Synthesis and Properties of Acrylonitrile–EPDM–N-Vinylcarbazole Graft Terpolymer

BEOM-DOO SEO, DUCK-JEI PARK, CHANG-SIK HA, and WON-JEI CHO*

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

SYNOPSIS

A graft terpolymer of acrylonitrile (AN) and N-vinylcarbazole (NVC) onto ethylene–propylene–diene terpolymer (EPDM) was synthesized in toluene using benzoyl peroxide. The effects of EPDM content, mole ratio of NVC to AN, reaction time, reaction temperature, and initiator concentration in the graft copolymerization were examined. The synthesized AN–EPDM–NVC graft terpolymers (AEVC) were identified by infrared (IR) and ^{1}H-NMR (nuclear magnetic resonance) spectra. The thermal stability, tensile strength, and light resistance of AEVC were investigated by using a Fade-o-Meter, thermogravimetric analyzer, and tensile tester. It was found that the heat resistance of AEVC is considerably better than that of acrylonitrile–butadiene–styrene (ABS) copolymer. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

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.[1,2] Thus, modification of the ABS terpolymer has attracted much interest for years. Among several attempts to improve the poor aging performance, the substitution of ethylene–propylene–diene terpolymer (EPDM) for butadiene has been investigated in this laboratory.[3–13] A typical example is acrylonitrile–EPDM–styrene (AES) copolymer.[14] It has been known that EPDM has outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component.[15–22]

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

EXPERIMENTAL

Materials

NVC (Aldrich Chemical Co.) and AN (Junsei Chemical Co.) were purified by standard procedures. BPO (Hayashi Chemical Co.) was purified by recrystallization from methanol. EPDM, having ethylidene norbornene as a termonomer (Aldrich; ethylene/propylene $= 50/42$ by mol %, ML50, $M_n = 50,500$; $M_w = 102,000$), was used as received. 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), toluene, and tetrahydrofuran (THF) were distilled prior to use.

Synthesis of Acrylonitrile–EPDM–N-Vinylcarbazole Graft Terpolymer (AEVC)

The grafting reactions were carried out in a 1-L separable flask equipped with a modified-Hopkins

cooler,[3] a thermometer, and an argon gas inlet. A given amount of EPDM was dissolved in 200 mL of toluene in the flask. A mixture of AN and NVC at a given mole ratio was dissolved in 50 mL of toluene and then added with 0.21 g of BPO. After stirring, the reaction was carried out under various experimental conditions (see Table I). After the reaction, the products were precipitated with methanol and the precipitates were filtered and dried in vacuo.

Isolation of Graft Terpolymer

In the synthesis, the products obtained consist of ungrafted EPDM, AEVC, and several copolymers and unbound homopolymers. The nongrafted EPDM was separated from the rest of the products by extraction using n-hexane. The acrylonitrile–EPDM–N-vinylcarbazole (AEVC) was isolated from a mixture of several copolymers and homopolymers, such as poly(AN-co-NVC), poly(acrylonitrile) (PAN), poly(N-vinylcarbazole) (PNVC), and crosslinked AEVC, using DMF and THF solvents. Details of isolation procedures of the graft terpolymer obtained are shown schematically in Figure 1.

The total conversion was calculated from the ratio of the total weight of crude product to the weight of monomers charged. The grafting ratio and grafting efficiency were determined on the basis of changes in polymer weight during the reaction process and the total amount of polymer formed, respectively, by using the following equations[23]:

Total conversion (%)

$$= \frac{\text{total weight of polymer formed}}{\text{weight of monomer charged}} \times 100 \quad (1)$$
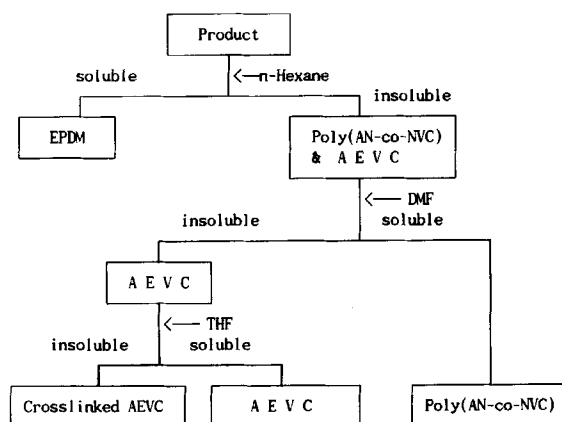
Grafting ratio (%)

$$= \frac{\text{weight of polymer in grafts}}{\text{weight of substrate}} \times 100 \quad (2)$$

