

Graft Copolymerization of Styrene and Acrylonitrile onto EPDM

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ABSTRACT: Acrylonitrile–EPDM–styrene (AES) graft copolymers were synthesized by solution graft polymerization of styrene (St) and acrylonitrile (AN) onto EPDM in an *n*-hexane/benzene solvent with benzoyl peroxide (BPO) as an initiator. The structure changes were studied by an FTIR spectrophotometer. The grafting parameters were calculated gravimetrically. The influence of the polymerization conditions, such as the reaction time, concentration of the initiator, EPDM content, and weight ratio of St/AN, on the structure of the products was investigated. It was found that a proper initiator concentration and EPDM content will give a high

grafting ratio of the AES resin. The thermal property of the copolymer was studied using programmed thermogravimetric analysis (TGA). The results showed that the copolymer has a better heat-resistant property than that of ABS, especially for the initial decomposition temperature (T_{in}) and the maximum weight loss rate temperature (T_{max}). Also, the mechanism of the graft reaction was discussed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 428–432, 2002

Key words: copolymerization; graft copolymers; thermogravimetric analysis (TGA); AES resin; EPDM

INTRODUCTION

The acrylonitrile–butadiene–styrene (ABS) copolymer is one of the most commonly used engineering plastics.¹ For rapid prototyping manufacturing (RPM) technology, the ABS copolymer has also been used.² However, its poor heat resistance and weatherability limit the outdoor use of the material and its blends. Also, the use of ABS resin in fused deposition manufacturing (FDM) technology has been limited because of its decomposition in high extrusion temperatures. So, how to improve the heat resistance and rheological property of ABS resin has become more and more important. Among the several attempts to improve the poor performance, the substitution of the ethylene–propylene–diene terpolymer (EPDM) for butadiene has been widely investigated.^{3,4} The usual method is to replace the butadiene with EPDM, which might be expected to improve the thermal stability of ABS, for it is known that EPDM has outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component. In this study, styrene (St) and acrylonitrile (AN) were grafted onto EPDM under a nitrogen atmosphere in the presence of benzoyl peroxide (BPO) as an initiator. The effects of the reaction time, initiator concentration, EPDM content, and

weight ratio of St to AN on the graft reaction were investigated. The conversion, grafting efficiency, graft ratio, and thermal stability of the graft copolymers were analyzed. Also, the mechanism of the graft reaction is discussed.

EXPERIMENTAL

Materials

AN and St (Tianjin Chemical, Tianjin, China) were purified by standard procedures. BPO (Tianjin Chemical, Tianjin, China) was recrystallized from methanol. EPDM, having ethylidene norbornene as a terpolymer and ethylene/propylene = 50/50 by mol % (Jilin Chemical Industry Corp., Jilin, China, ML 38-52) was used as received. *n*-Hexane and benzene were of analytical purity and distilled prior to use.

Copolymerization

The copolymerization was conducted in a 250-mL four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct. A given amount of EPDM was dissolved in *n*-hexane/benzene (50/50, vol %) in the flask, and then a mixture of St and AN at a given ratio was added with BPO after charging with nitrogen. Then, the reaction was carried out under various experimental conditions (see Table I).

After a chosen period of reaction, the contents were poured into methanol with stirring; the precipitate

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TABLE I
Grafting Copolymerization Conditions

Initiator concentration (%)	0.5, 1, 1.5, ^a 2, 2.5
EPDM content (%)	10, 15, ^a 20, 25, 30
Weight ratio of St/AN	1.5, 2, 2.5, 3 ^a , 4, 5
Solvent	<i>n</i> -Hexane/benzene (vol 50/50)
Reaction temperature, °C	70

^a Fixed when other condition changes.

was filtered and dried in a vacuum oven until a constant weight was achieved. The AN-EPDM-St graft copolymer (AES) was separated from St-co-AN using acetone by extraction using a Soxhlet extractor.⁵

Measurements

The total conversion, grafting ratio, and grafting efficiency of the copolymerization were calculated using the following equations:

$$\text{Total conversion (C) (\%)} = \frac{\text{weight of polymer in grafts}}{\text{weight of monomer charged}} \times 100\%$$

$$\text{Grafting ratio (GR) (\%)} = \frac{\text{weight of polymer in grafts}}{\text{weight of substrate}} \times 100\%$$

$$\text{Grafting efficiency (GE) (\%)} = \frac{\text{weight of polymer in grafts}}{\text{total weight of polymer formed}} \times 100\%$$

Thermal stability was examined with a DuPont 2000 STD-2960 instrument at a scanning rate of 10°C/min in a static air atmosphere. The half-weight loss temperature (T_{50}) was obtained when the weight loss of the copolymer reached 50%. The initial decomposition temperature (T_{in}) and maximum weight loss rate temperature (T_{max}) were given by the computer program. Inherent viscosity was measured using an Ubbelohde viscometer and a 0.1 g/dL solution at 25°C and trichloromethane was used as a solvent.

