Journal of Macromolecular Science, Part A

Synthesis and Characterization of Acrylonitrile-EPDM-1-Vinylnaphthalene Graft Terpolymer

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SYNTHESIS AND CHARACTERIZATION OF ACRYLONITRILE–EPDM–1-VINYLNAPHTHALENE GRAFT TERPOLYMER

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Key Words: Graft copolymerization; Acrylonitrile–EPDM–1-vinylnaphthalene graft terpolymer; Ethylene–propylene–diene terpolymer (EPDM); Characterization; Light resistance; Thermal stability; Tensile properties; Acrylonitrile–butadiene–styrene copolymer (ABS); Acrylonitrile–EPDM–styrene copolymer (AES)

ABSTRACT

The graft copolymerizations of acrylonitrile (AN) and 1-vinylnaphthalene (1-VN) onto ethylene–propylene–diene terpolymer (EPDM) were carried out with benzoyl peroxide (BPO) as an initiator in toluene. The effects of the mole ratio of 1-VN to AN, initiator concentration, reaction time, reaction temperature, and EPDM concentration on the graft copolymerizations were examined. The synthesized graft terpolymers, acrylonitrile–EPDM–1-vinylnaphthalene (AEV_1), were identified by IR spectra. The thermal stability and tensile strength of AEV_1 were greatly improved compared with those of ABS. The light resistance and weatherability of AEV_1 were better than those of ABS when subjected to UV light for longer than 96 hours.

INTRODUCTION

As is well known, the acrylonitrile–butadiene–styrene (ABS) terpolymer is one of the most commonly used engineering plastics because of its high impact strength

and rigidity. However, its poor heat resistance and weatherability limit the outdoor use of the material and its blends [1–3]. Thus, modification of the ABS terpolymer has attracted much interest over the years. Among several attempts to improve the poor performance, the substitution of ethylene–propylene–diene terpolymer (EPDM) for butadiene has been investigated in this laboratory [3–6]. EPDM has outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component [7–15].

The aim of this study is to improve the heat resistance, light resistance, and weatherability of ABS resin using EPDM in place of butadiene rubber (BR) and 1-vinylnaphthalene (1-VN) in place of styrene. 1-VN was selected because of its high glass transition temperature. Acrylonitrile (AN) and 1-VN were grafted onto EPDM under argon atmosphere in the presence of benzoyl peroxide (BPO) as an initiator. The effects of the mole ratio of 1-VN to AN, initiator concentration, reaction time, reaction temperature, and EPDM concentration were investigated in graft copolymerizations. The light resistance, weatherability, thermal stability, and tensile properties of the graft terpolymer were analyzed.

EXPERIMENTAL

Materials

Acrylonitrile (Junsei Chemical) was purified by standard procedures. Benzoyl peroxide (Hayashi Chemical) was recrystallized from methanol. Ethylene–propylene–diene terpolymer (EPDM), with ethylidene norbornene as a termonomer (Aldrich Chemical: ethylene/propylene = 50/50 mol%, ML50, $\overline{M}_n$ = 50,500; $\overline{M}_w$ = 102,000), was used as received. 1-Vinylnaphthalene (1-VN) monomer was prepared by dehydration of 1-naphthalene ethanol [16]. ABS (Japan Synthetic Rubber Co.; JSR 10 grade) and AES (Japan Synthetic Rubber Co.; JSR 110 grade) were used for comparison. n-Hexane, dimethylformamide (DMF), acetone, toluene, and tetrahydrofuran (THF) were distilled prior to use.

Synthesis of Acrylonitrile–EPDM–1-Vinylnaphthalene Graft Terpolymer (AEV₁)

A given amount of EPDM was dissolved in 250 mL toluene in a 1-L separable flask provided with a modified Hopkins cooler, a thermometer, and a gas inlet [5]. After dissolution, a mixture of 1-VN and AN with BPO was added into the flask. Taking a copolymerization of 1.0 mole ratio of 1-VN to AN and 7.5 wt% of BPO as an example, a solution of 15.5 g (0.1 mol) 1-VN, 5.3 g (0.1 mol) AN, and 1.56 g (7.5 wt%) BPO in 30 mL toluene was introduced into the flask. The flask was sealed after charging with argon, and the reaction was carried out under various experimental conditions (see Table 1). After a predetermined period of reaction, the contents were poured into methanol under stirring, the precipitate was filtered and dried in vacuo. The nongrafted EPDM was extracted by using n-hexane. The acrylonitrile–EPDM–1-vinylnaphthalene (AEV₁) graft terpolymer was isolated from

