

Effect of Aging on Synthesis of Graft Copolymer of EPDM and Styrene (EPDM-g-PS)

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Received 30 September 2004; accepted 14 March 2006

DOI 10.1002/app.24673

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of aging on synthesis by the graft copolymerization of styrene onto random ethylene-propylene–diene monomer with benzoyl peroxide (BPO) as the initiator is described. Results showed that yields of graft copolymer are increased in the first 10 min. After 10 min, the total polymer produced has a maximum at about 25 min. However, the portion of the graft copolymer is decreased and the portion of the pure polystyrene is increased. In addition, the influence factors, such as reac-

tion time, temperature, BPO concentrations and styrene concentrations, effect of solvents on the extent of graft copolymerization were discussed. The extent of grafted copolymerization was verified by hexane and acetone Soxhlet (solvent extraction). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4809–4813, 2006

Key words: EPDM/styrene graft copolymer; benzoyl peroxide; aging effect

INTRODUCTION

Graft copolymer of styrene (St) with ethylene-propylene–diene monomer (EPDM) has been widely studied in recent years. Among the several attempts to improve the weak points of high impact polystyrene (HIPS), the substitution of EPDM for butadiene has been widely investigated.^{1,2} The usual method is to replace the butadiene with EPDM because it has long been known that EPDM has outstanding resistance³ to heat, light, oxygen, and ozone because of its nonconjugated diene component.⁴ In this study, St monomers were grafted onto EPDM under argon atmosphere in the presence of benzoyl peroxide (BPO) as an initiator. Various variables were observed to maximize the yield of product copolymer, such as aging of the solution, the concentration of St and others. The previous BPO reaction on EPDM and St monomer has been preliminary studied.⁵ However, effects of aging the solution before mixing with St has not been mentioned earlier, which could further increase the yield of the copolymer. The excellent properties of the copolymer are that the EPDM-g-PS has a good miscibility between blends with PS⁶ than the normal EPDM and can be distributed in small domain size.⁷

The effects of the reaction time, temperature, initiator concentration, solvents, and aging time on the graft reaction were investigated. The yields of graft

copolymer were analyzed by hexane Soxhlet and acetone Soxhlet. The hexane will dissolve EPDM or the short branch chain of EPDM-g-PS, while acetone will dissolve the polystyrene formed.⁷

EXPERIMENTAL

Materials

The Dupont EPDM 4640 rubber used was donated by S.K. Polymer Co., Thailand. The St monomer used to prepare the copolymer was manufactured by Fluka Chemie A.G., Switzerland, and purified with NaOH and distilled under vacuum before use. The BPO, as a free radical initiator, was manufactured by Merck, Muchen, Germany, and recrystallined in ethanol before use. The solvents such as *n*-hexane, heptane, THF, and toluene were of analytical purity and used as received.

Preparation

EPDM (~ 5 g) was dissolved in 50 mL of toluene and heated at 80°C. The solution was stirred until the EPDM was completely dissolved. Free radical initiator used was BPO, which was recrystallined in ethanol to remove the impurities. St monomer was extracted with NaOH solution (5% w/w) in distilled water, and then was further purified by distilling over sodium under vacuum atmosphere before use.

Graft copolymer polymerization

The copolymerization was conducted in a 250-mL three-neck flask equipped with stirrer, under argon

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Contract grant sponsors: Thailand Research Fund (TRF); TJTTP-J.

atmosphere. The graft reaction was carried out in toluene solvent at 60 or 90°C. To stop the polymerization reaction, excess acidic methanol was added to the reaction solution. The precipitated polymer was washed with methanol and dried under vacuum. The unreacted EPDM was extracted in hexane Soxhlet extractor and the produced polystyrene was further extracted in acetone Soxhlet extractor⁸ for 12 h and the remaining graft copolymer of EPDM and St (EPDM-g-St) was obtained after drying.

RESULTS AND DISCUSSION

The purpose of this work is to limit the optimum condition in the synthesis of graft copolymer of EPDM and polystyrene to improve the properties of the obtained polymer blends. Therefore, this section provides information about some preliminary results concerning the reaction conditions such as polymerization time, polymerization temperature, concentration of initiator, condition of synthesis, effect of solvent as a synthesis medium, and effect of aging for initializing the synthesis. The characterizations of graft copolymer were conducted by NMR and DSC.⁷ Moreover, the tensile strength tests have been used to investigate the mechanical properties reported elsewhere.⁷

Effect of time on synthesis of graft copolymer of EPDM and St

The effect of reaction time was investigated by varying the time for polymerization of EPDM and St in the range of 1–4 h while using BPO as the initiator. The copolymerization was performed in toluene at

90°C using ~ 5 g of EPDM, 1.50×10^{-3} to 2.08×10^{-3} mol/L BPO concentration, with total St concentration of 2.49 mol/L. The influence of time on the synthesis of graft copolymer is shown in Figure 1.