Grafting efficiency (%)

$$= \frac{\text{weight of polymer in grafts}}{\text{total weight of polymer formed}} \times 100 \quad (3)$$

Figure 1 Block diagram of graft terpolymer (AEVC) isolation procedure.

Measurements

IR and ¹H-NMR Spectroscopy

The infrared spectrum of the graft copolymer was recorded on Perkin-Elmer 1330. ^{1}H-NMR spectra were obtained in CDCl$_3$ on a JEOL GSX-270 NMR spectrophotometer.

Gel Permeation Chromatography (GPC)

The molecular weight was determined using THF as an eluent by GPC (Waters–Water 244). The apparatus was calibrated with polystyrene standards.

Thermogravimetric Analysis (TGA)

Thermal stability was examined with a Shimadzu DT 30A TGA instrument at a scanning rate of 15°C/min in nitrogen.

Tensile Properties

The tensile tests were carried out using an Instron Tensile Tester (Model 4204). The samples were prepared following the procedure of ASTM D638-84. The crosshead speed was 5 mm/min, and the initial gauge length was set at 25 mm.
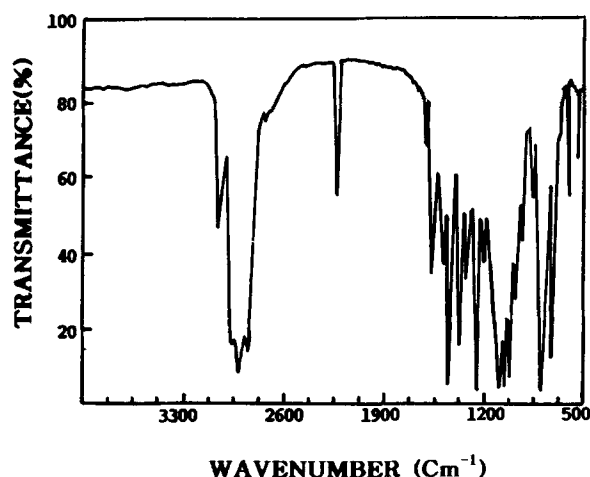
Table I Graft Copolymerization Conditions Used

Condition	Description				
EPDM concentration (%)	8	13		19	27
Mole ratio of [NVC]/[AN]	0.50	0.75	1.00	1.50	2.00
Reaction time (h)	3	8		12	17
Reaction temperature (°C)	60	70		80	90
Initiator concentration (based on the vinyl monomers) (mol %)	0.5	1.0		3.0	5.0

WAVENUMBER (Cm⁻¹)

Figure 2 IR spectrum of AEVC graft terpolymer.

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 (ND-101 DP). The film specimens were cast from THF solutions (ca. 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 5×10 cm², with a thickness of 35 μm. The ΔE of the films after exposure to ultraviolet (UV) light was calculated using the Hunter–Schofield equation.[4]

Weatherability

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

RESULTS AND DISCUSSION

Characterization

The structure of AEVC was identified by IR spectrophotometry (Perkin–Elmer 1330). The IR spectra of AEVC exhibited characteristic absorption bands at 3060 cm⁻¹ (stretching vibration of aromatic C—H bond), 2900 cm⁻¹ (stretching vibration of aliphatic C—H bond), 2250 cm⁻¹ (stretching vi-

bration of —C≡N bond), 1157 cm⁻¹ (stretching vibration of —C—N bond), and 900 ~ 690 cm⁻¹ (out-of-plane rotational vibration of aromatic C—H) (Fig. 2). The graft terpolymer was also characterized by its ¹H-NMR spectra. The AEVC spectra showed multiple peaks at 0.7, 1.0–2.2, and 7.2 ppm, which are due to the methyl protons of the polymer backbone chain, the methine and methylene protons, and the phenyl protons of the NVC unit, respectively.