RESULTS AND DISCUSSION

The molecular structure of the AES copolymer and EPDM were identified by a FTIR spectrophotometer (Bruker vector 22). The FTIR spectra of EPDM and the AES resin with different reaction times are shown in Figure 1. The FTIR spectrum of AES exhibited characteristic absorption bands at 2238 cm^{-1} (stretching vibration of $\text{CN}\equiv\text{N}$) and 760 and 700 cm^{-1} (characterization of the monosubstituted benzyl ring) which did

not appear in the spectrum of EPDM. Therefore, the monomers of St and AN were grafted onto the molecular chain of EPDM. The absorbance of these groups also increased when the reaction time lasted from 1 to 10 h. This indicates that the grafting ratio increased.

Effect of reaction time

The grafting reaction was carried out with a fixed BPO concentration (1.5% wt) and EPDM content (15% wt) at 70°C. The reactivity ratios of St and AN were reported to be 0.40 and 0.04, respectively.⁶ This indicates that St and AN are easily copolymerized with each other and it is difficult to form a homopolymer unless the conversion becomes too high even if the feed composition is far from the azeotropic point. The weight ratio of St to AN was fixed at 3.0, which is close to the azeotropic point of copolymerization of St with AN. The weight ratio of St/AN at the azeotropic point was calculated to be 3.13/1 according to the reactivity ratios of St and AN.

The effect of the reaction time on the graft copolymerization is shown in Table II. As shown, the grafting efficiency decreased rapidly with a reaction time increase and then leveled off when the reaction proceeded. This may be because the active spot of EPDM rapidly reacted and decreased with the proceeding of the graft reaction. With the proceeding of the reaction, the radical has much less chance to react with the EPDM macromolecule, which is in accord with that the graft ratio almost reached its maximum value soon

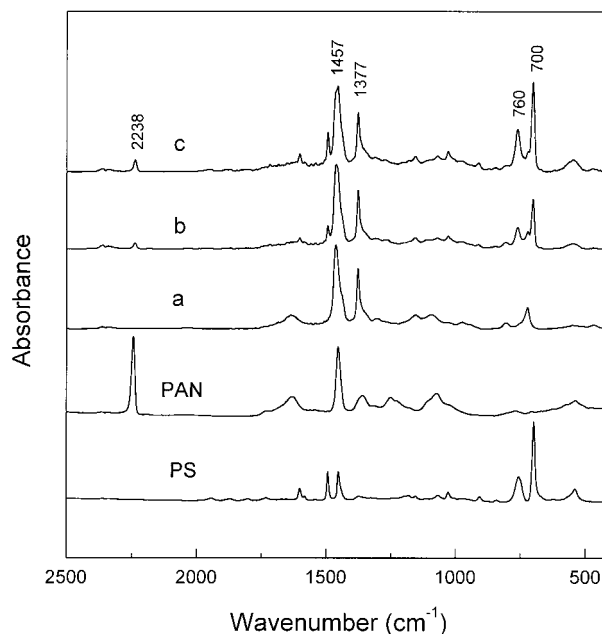


Figure 1 FTIR spectra of AN-EPDM-St graft copolymer and EDPM terpolymer: (a) EDPM; (b) reaction time, 1 h; (c) reaction time, 10 h.

TABLE II
Graft Copolymerization at Different Reaction Times

Measurement	Time (h)									
	1	3	5	6	8	10	11	12	14	14 ^a
C (%)	4.12	17.00	34.14	42.69	61.96	73.33	75.95	78.93	81.72	63.3
GR (%)	12.41	22.32	25.98	25.78	33.33	36.88	37.46	38.38	38.76	35.97
GE (%)	60.63	29.82	18.14	14.35	14.25	14.06	13.91	13.94	13.68	15.66

^a Semibatch method; reaction time, 14 h.

after the reaction started and then did not change. When the reaction time reached 10 h, the graft reaction almost stopped. So, for all the graft reactions, the reaction times were kept at 14 h to reach a high conversion of the monomers.