TABLE 1.   Graft Copolymerization Conditions Used in This Study

Condition	Description
Mole ratio of [1-VN]/[AN]	0.5, 1.0, 2.0
Initiator concentration (based on the	
Monomers + EPDM) (wt%)	0.5, 2.5, 5.0, 7.5, 10
Reaction time (hours)	20, 40, 60, 90
Reaction temperature (°C)	50, 60, 70, 80
EPDM concentration (%)	5, 7.5, 10, 15, 20

precipitated mixtures using DMF, toluene, and acetone. Details of the isolation procedure of the graft terpolymer are schematically shown in Fig. 1.

The total conversion (%), grafting ratio (%) and grafting efficiency (%) were estimated from the following equation [17]:

$$\text{total conversion (\%)} = \frac{\substack{\text{weight of monomers (AN + 1VN)} \\ \text{reacted onto EPDM}}}{\text{weight of monomer charged}} \times 100$$

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

$$\text{grafting efficiency (\%)} = \frac{\text{weight of polymer in grafts}}{\substack{\text{weight of monomers (AN + 1VN)} \\ \text{reacted onto EPDM}}} \times 100$$

Measurements

Structure Identification.   The chemical structure of polymers was identified by IR spectrophotometry (Perkin-Elmer 1330).

Thermogravimetric Analysis (TGA).   Thermal stability was examined with a Shmadzu DT 30A TGA instrument at a scanning rate of 15°C/min in nitrogen.

Viscosity.   The viscosities of AEV_1 terpolymers were measured at 30°C in THF by using a Cannon-Fenske viscometer.