Elemental analysis (Carlo Erba 1108) for a typical AEVC with a 1.00 feed mole ratio of NVC to AN gives the following results:

ANAL: C, 72.50%; H, 10.69%; N, 2.41%

In this case, the grafted AEVC was synthesized with 0.21 g of BPO at 70°C for 17 h. The weight-average molecular weight of the typical AEVC was determined as 160,000 ($M_w/M_n = 2.13$).

Effects of Reaction Conditions on Graft Copolymerization of an and NVC onto EPM

Effect of EPDM Content

The effect of EPDM content on the graft copolymerization is shown in Figure 3. The reaction was carried out at 70°C for 17 h with a mole ratio of
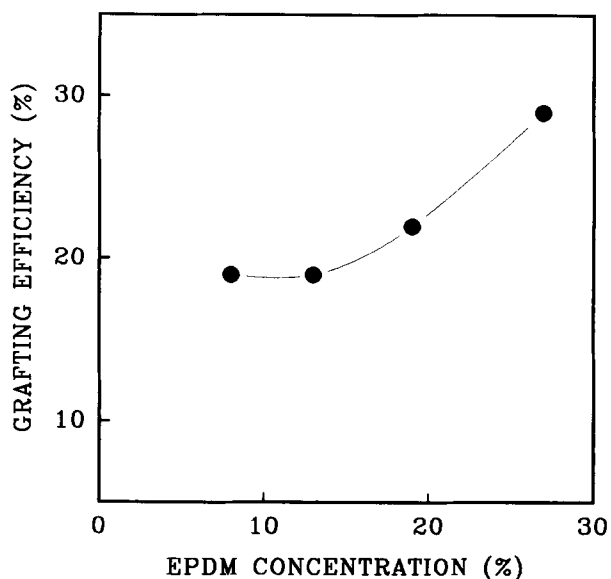

Figure 3 Plot of grafting efficiency vs. EPDM concentration: [NVC]/[AN] = 1.00; reaction temp.: 70°C; solvent: toluene; reaction time: 17 h; BPO: 0.21 g.

*N*VC to AN of 1.0. The grafting efficiency increased with increasing concentration of EPDM. With higher concentrations of EPDM, more active centers are formed in the system and thus the grafting efficiency increases. On the other hand, it seems that the lower the concentration of EPDM, the fewer the active centers,[20] and thus the higher degree of copolymerization of poly(AN-co-*N*VC).

Effect of Mole Ratio

Table II shows the effect of mole ratio of *N*VC to AN on the graft copolymerization onto EPDM. The reaction was carried out in toluene with 3 mol % of BPO at 70°C for 17 h. As can be seen, the grafting efficiency decreases with increases in the mole ratio of *N*VC to AN. The grafting efficiency is as high as 27% at the 0.50 mole ratio of *N*VC to AN. Table II also lists the molecular weight characteristics of the graft copolymers that have various mole ratios in feed. It is seen that the molecular weights of the graft copolymers become smaller as the grafting efficiency is lower. It is interesting that the polydispersity declines continuously with increasing ratio of *N*VC to AN. The result may be closely related to decreasing grafting efficiency with increasing mole ratio of *N*VC to AN (i.e., as the grafting efficiency decreases, the amounts of homopolymers and copolymers become higher and can be easily isolated during the extraction process). Then it may be assumed that the remaining graft terpolymers have a narrower polydispersity. A similar tendency has been shown in our previous work[10] for the graft copolymerization of methyl methacrylate and 2-vinylnaphthalene onto EPDM.

