

Grafting of Maleic Anhydride onto Styrene–Butadiene–Styrene Triblock Copolymer Using Supercritical CO₂ as a Swelling Agent

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ABSTRACT: Grafting of maleic anhydride (MA) onto styrene–butadiene–styrene triblock copolymer (SBS) was carried out by free radical polymerization using supercritical carbon dioxide (SC CO₂) as a solvent of MA and swelling agent of SBS. The effect of various factors such as monomer concentration, initiator concentration, SC CO₂ pressure, and reaction time on grafting ratio was studied. SBS and the product (SBS-g-MA) were characterized by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). GPC data showed that the molecular weight of SBS-g-MA is bigger than that of

SBS. DSC testing indicated that the glass transition temperature (T_g) of SBS-g-MA is higher than that of SBS. By SEM photo, we can observe that some particles which contain more oxygen atom grew out from the surface of SBS-g-MA when grafting ratio reached at 5.6%, and the amount and diameter of particles increased with increasing of grafting ratio. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4425–4429, 2006

Key words: supercritical carbon dioxide; styrene–butadiene–styrene triblock copolymer; maleic anhydride; grafting

INTRODUCTION

As a thermoplastic elastomer, styrene–butadiene–styrene triblock copolymer (SBS) has many good properties such as good elasticity, high strength, low temperature durability, etc. But it is a nonpolar polymer, and so its cohesion is low and that limits its application. Because there are double-bonds in the SBS macromolecule structure, it can be grafted using polar olefine monomers (e.g., maleic anhydride, acrylic acid, methyl methacrylate, etc), and it becomes carboxylic polymer. Such grafted SBS contain polar groups, so that its glass transition temperature, elastic modulus, melting viscosity, electric behavior, and other properties are changed and its application area is expanded.

There are two conventional methods for the grafting of SBS. (1) In solution grafting,^{1,2} SBS, monomer, and initiator are dissolved in an organic solvent (e.g., benzene and toluene) and allowed to react. The handling is simple and the reaction process is smooth. But it needs lots of poisonous organic solvents, which cause great trouble during the post-treatment. To obtain a solid product, these organic solvents must be removed

from the product, and this consumes high energy and pollutes the environment. (2) In melting grafting,³ SBS, monomer, and initiator are added together into an extruder. They react during the melting extrusion process. This method avoids using poisonous organic solvent. But because the viscosity in the system is very high and reaction time in the extruder is very short, the grafting ratio usually is low.

Supercritical carbon dioxide (SC CO₂; critical temperature 31.1°C, critical pressure 7.38 MPa) provides an environmentally benign alternative to the organic solvents traditionally employed in the chemical industry. SC CO₂ has many advantages as a reaction medium: nontoxic, not inflammable, chemical inertia, inexpensive. Comparing with other supercritical fluids, it also has moderate critical pressure and low critical temperature (close to room temperature). Because of its low viscosity and zero surface tension, the mass-transfer speed in SC CO₂ fluid is much faster than that in conventional liquid.

The study on polymerization using SC CO₂ as reaction medium has made great progress. For example, solution polymerization,⁴ dispersion polymerization,^{5–8} precipitation polymerization,^{9,10} and emulsion polymerization.^{11,12} It has been found that SC CO₂ can dissolve most of the small molecular organic compounds. Although it cannot dissolve most of the polymers, it can swell them in different degrees. So, SC

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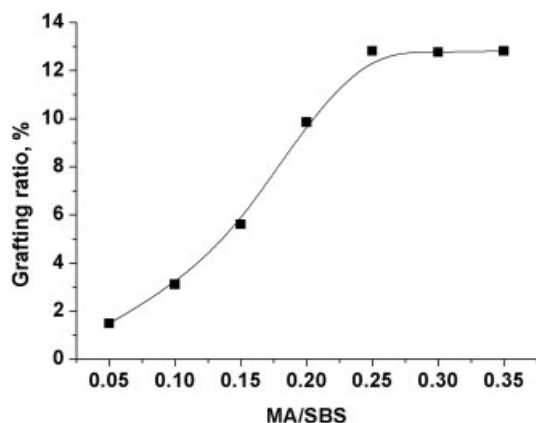


Figure 1 Effect of MA concentration on grafting ratio (reaction condition: BPO/SBS = 0.02, $T = 70^{\circ}\text{C}$, $P = 20\text{ MPa}$, $t = 12\text{ h}$).