The mechanism of the graft copolymerization of St and/or AN onto EPDM was reported. Some researchers thought that the initiator radicals react with EPDM at first and then induce the polymerization of monomers.⁷ But some thought that the graft copolymerization was caused by the monomer radicals.⁸ To make this clear, a semibatch reaction was carried out. The monomers of St and AN were added to the reaction system gradually. So, the concentration of the monomer in the system became very low. If the graft reaction was induced by the reaction of EPDM with the initiator radical, a considerably high grafting efficiency will be obtained by this method. But the results in Table II showed that this is not the case. The grafting efficiency increased insignificantly, which indicates that the monomer radical formed at first. Also, the grafting ratio is a little lower because of the lower monomer concentration.

Effect of initiator concentration

Figure 2 shows the effect of the initiator concentration on the graft copolymerization. The reactions were also performed at 70°C for 14 h in *n*-hexane/benzene (50/50 vol %) with a weight ratio of St to AN fixed at 3.0. It is reasonable to observe that the total conversion increases with an increasing BPO concentration. But the grafting efficiency decreases with an increasing initiator concentration. The result is expected since the random copolymer formed more readily than did the graft copolymer as the initiator concentration increased. When the BPO concentration is more than 1.0%, the grafting efficiency is always around 14%. The grafting ratio is determined by both the total conversion and the grafting efficiency. With a low BPO concentration, the low total conversion predominated, in spite of the rather high grafting efficiency. But when the total conversion increases insignificantly, the decreasing grafting efficiency be predominate over the grafting ratio. So, the grafting ratio passes a maximum with increase of the BPO concentration.

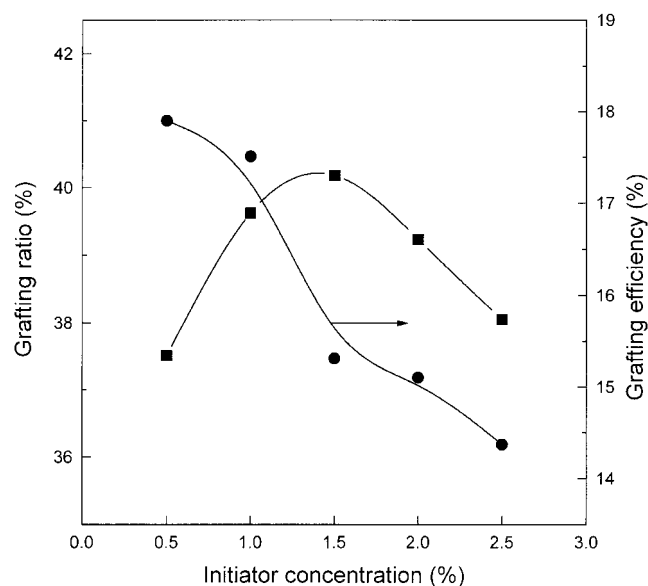


Figure 2 Effect of initiator concentration on graft copolymerization.

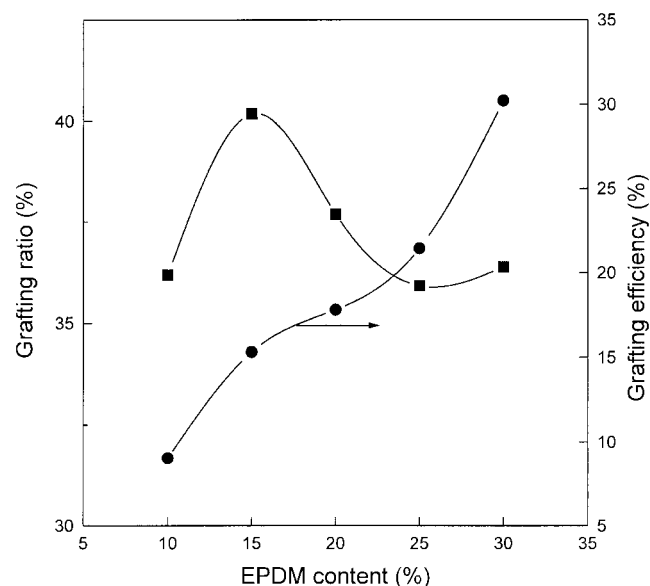


Figure 3 Effect of EPDM content on graft copolymerization.