Light Resistance.   The light resistance was determined using a Fade-o-Meter (Atlas) (at 60°C and 65% relative humidity) and a color difference meter (NP-101DP). The film specimens were cast from THF solutions (3 wt%) on a nonyellowing urethane-coated hiding paper. The films were slowly dried at room temperature and then kept under vacuum until they reached constant weight. The cross-sectional area of the films was 3×5 cm^2 and the thickness was 35 μm. The color difference (ΔE) of the samples after exposure to UV was calculated by using the Hunter–Schofield equation [6].

```
                        ┌─────────────────┐
                        │    Product      │
                        │    (11.7g)      │
                        └─────────────────┘
                                 │
     soluble                     │  <──n-Hexane
  ┌──────────────────────────────┴────────────────────────┐
  │                                          insoluble     │
  │                                                        │
┌───────────┐                          ┌──────────────────────────┐
│  EPDM     │                          │  Poly(AN-co-1-VN)         │
│  (0.5g)   │                          │  Poly(AN-g-EPDM)          │
│           │                          │  Poly(EPDM-g-1-VN)        │
└───────────┘                          │   &   AEV₁   (11.2g)      │
                                       └──────────────────────────┘
                                                   │
                                                   │  <── DMF
                      insoluble                    │     soluble
           ┌──────────────────────────────────────┴──────────────────────────┐
           │                                                                  │
   ┌────────────────────────┐                              ┌─────────────────────────┐
   │ Poly(AN-g-EPDM) &       │                              │ Poly(AN-co-1-VN)        │
   │ Poly(EPDM-g-1-VN)       │                              │   & AEV₁   (10.5g)      │
   │      (0.7g)             │                              │                         │
   └────────────────────────┘                              └─────────────────────────┘
              │                                                        │
              │  <── Toluene                                           │  <── Acetone
   insoluble  │   soluble                                  soluble     │  insoluble
   ┌──────────┴──────────┐                              ┌──────────────┴──────────┐