CO_2 has been used as a swelling agent to produce polymer blends^{13–15} and grafted polymer.¹⁶

In this work, we studied the grafting reaction of MA onto SBS, using SC CO_2 as a solvent of MA and swelling agent of SBS and got some good results.

EXPERIMENTAL

Materials

Pellet styrene–butadiene–styrene triblock copolymer (SBS) supplied by Baling Petrochemical Company (Hunan Province, China) was used as received. MA produced by Beijing Yili Fine Chemical Company (Beijing City, China) was used after recrystallization in methanol. Benzoyl peroxide (BPO) produced by Tianjin Damao Chemical Reagent Company (Tianjin City, China) was used after recrystallization in chloroform. Acetone (AR grade) received from Tianjin Fuchen Chemical Reagent Factory (Tianjin City, China) was used without further purification. Carbon dioxide with purity of 99.9% was purchased from Jinan Gas Factory (Shandong Province, China) and used as received.

Grafting procedures

In this work, SBS (3 g), MA, and BPO were added into a 100-mL stainless steel high-pressure reactor. After the reactor was sealed, the inside air was drawn out by a vacuum pump, and the liquid CO_2 (about 50 g) was injected into the reactor by a high-pressure injection pump. Then the reactor was put into a water bath and heated to the desired reaction temperature (70°C) to start the reaction. When the reaction ended, we cooled down the reactor to room temperature, deflated CO_2 slowly, and collected the solid substance. The sample was Soxhlet-extracted using hot acetone for 48 h to remove the unreacted monomer and was dried to

stable weight. Finally, we obtained purified grafted SBS (SBS-g-MA). The grafting ratio (percentage) was calculated as follows:

$$G = \frac{W_1 - W_0}{W_0} \times 100\%$$

where G is grafting ratio; W_0 is SBS weight before reaction; W_1 is SBS-g-MA weight.

Characterization

FTIR (Perkin–Elmer spectrum one) was used to characterize the grafting of polymer. GPC (Waters1525) was used to measure the average molecular weight and its distribution. DSC (Perkin–Elmer diamond) was used to analyze the thermo behavior. SEM (Hitachi S-2500 with X-ray dispersion function) was used to observe the morphology of products and analyze the surface element.

RESULTS AND DISCUSSION

Effect of MA concentration on the grafting ratio

Figure 1 indicates that the grafting ratio increases initially with increasing of MA concentration. But when MA/SBS (mass ratio) is more than 0.25, the grafting ratio tends to be unchangeable. The reason is that increasing of MA concentration increases the reaction probability of MA and SBS, and the grafting ratio increases. Because the homopolymerization of MA is difficult,¹⁷ and the quantity of reactive double-bonds in SBS is invariable, increase of MA concentration continuously will lead the grafting ratio to saturation.

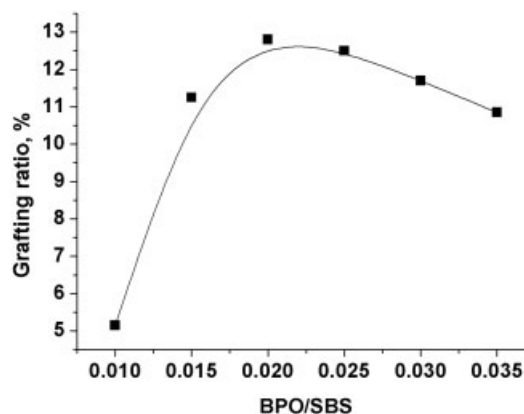


Figure 2 Effect of BPO concentration on grafting ratio (reaction condition: MA/SBS = 0.25, $T = 70^{\circ}\text{C}$, $P = 20\text{ MPa}$, $t = 12\text{ h}$).