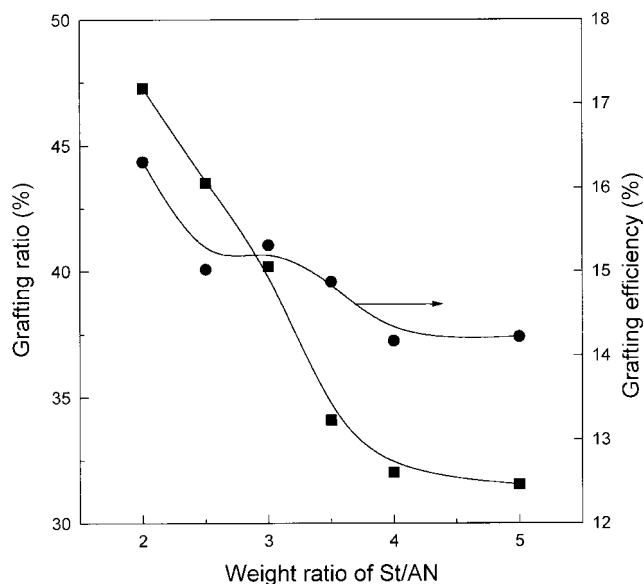


Figure 4 Effect of weight ratio of St/AN on graft copolymerization.

Effect of EPDM content

Figure 3 shows the effect of the EPDM content on the graft copolymerization. The results show that the grafting efficiency increases with the EPDM content. This is because the higher EPDM content will afford more opportunities for monomer radicals to react and then more monomer will graft onto EPDM. But the grafting ratio appears to be maximum when the EPDM content is 15 wt % of the total monomer and the EPDM content. The result is reasonable because the grafting ratio was determined not only by the grafting efficiency, but also by the EPDM content. No doubt, a too high EPDM content will cause a lower grafting ratio even if the grafting efficiency increases. So, the maximum grafting ratio appears when the EPDM content is proper.

Effect of weight ratio of St/AN

The effect of the weight ratio of St to AN on the graft copolymerization is shown in Figure 4. It can be seen that the grafting efficiency decreases with an increasing weight ratio of St to AN to 5.0. This effect may be explained by considering the different activities of the St and AN radicals. It is known that the AN radical is 10 times more active than is the radical of St because of the resonance stabilization of the benzyl ring to St.⁶ When more AN is charged, more AN radicals will form and then will cause a greater graft reaction. So, more radicals will graft onto the EPDM macromolecule. Thus, grafting efficiency will increase.

TABLE III
Inherent Viscosities of Graft Copolymers

Initiator concentration (%)	$[\eta]$ (dL/g)	EPDM content (%)	$[\eta]$ (dL/g)	St/AN	$[\eta]$ (dL/g)
0.5	1.92	10	1.93	2	2.55
1	2.03	15	2.35	2.5	2.40
				3	2.35
1.5	2.35	20	2.31	3.5	2.26
2	2.10	25	2.10	4	1.79
2.5	1.84	30	2.01	5	1.72

Inherent viscosities

The inherent viscosity, as a measure of molecular weight, was obtained using an Ubbelohde viscometer and is summarized in Table III. It is seen that the inherent viscosity of AES strongly depends on the concentration of the initiator, the EPDM content, and the St/AN weight ratio, which is closely related to the grafting ratio, as described in the previous section.

A plot of inherent viscosities versus grafting ratios is shown in Figure 5. Obviously, the inherent viscosity was determined solely by the grafting ratio even when the weight ratio of St/AN was not fixed. Under this condition, the molecular structure of the AES resin was only affected by the ratio of the total amount of St and AN in the graft copolymer. A higher grafting ratio means that a higher molecular weight and a higher inherent viscosity will be observed.

Thermal stability

TG curves of commercially available ABS (Taiwan Qimei Ltd. 747, Tainan, Taiwan), the EPDM used, and