   │                     │                              │                         │
┌────────────┐  ┌────────────────┐              ┌────────────────┐  ┌──────────┐
│Poly(AN-g-  │  │Poly(EPDM-g-1-VN)│             │Poly(AN-co-1-VN │  │  AEV₁    │
│EPDM)       │  │                 │             │                │  │          │
│(0.5g)      │  │    (0.2g)       │             │    (0.9g)      │  │ (9.6g)   │
└────────────┘  └────────────────┘              └────────────────┘  └──────────┘
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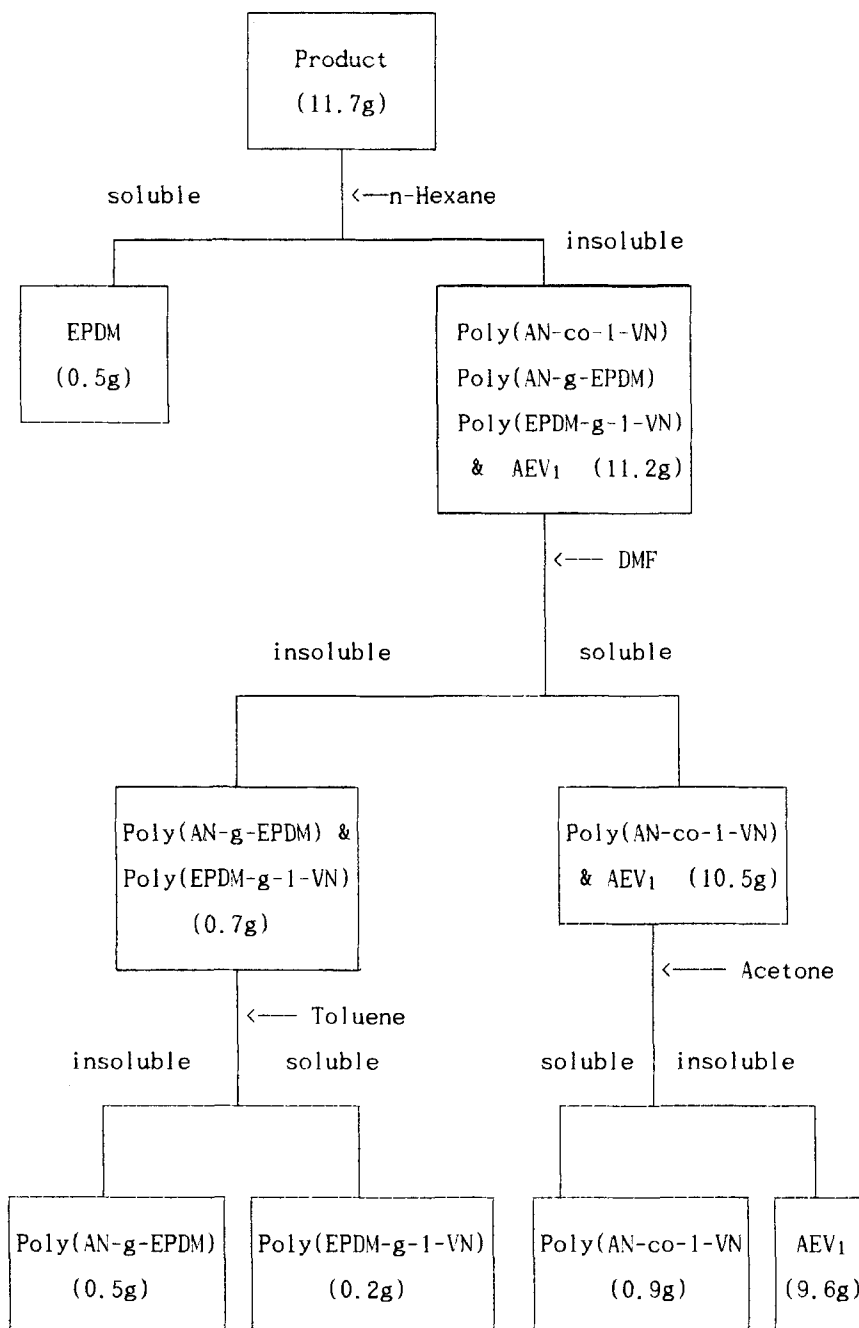
FIG. 1.   Block diagram of graft terpolymer (AEV₁) isolation process. The numbers in parentheses denote the weights of each isolated polymer. (Notations are described in the text.)

Weatherability

The weather resistance (ASTM G53) was measured at 60°C by using a Q panel UV B 313 Weathering Tester coupled with a UV lamp of 315–280 nm in wavelength. The film specimens were prepared by the same method as described for the measurement of light resistance. The color difference (ΔE) of the samples after exposure to UV and moisture was compared by the same method as applied to test light resistance.

Tensile Properties

The tensile tests were carried out using an Instron tensile tester (Model 4204). The samples were prepared following the procedure of ASTM D 638-84. The crosshead speed was 5 mm/min, and the initial gauge length was adjusted to 25 mm.

RESULTS AND DISCUSSION

Characterization

The structure of AEV_1 was confirmed by IR examination (Perkin-Elmer 1330). The IR spectrum of AEV_1 exhibited characteristic absorption bands at 3025 cm^{-1} (stretching vibration of aromatic C–H bond), 2920 cm^{-1} (stretching vibration of aliphatic C–H bond), 2225 cm^{-1} (stretching vibration of C≡N group), 1465 cm^{-1} (scissoring of CH_2), 1368 cm^{-1} (bending of CH_3), and 860 and 820 cm^{-1} (out-of-plane bending vibration of aromatic C–H). The inherent viscosities of the graft terpolymers with different copolymerization conditions are shown in Table 2. The inherent viscosities of AEV_1 terpolymers ranged from 0.21 to 0.44 dL/g. It is seen that the inherent viscosity of AEV_1 increases as the grafting efficiency increases, regardless of the copolymerization conditions.

