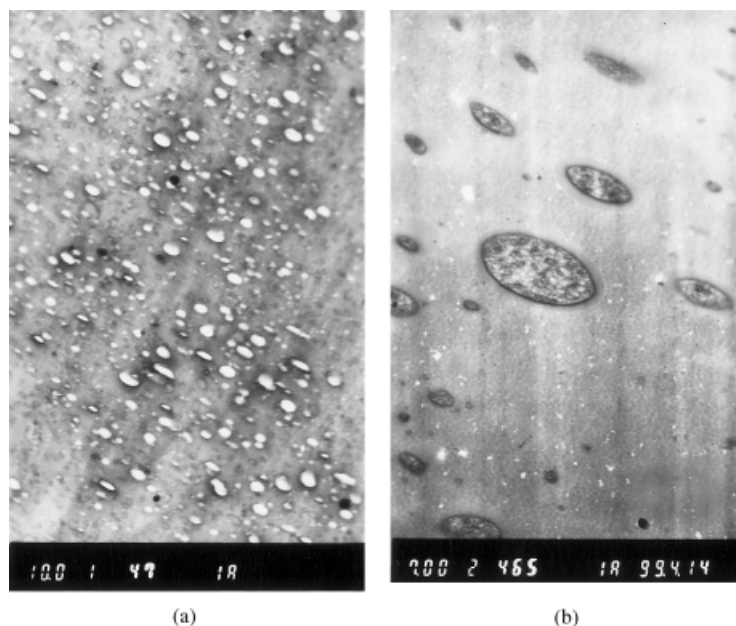


Figure 4 TEM micrographs of PS–PBA alloys polymerized with PBA seeds of different sizes. The amounts of the emulsifier for the PBA seed emulsion polymerizations were (a) 0.05 and (b) 0.01 g/g of H₂O. The amount of PBA for the seed emulsion polymerizations was 10.0 wt %.

was. This increase occurred for two reasons. First, PBA, as a type of rubber, had good toughness. Second, the higher amount of BA resulted in an increase in the graft copolymers. The small amounts of the graft copolymers, as compatibilizers, reduced the interfacial tension and increased the compatibility between the PS and PBA phases.

Effect of the BA Content on the Microstructure

PBA was designated as the rubber phase, which resulted in the increased toughness of the PS–PBA alloy. Figure 3 shows that as the amount of PBA increased, the amount of PS in the PBA phase increased. This happened because the higher the amount of PBA was, the higher the amount of the graft copolymers was. St–BA graft copolymers constituted the compatibilizer of the PS–PBA phases. As a result, the more graft copolymer there was, the fuzzier the PS–PBA phases were. This particular microstructure resulted in excellent macroscopic behavior.

Effect of the Size of the PBA Particles on the Microstructure and Impact Strength

Figure 4 shows that PBA particles of different sizes dispersed in the continuous phase of PS. When the PBA particles became larger, a greater

amount of PS was occluded in the PBA particles. This happened because there was a higher chain-transfer probability for the PBA phase with large particles than for the PBA phase with small particles. An obvious occlusion structure in the PBA phase for samples obtained by polymerization with large particles is shown in Figure 4. Because of this structure, the compact strength of the sample shown in Figure 4(b) was obviously higher than that of the sample shown in Figure 4(a). The results of the compact strengths are listed in Table I.

Table I Impact Strength and Graft Ratio of Samples with Different PBA Particle Sizes

Sample	PBA Contents (wt %)	Concentration of SDS for Seed Polymerization (g/g of H ₂ O)	Graft Ratio (%)	Impact Strength (kJ/m ²)
a	10.0	0.05	3.0	3.6
b	10.0	0.01	4.8	4.7

Polymerization conditions: temperature = 60°C; volume fraction of the dispersed phase = 0.87; concentration of AIBN initiator = 0.6 g/100 g of H₂O; concentration of BPO initiator = 0.6 g/100 g of St.