From the previous data of Sheng,⁵ the yield of the copolymer will increase as time goes by and slightly increase after 1 h of polymerization. In a trend similar to that in Sheng's work, the copolymer formed (after extracting with acetone) has the tendency to saturate at certain yield. However, when the polymerization time reaches 4 h, the portion that did not dissolve in acetone (the moderate branch EDPM-g-PS) starts to increase abruptly, which indicated that the growth of the side chains exceeds the solubility limit in hexane (EDPM and short branch EDPM-g-PS will dissolve in hexane), while the quantity of PS formed (that dissolved in acetone) is quite constant. The experiments ceased after 4 h because the activity of the catalytic process are not worth to perform. The difference between Sheng's data and our data is the properties of the EDPM and reaction conditions used, which might lead to different results; but, however the tendency of the graph is very similar.

Effect of BPO initiator concentration on the synthesis of graft copolymer of EPDM and St

The effects of the initiator concentration were investigated under 3 h polymerization times. The concentration of BPO initiator was varied in the range of 2.08×10^{-3} to 6.25×10^{-3} mol/L. The polymerizations were performed in toluene at 90°C using ~ 5 g of EPDM, with St concentration of 2.49 mol/L. The influence of BPO concentration on synthesis of graft copolymer is shown in Figure 2.

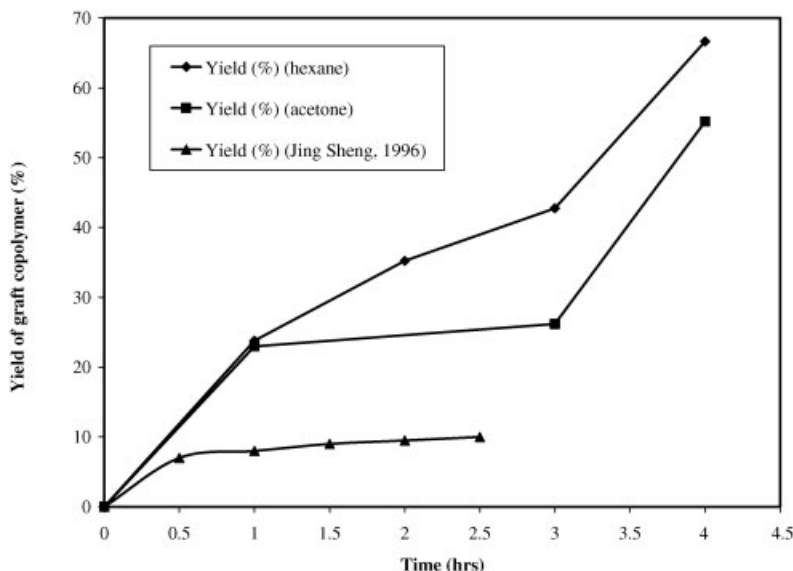


Figure 1 Yield of graft copolymer at different times. Polymerization conditions: EPDM, 3–5 g; [St], 2.49 mol/L (20 mL); BPO, 1.50×10^{-3} to 2.08×10^{-3} mol/L; solvent, toluene; polymerization temperature, 90°C.

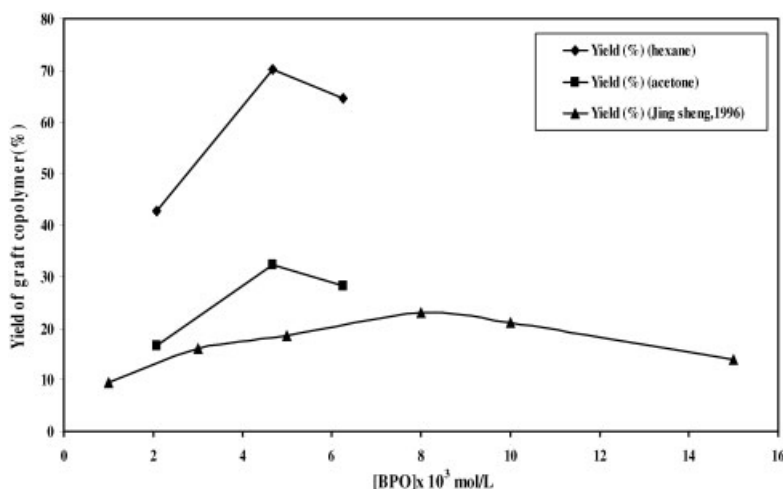


Figure 2 Yield of graft copolymer at different BPO concentrations. Polymerization conditions: EPDM, 5.687 g; [St], 2.49 mol/L (20 mL); time, 3 h; solvent, toluene; polymerization temperature, 90°C.