Further studies should be carried out on the accurate characterization of the terpolymer compositions, such as mole percentages of AN and 1-VN in the graft terpolymer, even though the determination of a terpolymer composition is not easy. For reference, elemental analysis (Carlo Erba 1108) for a typical AEV_1 with a 1/1 feed mole ratio of 1-VN to AN gives the following results: C, 86.52; H, 8.78; N, 2.36%. In this case, the grafted AEV_1 was synthesized with 7.5 wt% of BPO at 70°C for 40 hours.

Effect of Reaction Conditions on the Graft Copolymerizations of AN and 1-VN onto EPDM

Effect of Mole Ratio

The effect of the mole ratio of 1-VN to AN on the graft copolymerization onto EPDM is shown in Table 3. The reaction was carried out in toluene with BPO (7.5 wt%) as an initiator at 70°C for 40 hours. It can be seen that the grafting efficiency as well as the total conversion and grafting ratio increased with an increasing mole ratio of 1-VN to AN.

TABLE 2.   Inherent Viscosity of AEV_1s

Experiment No.[a]	Samples	η_{inh}[b]	Experiment No.[a]	Samples	η_{inh}[b]
1	AEV_1 (20h)	0.24	4	AEV_1 (50°C)	0.23
	AEV_1 (40h)	0.32		AEV_1 (60°C)	0.36
	AEV_1 (60h)	0.33		AEV_1 (70°C)	0.32
	AEV_1 (90h)	0.34		AEV_1 (80°C)	0.27
2	AEV_1 (5%)	0.21	5	AEV_1 (0.5%)	0.29
	AEV_1 (7.5%)	0.26		AEV_1 (2.5%)	0.33
	AEV_1 (10%)	0.32		AEV_1 (5.0%)	0.44
	AEV_1 (15%)	0.33		AEV_1 (7.5%)	0.32
	AEV_1 (20%)	0.38		AEV_1 (10%)	0.31
3	AEV_1 (0.5)	0.26			
	AEV_1 (1.0)	0.32			
	AEV_1 (2.0)	0.31			

[a]Experiment No. 1, effect of reaction time; 2, effect of EPDM concentration; 3, effect of mole ratio of 1-VN to AN; 4, effect of reaction temperature; 5, effect of initiator concentration.

[b]η_{inh}: dL/g in THF at 30 ± 0.01°C.

Effect of Initiator Concentration

Figure 2 shows the effect of initiator concentration on graft copolymerization. In this case, the reaction was carried out in toluene with a 1.0 mole ratio of 1-VN to AN at 70°C for 40 hours. The grafting efficiency increased with increasing initiator concentration up to 5.0 wt%, but thereafter it decreased slightly with any further increase of initiator concentration. The decrease in the grafting efficiency at higher initiator concentrations is expected since the homopolymer is formed more readily than the graft copolymer as the initiator concentration is increased. This result is in agreement with Voek's work [18].

TABLE 3.   Effect of Mole Ratio of 1-VN and AN on the Graft Copolymerization of 1-VN and AN onto EPDM[a]

Mole ratio [1-VN]/[AN]	Total conversion, %	Grafting ratio, %	Grafting efficiency, %
0.50	46	265	61
1.00	50	378	82
2.00	51	400	83

[a]EPDM, 15%. Solvent, Toluene. Reaction temperature, 70°C. Reaction time, 40 hours. BPO, 7.5 wt%.