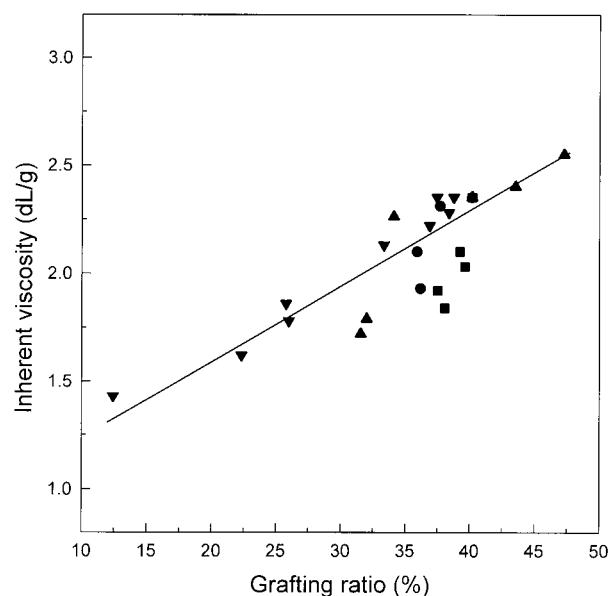


Figure 5 Inherent viscosities of AES resin versus grafting ratios.

the synthesized AES resin are shown in Figure 6 and the results data are listed in Table IV for comparison. The initial decomposition temperature of ABS is 387.3°C and those of EPDM and AES synthesized with different reaction times are 412.8 and 405.1°C and 398.8 and 394.6°C, respectively. Similar behavior was also observed for T_{50} . It is seen that the heat resistance follows the order $AES \approx EPDM > ABS$. It should be pointed out that all the AES resins show superior thermal stability with a higher thermal degradation temperature to ABS regardless of the copolymerization conditions. The good thermal stability of AES may be attributed to the EPDM unit in the copolymer having a high heat-resistance property. It can also be seen that the T_{in} of AES decreases with an increasing reaction time, that is, the grafting ratio. This is because the SAN copolymer has a lower decomposition temperature. When the weight ratio of St/AN is 3/1, T_{in} and T_{50} were reported to be 328.4 and 378.2°C, respectively.⁹ No doubt, the introduction of St and AN to the macromolecular chain of EPDM will decrease its T_{in} . The maximum weight loss rate temperature, T_{max} , of

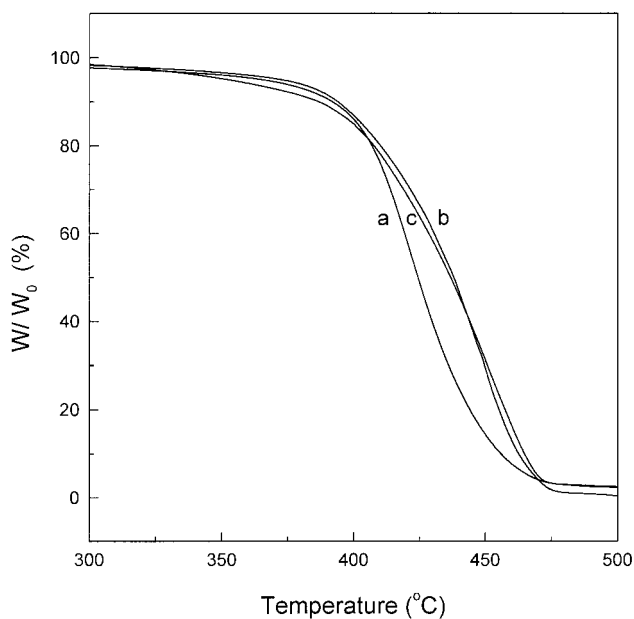


Figure 6 TG curves of ABS, EPDM, and AES resins: (a) ABS; (b) EPDM; (c) AES of reaction time 1 h.

TABLE IV
TG Results of ABS, EPDM, and Synthesized AES Resin

Temperature	ABS	EPDM	AES ^a	AES ^b	AES ^c
T_{in} (°C)	387.3	412.8	405.1	398.8	394.6
T_{50} (°C)	430.3	438.1	436.9	435.4	432.9
T_{max} (°C)	419.3	450.0	450.4	451.6	454.3

^a Reaction time: 1 h.

^b Reaction time: 10 h.

^c Reaction time: 14 h.

EPDM was found to be about 31°C higher than that of ABS and the T_{max} of the AES resin further increased when the grafting ratio was increased. This may be because the weight loss in this temperature range should be attributed to the EPDM chain and the diene component has reacted with St and/or AN.

CONCLUSIONS

The molecular structure of the synthesized AES resin, the grafting efficiency, and the grafting ratio of the copolymerization were affected by the concentration of the initiator, the EPDM content, and the weight ratio of St/AN. A high grafting ratio will be reached with proper copolymerization conditions. The synthesized AES resin has a good heat-resistant property, near to that of EPDM but higher than that of ABS. It may substitute ABS in the FDM technology because of its high heat-resistant property.

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