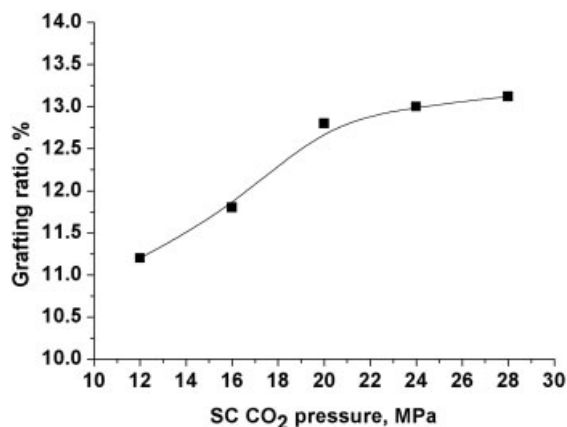


Figure 3 Effect of SC CO₂ pressure on grafting ratio (reaction condition: MA/SBS = 0.25, BPO/SBS = 0.02, $T = 70^{\circ}\text{C}$, $t = 12$ h).

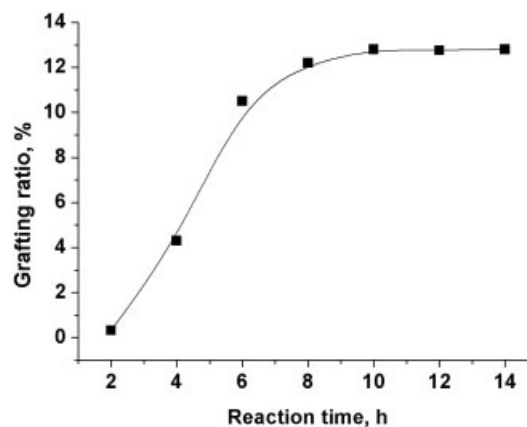


Figure 4 Effect of reaction time on grafting ratio (reaction condition: MA/SBS = 0.25, BPO/SBS = 0.02, $T = 70^{\circ}\text{C}$, $P = 20$ MPa).

Effect of BPO concentration on the grafting ratio

Figure 2 shows that the grafting ratio increases initially with increasing of BPO concentration. But when BPO/SBS (mass ratio) is more than 0.02, the grafting ratio decreases. We explain this phenomenon as follows: when we increase BPO concentration initially, the free radical concentration in the system increases, and this increases the grafting ratio. But because there are lots of double-bonds in the SBS macromolecule structure, excessive BPO may cause crosslinking reaction between SBS molecule chains, and this decreases the reaction probability between SBS and MA, so that the grafting ratio decreases.

Effect of SC CO₂ pressure on the grafting ratio

Figure 3 shows that the grafting ratio increases with increasing of supercritical carbon dioxide (SC CO₂) pressure, in our experimental pressure range from 12 to 28 MPa. The reason is that increasing of SC CO₂ pressure increases the swelling degree of SBS and the soaking amount of MA. So, the grafting reaction probability increases, and the grafting ratio increases.

Effect of reaction time on the grafting ratio

Figure 4 indicates that the grafting ratio increases initially with reaction time and reaches a plateau in 9 h. The reason is that there are lots of reactive double-bonds in SBS and MA monomers in the system in the beginning of the reaction, so that the reaction speed increases rapidly after induction period. With the reaction time prolonging, the quantity of reactive double-bonds in SBS and MA concentration are decreasing. Gradually, the grafting ratio tends to saturate.