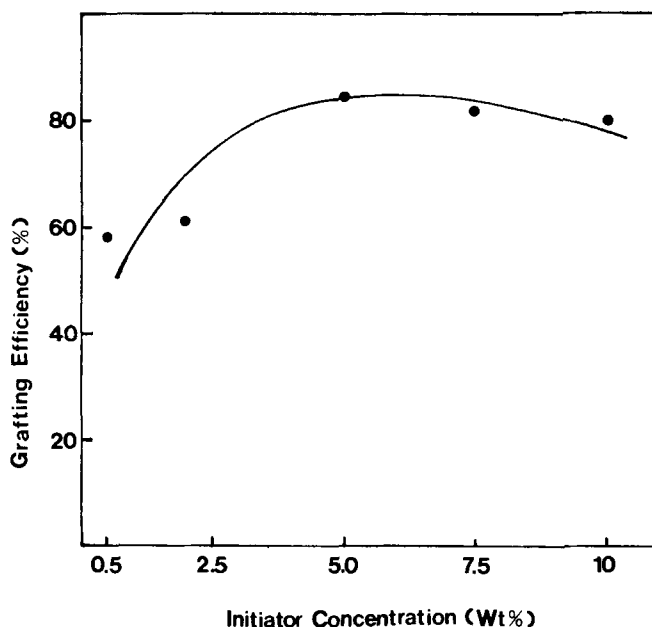
FIG. 2.   Plot of grafting efficiency vs initiator concentration: [1-VN]/[AN]; 1.0; reaction temperature, 70°C; solvent, toluene; reaction time, 40 hours. The initiator concentration is based on the monomers + EPDM.

Effect of Reaction Time

The effect of reaction time on the grafting process is shown in Fig. 3. In this case, the mole ratio of 1-VN to AN was 1.0 and the reaction was at 70°C. The grafting efficiency increased with reaction time up to 40 hours but thereafter leveled off. With an increase in reaction time, the radicals have more time for reaction, and as a result an increase in grafting efficiency is observed. After some time, all the initiator is used up, and no further change in grafting efficiency with reaction time is observed.

Effect of Reaction Temperature

Figure 4 shows the effect of reaction temperature on graft copolymerization. The reaction was performed in toluene with 7.5 wt% BPO and 1.0 mole ratio of 1-VN to AN for 40 hours. On increasing the temperature, the grafting efficiency pass through a maximum. The grafting efficiency depends on the number of active sites available. An increase in temperature is expected to increase the rate of grafting. With an increase in temperature, however, the rate of homopolymerization also increases. As a result, the grafting efficiency increases initially, but on any further increase in temperature the grafting efficiency decreases. A similar observation was made by Porejko et al. [19, 20] for the grafting of maleic anhydride onto LDPE.
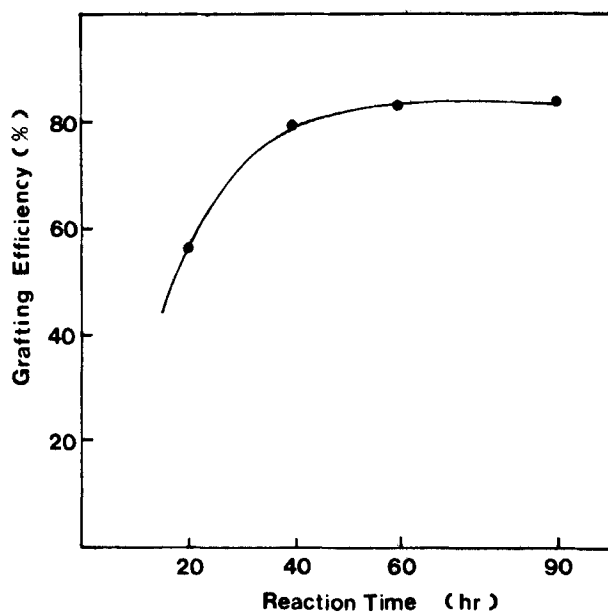
FIG. 3.   Plot of grafting efficiency vs reaction time: [1-VN]/[AN], 1.0; reaction temperature, 70°C; solvent, toluene; BPO, 7.5 wt%.
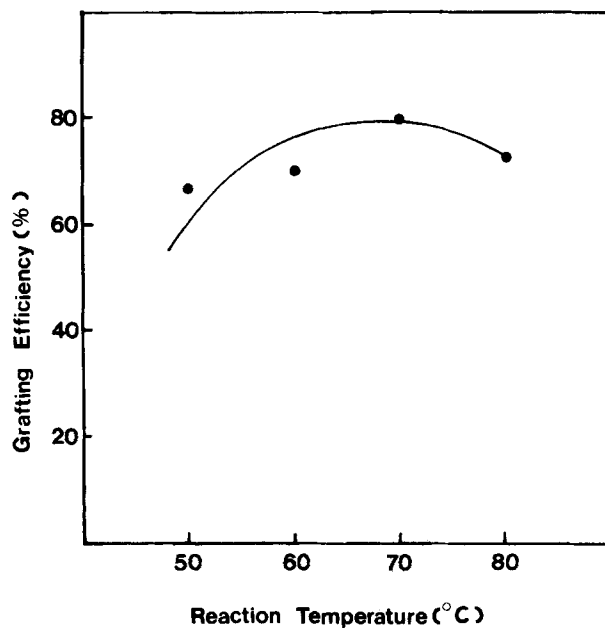

FIG. 4.   Plot of grafting efficiency vs reaction temperature: [1-VN]/[AN], 1.0; reaction time, 40 hours; solvent, toluene; BPO, 7.5 wt%.
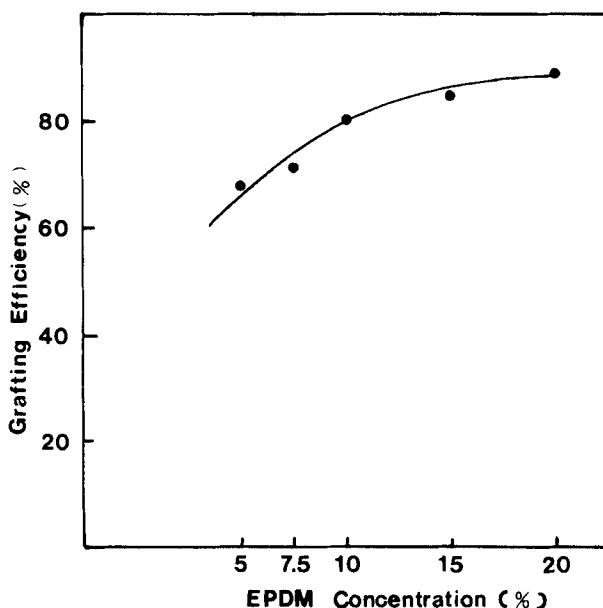
FIG. 5.   Plot of grafting efficiency vs EPDM concentration: [1-VN]/[AN], 1.0; reaction temperature, 70°C; solvent, toluene; reaction time, 40 hours; BPO, 7.5 wt%.

Effect of EPDM Contents

The effect of EPDM contents on graft copolymerization is shown in Fig. 5. The grafting efficiency gradually increases with the EPDM content. This result is probably due to the increasing diene content of the graft site in EPDM as the EPDM content is increased [21]. The reaction was carried out at 70°C for 40 hours in toluene at a mole ratio of 1-VN to AN of 1.0.