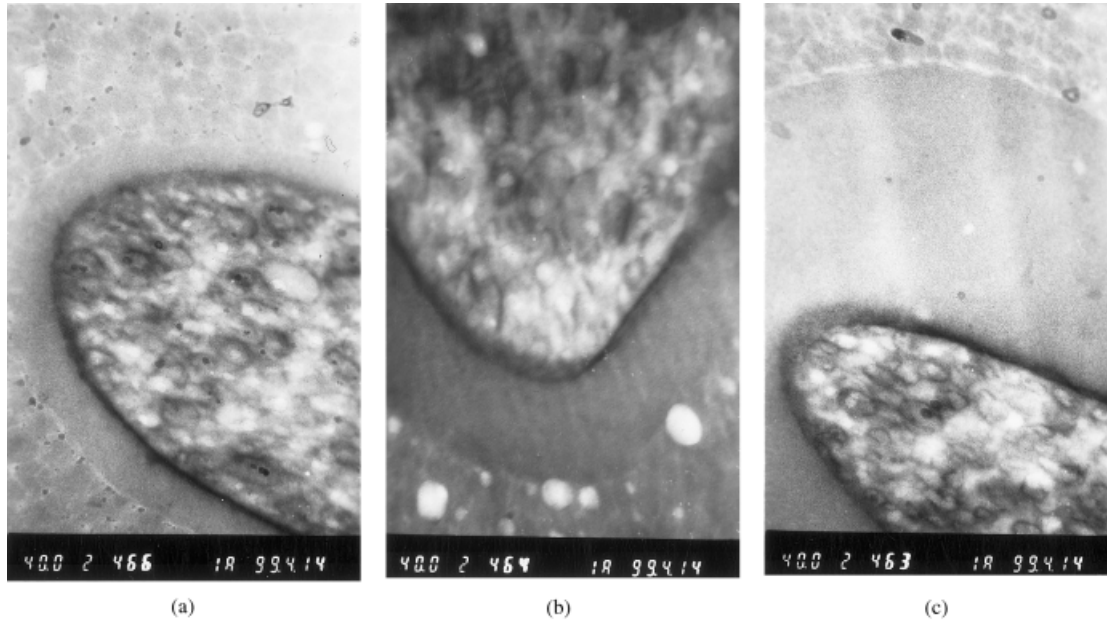


Figure 5 TEM micrographs of samples obtained by the polymerizations of concentrated emulsions at different polymerization temperatures. The temperatures for the concentrated-emulsion polymerizations were (a) 60, (b) 70, and (c) 80°C.

Effect of the Polymerization Temperature on the Microstructure and Impact Strength

The compatibilizing effect is revealed clearly by the morphologies of the PS-PBA alloys. Figure 5 presents micrographs of samples obtained by transmission electron microscopy (TEM) that illustrate that dispersed PBA particles containing PS strongly adhered to the PS matrix. When the reaction proceeded at 60°C, the thickness between the PS and PBA phases was about 0.1 μm , whereas the thickness became 0.5 μm when the reaction proceeded at 80°C. This occurred because a higher temperature resulted in a higher proba-

bility of a chain-transfer reaction, which led to an increase in graft copolymers. The higher the temperature was, the thicker the interface layers were. The graft copolymers, as compatibilizers, dispersed uniformly between the PS and PBA phases; this was very helpful for the compatibility of the PS and PBA phases.

Figure 6 presents micrographs of fractured surfaces obtained with scanning electron microscopy (SEM). The surfaces are a measure of the brittleness of a sample: when a brittle sample broke, there was hardly any deformation, and the fractured surface was smooth. The smooth sur-

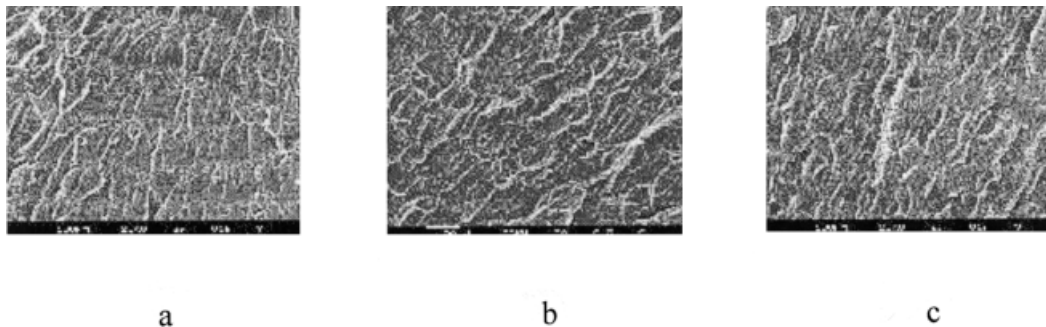


Figure 6 SEM micrographs of freshly fractured surfaces of PS-PBA alloys. The temperatures for the concentrated-emulsion polymerizations were (a) 60, (b) 70, and (c) 80°C.

Table II Graft Ratio and Impact Strength of Samples Obtained at Different Polymerization Temperatures

Sample	Graft Copolymerization Temperature (°C)	Graft Ratio (%)	Impact Strength (kJ/m ²)
a	60	5.2	4.3
b	70	5.6	4.8
c	80	6.2	4.9

Polymerization conditions: volume fraction of the dispersed phase = 0.87; PS/PBA weight ratio = 85/15; concentration of AIBN initiator = 0.6 g/100 g of H₂O; concentration of BPO initiator = 0.6 g/100 g of St.

face reflects a poor combination of the PS matrix and PBA seeds. However, a tough sample underwent relatively large deformation before breaking, and the fractured surface was coarse. Figure 6 shows that the higher the reaction temperature was, the finer the wrinkles were. It is obvious that this phenomenon was due to the increased amount of graft copolymers with the increasing reaction temperature. Therefore, one can conclude that compatibilization between the PS and PBA phases can be obtained with an increased reaction temperature during concentrated-emulsion polymerizations.

The graft ratios and compact strengths of samples obtained at different polymerization temperatures are listed in Table II. The higher the polymerization temperature was, the higher the graft ratio was, and the same tendency was found for the compact strength. As expected, these results were consistent with those previously mentioned.

CONCLUSIONS

When a concentrated emulsion of St monomer containing PBA seeds was polymerized, some

graft copolymers were generated *in situ* between the PS and PBA phases. An excellently combined self-compatibilized alloy was thus obtained. A high polymerization temperature was necessary to ensure good compatibilization, which made the domain of the PBA phase finer and improved the impact strength of the self-compatibilized alloy.

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