FTIR analysis

Figure 5 is the FTIR spectra of SBS and SBS-g-MA. Comparing these two spectra, we can find that there are stretching bands at 1779cm^{-1} and 1856cm^{-1} for the carbonyl group ($-\text{C}=\text{O}$) and ether carbon bands at $1300\text{--}1100\text{cm}^{-1}$ in the spectra of SBS-g-MA, indicating that MA has been grafted onto SBS.

GPC and DSC analysis

GPC data represent that the molecular weight of SBS-g-MA is bigger than that of SBS, and its distribution is wider also. The reason is that those MA grafted on SBS molecular chains made the molecular weight of SBS-g-MA big, and the randomness of grafting reaction made the molecular weight distribution wide. DSC testing shows that the T_g of SBS-g-MA are higher than that of SBS, indicating that polar MA grafted on SBS causes high T_g (Table I).

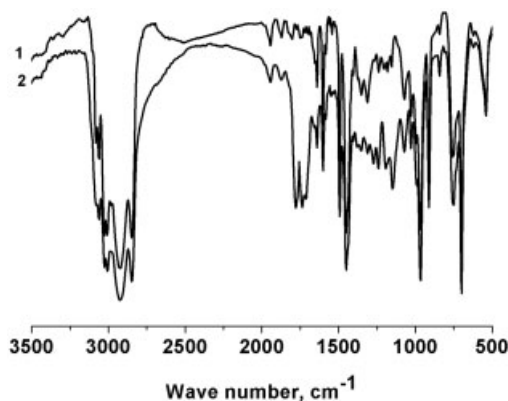


Figure 5 FTIR spectra of SBS and SBS-g-MA; (1) SBS and (2) SBS-g-MA ($G = 12.8\%$).

TABLE I
 M_n , M_w/M_n , and T_g of SBS and SBS-g-MA^a

Sample	M_n (10^{-4} g/mol)	M_w/M_n	T_g (°C)
SBS	16.64	1.153	-75, 72 ^b
SBS-g-MA (G = 5.6%)	18.16	1.198	-74, 77
SBS-g-MA (G = 12.8%)	20.11	1.204	-70, 86

^a M_n , number-average molecular weight; M_w , weight-average molecular weight; T_g , glass transition temperature.

^b The negative data are T_g of polybutadiene chain; the positive data are T_g of polystyrene chain.

Morphology and surface element analysis

The surface of SBS and SBS-g-MA were examined by SEM. The results are shown in Figure 6. When compared with the photo of SBS, the photo of SBS-g-MA showed wrinkles on the surface of SBS-g-MA, when the grafting ratio reached 3.2%. However, when the grafting ratio reached 5.6%, some particles grew out from the surface, and the amount and diameter of the