As shown in Figure 2, the yield of the synthesized graft copolymer increased with increasing concentrations of BPO, leading to a maximum value at about 4.67×10^{-3} mol/L. When the percent of BPO was less than the maximum value, the amounts of monomer radical, polymer radical, and graft copolymer radical increased with increasing concentrations of BPO, which increased the probability of interaction of radicals. When the percent of BPO was in excess, the grafting percent of St onto EPDM was decreased because the reaction of BPO by itself gradually increases. The viscosity of polymerization was increased with synthesis time, and because of the increasing concentration of BPO, which was evident, the movement of radicals was more difficult.⁵ The trend of the results can be compared with Sheng's, but the differences arise due to the dissimilar reaction conditions. (In Sheng's work, concentration of EPDM was 60 g/L, St concentration was 0.3 mol/L, and time of reaction was 2 h.)

Effect of solvents on synthesis of graft copolymer of EPDM and St

The effects of solvents were investigated by using polymerization time of 1 h. The temperature for polymerization of EPDM and St was 60 and 90°C. The

TABLE I
Yield of Graft Copolymer of Each Solvent at 60°C

| Solvent | Yield (%) (hexane) | Activity (g of polymer/(mol of BPO) h) |
|---------|--------------------|--|
| Toluene | 1.65 | 147.83 |
| Hexane | 0.24 | 21.357 |
| Heptane | 2.71 | 203.25 |
| THF | 0.03 | 2.72 |

Polymerization conditions: EPDM, 4–5 g, [St], 1.24 mol/L (10 ml); BPO, 1.507×10^{-3} to 2.039×10^{-3} mol/L; polymerization temperature, 60°C.

polymerizations were performed using ~ 5 g of EPDM, 1.507×10^{-3} to 2.039×10^{-3} mol/L BPO concentrations, with total St concentration of 1.24 mol/L. The influences of solvent on synthesis of graft copolymer are shown in Table I for the reaction at 60°C and in Table II for the reaction at 90°C.

As shown in Table I, at 60°C, yields of graft copolymer were increasing from THF, hexane, toluene, and heptane respectively. However, at the temperature of 90°C, toluene gave more yield than heptane and eight times higher yield from the same solvent at 60°C (Table I). The nature of solvent may also affect k_d (rate of thermal decomposition).⁹ Therefore, rate of thermal decomposition of BPO to give free radical depends on various solvents and temperature, as can be seen. Therefore, at temperature of 90°C, cyclic solvent gives higher initiator radical than linear solvent in the process of high grafting polymer.

Effect of temperatures on the synthesis of graft copolymer of EPDM and St in toluene solvent

The effect of temperature was investigated by using BPO concentrations of 1.507×10^{-3} and 2.039×10^{-3} mol/L at 1 h for polymerization of EPDM and St. The polymerizations were performed in toluene and using ~ 5 g of EPDM and 1.24 mol/L concentration

TABLE II
Yield of Graft Copolymer of Each Solvent at 90°C

| Solvent | Yield (%) (hexane) | Activity (g of polymer/(mol of BPO) h) |
|---------|--------------------|--|
| Heptane | 25.57 | 1915.76 |
| Toluene | 29.30 | 2192.96 |

Polymerization conditions: EPDM, 4–5 g, [St], 1.24 mol/L (10 ml); BPO, 1.507×10^{-3} to 2.039×10^{-3} mol/L; polymerization temperature, 90°C.

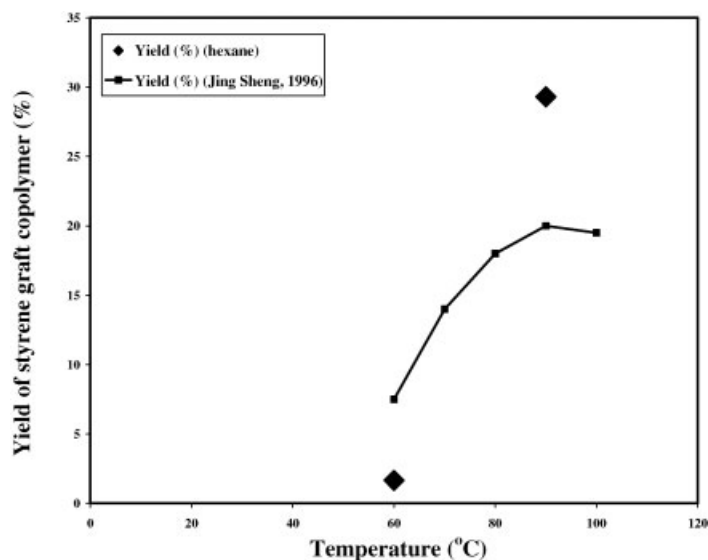


Figure 3 Yield of graft copolymer at different temperatures. Polymerization conditions: EPDM, 4–5 g; [St], 1.24 mol/L (10 mL); BPO, 1.507×10^{-3} to 2.039×10^{-3} mol/L; solvent, toluene.