Thermal Stability

The TGA curve of a synthesized AEV_1 is shown in Fig. 6. The thermal data of commercially available ABS and AES are also shown for comparison. For this figure, the grafted AEV_1 was synthesized with a 1.0 mole ratio of 1-VN to AN and 7.5 wt% of BPO at 70°C for 40 hours. It is clear that the AEV_1 shows superior thermal stability at the highest thermal degradation temperature compared to ABS and AES. As shown in Fig. 6, the decomposition temperatures of ABS, AES, and AEV_1 are 370, 390, and 430°C, respectively. The residual weight at 450°C of AEV_1 is 60% whereas those of the other polymers are below 25%. The good thermal stability of AEV_1 may be attributed to the synergistic effect of the EPDM and 1-VN components in the copolymer because of their inherent high heat resistances [22, 23].
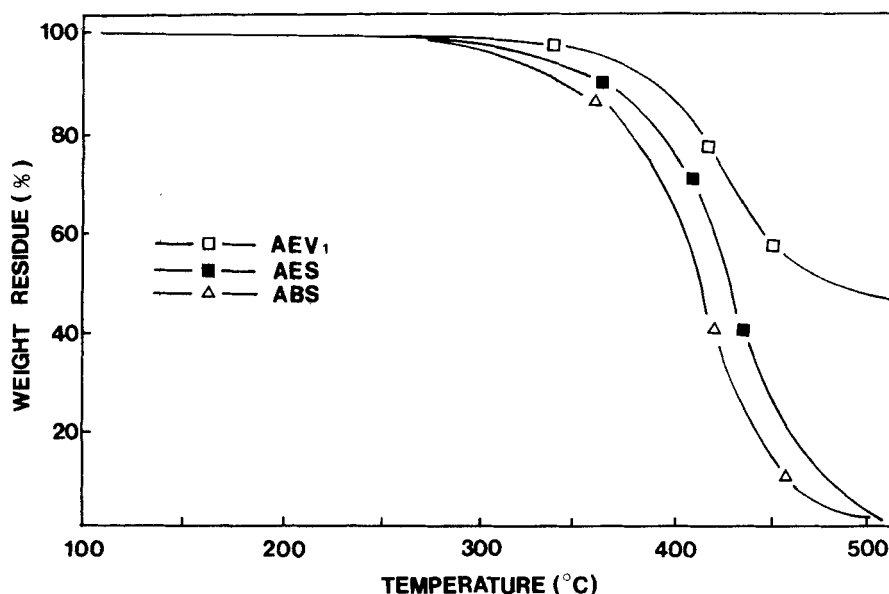
FIG. 6.   TGA curves of ABS, AES, and AEV$_1$: heating rate, 15°C/min in nitrogen.

Tensile Properties

The tensile properties of AEV$_1$, AES, and ABS are listed in Table 4. The grafted AEV$_1$ shown in this table was prepared at 70°C for 40 hours in toluene with a mole ratio of 1-VN to AN of 1.0. The effect of the reaction conditions on the tensile properties was not significant. Note that the AEV$_1$ has the highest tensile strength compared to AES and ABS.

Light Resistance and Weatherability

The weatherability of polymers is a very important factor governing other long-term properties. Primary causes of the deterioration of polymers include sunlight, temperature, moisture, and pollutants. There are some experimental tech-

TABLE 4.   Comparison of the Tensile Properties
of ABS, AES, and AEV$_1$[a]

Material	Tensile strength, kg/cm^2	Elongation at break, %
ABS	295	8.4
AES	311	3.7
AEV$_1$	356	2.1

[a]AEV$_1$ synthesized from graft copolymerization of 1-VN and AN onto EPDM. [1-VN]/[AN] = 1.0. Solvent, toluene. Reaction time, 40 hours. Reaction temperature, 70°C. BPO, 7.5 wt%.

niques for testing the weather resistance of materials [24]. We applied two kinds of accelerated weathering tests to compare the weatherability and the light resistance; Fade-o-Meter and Weather-o-Meter. The light resistance and weatherability were semiquantitatively expressed in terms of color difference (ΔE) with the National Bureau of Standards Unit. A smaller ΔE means better light resistance and weatherability [25, 26]. The samples were tested in a Fade-o-Meter for measurements of light resistance for 24, 