Effect of Reaction Time

The effect of reaction time on the graft copolymerization is shown in Figure 4. The graft copolymer-
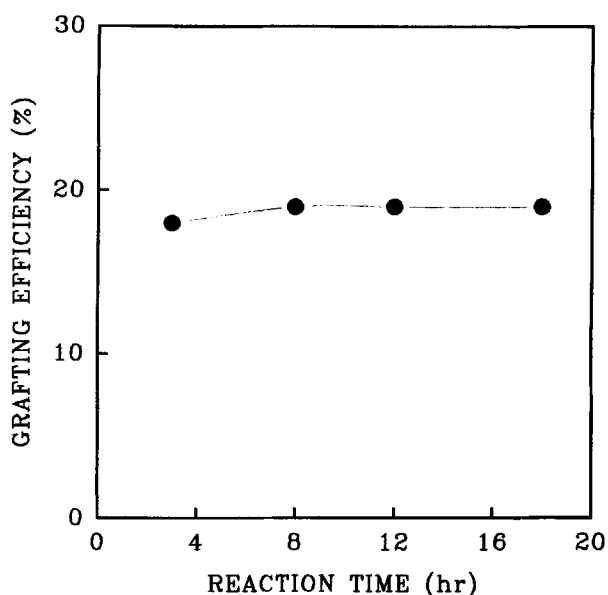
Figure 4 Plot of grafting efficiency vs. reaction time: [AEVC]/[AN] = 1.00; reaction temp.: 70°C; solvent: toluene; BPO: 0.21 g.

ization was carried out in toluene at 70°C with constant concentrations of EPDM and BPO. The mole ratio of *N*VC to AN was fixed at 1.00. The grafting efficiency was not changed up to 17 h, but total conversion and grafting ratio increased with increasing reaction time. This may be caused by the increase of graft terpolymer as well as the increase of homopolymers and copolymers along the reaction path.
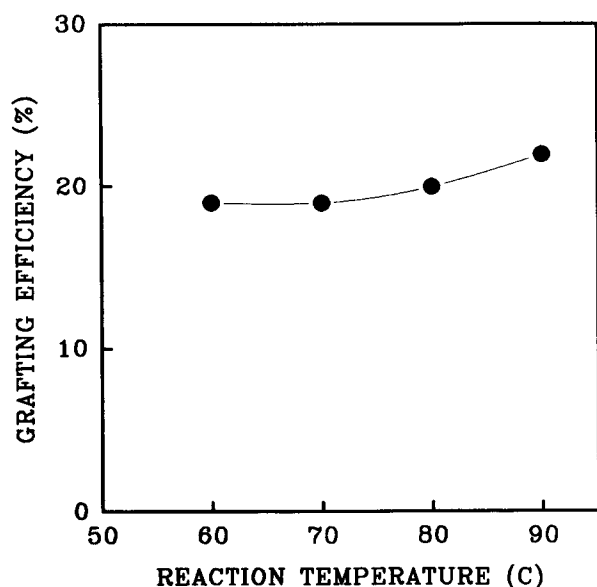
Effect of Reaction Temperature

The effect of reaction temperature on the graft copolymerization is shown in Figure 5. The grafting was carried out at 60, 70, 80, and 90°C, keeping all the variables constant. The mole ratio of *N*VC and AN was fixed at 1.00. The grafting efficiency in-

Table II Effect of Mole Ratio of NVC to AN on the Graft Copolymerization of NVC and AN onto EPDM and the Molecular Weight Characteristics

Exp. No.	Mole Ratio of NVC to AN	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)	M_n	M_w	M_w/M_n
AEVC(0.50)	0.50	94	166	27	78,000	182,000	2.33
AEVC(0.75)	0.75	86	142	21	76,600	174,000	2.27
AEVC(1.00)	1.00	84	134	19	74,500	160,000	2.13
AEVC(1.50)	1.50	73	108	16	74,000	131,000	1.77
AEVC(2.00)	2.00	70	93	15	68,900	115,000	1.67

Reaction time: 17 h; reaction temp.: 70°C; solvent: toluene; BPO: 0.21 g.