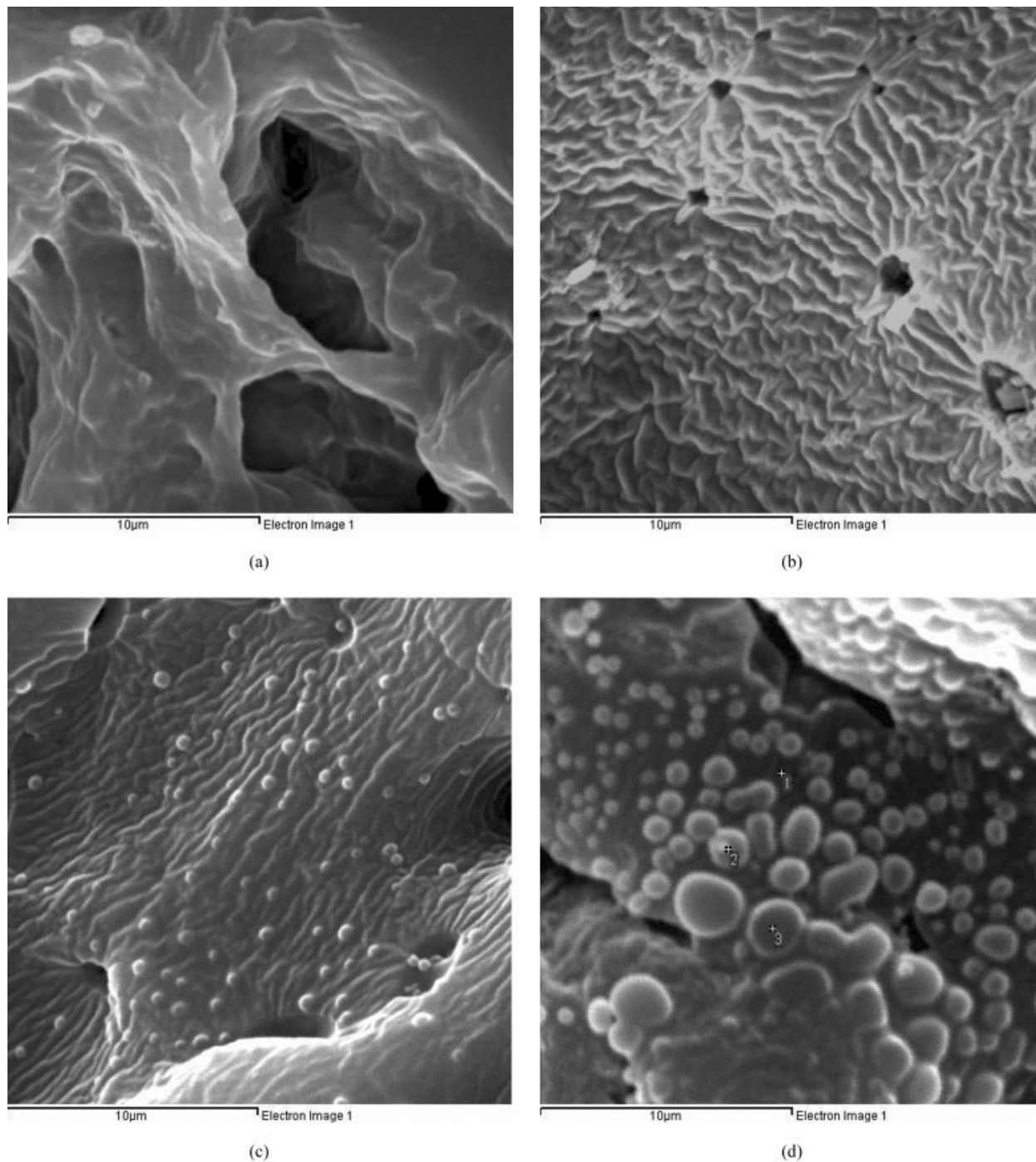


Figure 6 Scanning electron micrographs of SBS and SBS-g-MA; (a) SBS extracted by acetone, (b) SBS-g-MA (G = 3.2%), (c) SBS-g-MA (G = 5.6%), (d) SBS-g-MA (G = 12.8%).

TABLE II
The Concentration of Surface Atom^a

Spot	C (%)	O (%)
1	95.98	4.02
2	84.69	15.31
3	84.04	15.96

^a These data are atom amount ratio of carbon and oxygen; 1, flat place; 2 and 3, particles [Fig. 6(d)].

particles increased with increasing of the grafting ratio. The elements of the surface of SBS-g-MA were analyzed by X-ray dispersion. The result [Fig. 6(d) and Table II] shows that the concentration of oxygen atom in the surface of the particles is more than that in the flat place, indicating that these particles contain more MA than the flat place. We explain this phenomenon as follows: Because there is no compatibility between polar MA and nonpolar SBS, these particles are conglomerations of SBS chain grafted MA.

CONCLUSIONS

SC CO₂ can be used as a medium for grafting reaction of SBS and MA. High grafting ratio can be obtained by this method. The molecular weight of SBS-g-MA is

bigger than that of SBS. Also, the glass transition temperature of SBS-g-MA is higher than that of SBS. When grafting ratio reached 5.6%, there are some particles in which contain more oxygen atoms grew out from the surface of SBS-g-MA.

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