48, 72, 96, 120 and 144 hours, and in a Weather-o-Meter for measurements of weatherability for the same time intervals. Figure 7 shows the light resistance of EPDM, ABS, and AEV_1. The grafted AEV_1 with 1.0 mole ratio of 1-VN to AN was synthesized at 70°C for 40 hours in toluene. The ΔE data of commercially available EPDM and ABS (the same grade as referred to in Fig. 6) are also shown for comparison. When samples were exposed to UV light for less than 72 hours, the AEV_1 showed poorer light resistance than ABS or EPDM. It should be noted, however, that AEV_1 shows better light resistance than ABS when exposure to UV light in the Fade-o-Meter is for longer than 96 hours, even though AEV_1 does not show better light resistance than does EPDM.

Similar results were also observed in the weatherability data. The weatherabilities of EPDM, ABS, and AEV_1 are also shown in the insert of Fig. 7. The weather-
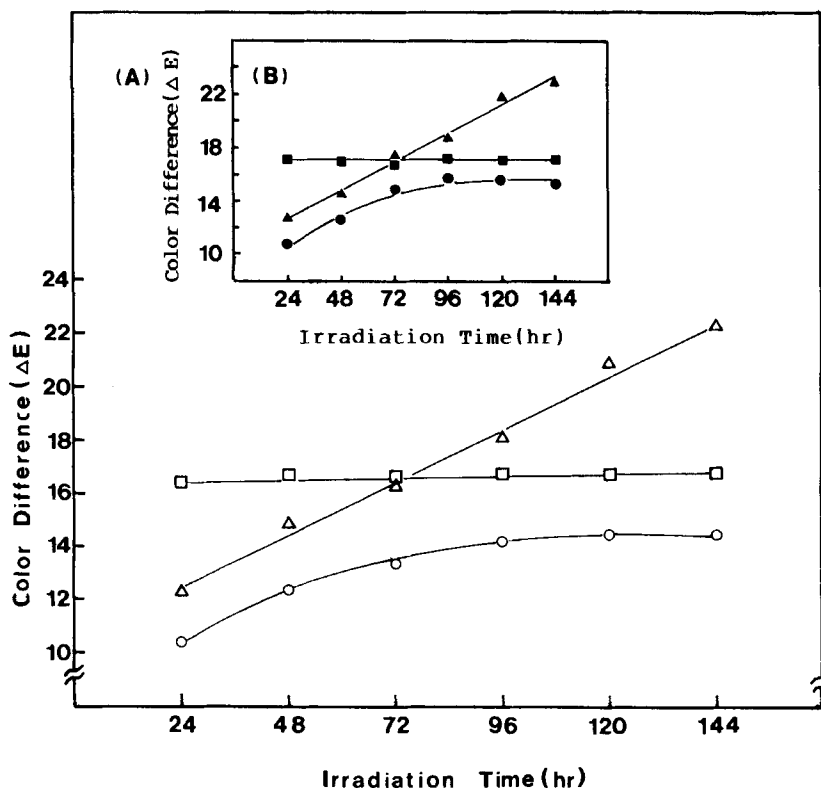

FIG. 7. Plots of color difference vs irradiation time for various samples (A) by Fade-o-Meter and (B) by Weather-o-Meter. EPDM (○, ●), ABS (△, ▲), AEV_1 (□, ■).

ability in terms of color difference of AEV_1 was almost constant over the entire irradiation times, whereas that of ABS increased with increasing irradiation time. Thus, it is concluded that our AEV_1 shows better weatherability than does ABS, and that the good weatherability of AEV_1 is more prominently observed when it is exposed to UV light for more than 96 hours.

CONCLUSIONS

Acrylonitrile–EPDM–1-vinylnaphthalene graft terpolymer (AEV_1) was synthesized with benzoyl peroxide by a solution polymerization technique. The dependence of material properties on the various reaction conditions was investigated. The important results are summarized as follows:

1. In the graft copolymerization of 1-vinylnaphthalene and acrylonitrile onto EPDM, the grafting efficiency increased with an increasing mole ratio of 1-VN to AN.
2. The grafting efficiency increased with increasing initiator concentration up to 5.0 wt% and then gradually decreased.
3. The grafting efficiency of AEV_1 increased with rising reaction time up to 40 hours but thereafter leveled off.
4. The grafting efficiency showed a maximum of 70°C and increased with EPDM content.
5. The thermal stability of AEV_1 was superior to ABS. The tensile strength, the light resistance, and the weatherability of AEV_1 were better than those of ABS.

ACKNOWLEDGMENTS

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