of St. The influence of temperature on synthesis of graft copolymer is shown in Figure 3.

As shown in Figure 3, yield of graft copolymer increased with increasing temperature, yielding a maximum value at 90°C and then decreased at the same time, presumably because of the reduction of the half-life of BPO with rising temperature,¹⁰ which would increase the number of BPO radicals. When the temperature of the reaction was more than 90°C, the extent of grafting decreased because the number of radicals was decreased while increasing velocity

of decomposition of BPO.⁵ Thus, most of the reactions are commenced at 90°C.

Effect of aging time on synthesis of graft copolymer of EPDM and St

The effect of aging time was investigated by using BPO as the initiator. The time for polymerization of EPDM and St was set at 2 h. The copolymerization was performed in toluene at 90°C using ~ 5 g of EPDM, BPO concentration about 1.50×10^{-3} to 2.08×10^{-3} mol/L,

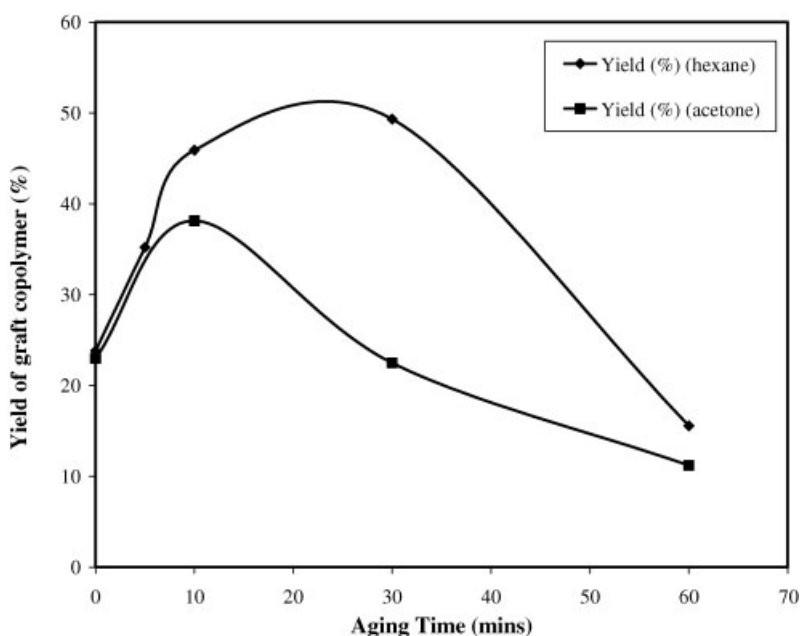


Figure 4 Yield of graft copolymer at different aging times. Polymerization conditions: EPDM, 3–5 g; BPO, 1.5×10^{-3} to 2.08×10^{-3} mol/L; solvent, toluene; polymerization temperature, 90°C; polymerization time, 2 h.

with total St concentration of 2.49 mol/L. The influence of aging time on synthesis of graft copolymer is shown in Figure 4.

As shown in Figure 4, yield of graft copolymer increased with increasing aging time, yielding a maximum value at 10 min (acetone) and 30 min (hexane). After 10 min, the portion that can be dissolved in acetone is increased, which indicates that more polystyrene is formed and can be detected by the portion that dissolved in acetone. However, the aging time is important for the reaction because the initial reaction solutions were very viscous and the reaction of the free radical is impeded by the viscosity of the solution. However, the BPO free radical can be decomposed by as many processes⁷ and too long aging may cause adverse effects on the reactions, which can be clearly seen in Figure 4.

CONCLUSIONS

This research revealed the importance of aging time besides all the process parameters. The increase of the aging time to an appropriate amount will increase the yield of EPDM-g-PS to a larger extent.

However, too much aging time will cause adverse effect on the polymerization reaction. All the process parameters were elucidated, which also comply with the results of Sheng.⁵ Effect of solvents at different temperatures were stated, and in this reaction, toluene is the best solvent.

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