Figure 5 Plot of grafting efficiency vs. reaction temperature: [AEVC]/[AN] = 1.00; reaction time: 17 h; solvent: toluene; BPO: 0.21 g.

creased with increasing reaction temperature. On increasing the temperature, the grafting efficiency gradually increased with increasing reaction time. This may be explained by the decomposition rate of BPO as a function of temperature; it has been reported that the decomposition rate of BPO as an initiator is largest at 80 to 85°C.[24,25]

Effect of Initiator Concentration

Figure 6 shows the effect of the initiator concentration on the graft copolymerization. The grafting was carried out with various concentrations of initiator at 70°C for 17 h. The mole ratio of NVC to AN was the same as described earlier. The grafting efficiency decreased with increasing initiator concentrations. The increase in the initiator concentrations favors the formation of more homopolymers from the graft copolymer, and consequently there is a decrease in grafting efficiency. A similar observation was made in Voek's work.[23]

Thermal Stability

The effect of mole ratio of NVC to AN in graft copolymerization on the decomposition temperature is shown in Figure 7. For this figure, the grafting reaction was carried out under the same conditions as those referred to in Table II. It was observed that the thermal stabilities of AEVC increased in the order of AEVC (0.50) < AEVC (0.75) < AEVC (1.00)

< AEVC (1.50) < AEVC (2.00), meaning that the AEVC with higher NVC content showed higher thermal stabilities.

Figure 8 shows TGA curves of ABS, AES, and AEVC. The thermal data of commercially available ABS (Japan Synthetic Rubber Co.; JSR 10 grade) and AES (Japan Synthetic Rubber; JSR 110 grade) were also shown for comparison. In this figure, the grafted AEVC was synthesized with 1.00 mole ratio of NVC to AN and 0.21 g of BPO at 70°C for 17 h. It is clear that the AEVC shows superior thermal stability with the highest thermal degradation temperature. As shown in Figure 8, the residual weight at 450°C of AEVC is 48%, whereas those of the other polymers are below 25%. The good thermal stability of AEVC may be attributed to the synergistic effect of EPDM and NVC components in the terpolymer because of their inherent high heat resistances.[26,27]

## Light Resistance and Weatherability

There are some experimental techniques to test weather resistivity of materials.[28] We applied two kinds of accelerated weathering tests to compare weatherability and light resistance: Fade-o-Meter and Weather-o-Meter. Light resistance and weatherability were semiquantitatively expressed in terms of ΔE with the National Bureau of Standards Unit. The smaller ΔE means better light resistance and weatherability.[29-31] The samples were tested in a Fade-o-Meter for measurements of light resistance
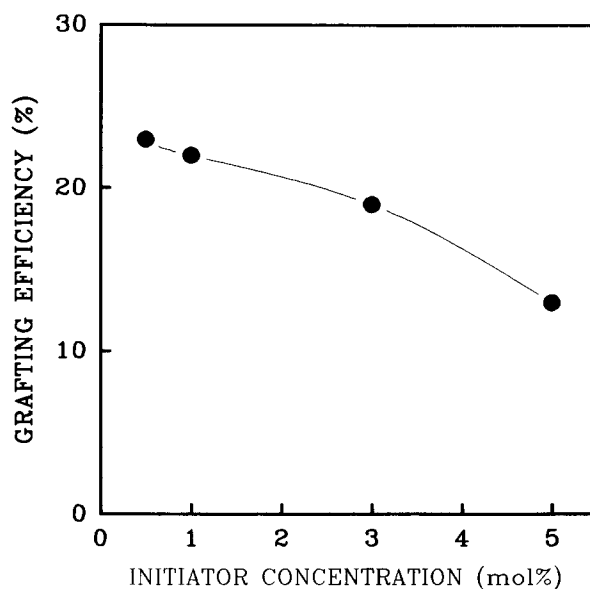

Figure 6 Plot of grafting efficiency vs. initiator concentration: [AEVC]/[AN] = 1.00; reaction temp.: 70°C; solvent: toluene; reaction time: 17 h; BPO: 0.21 g.
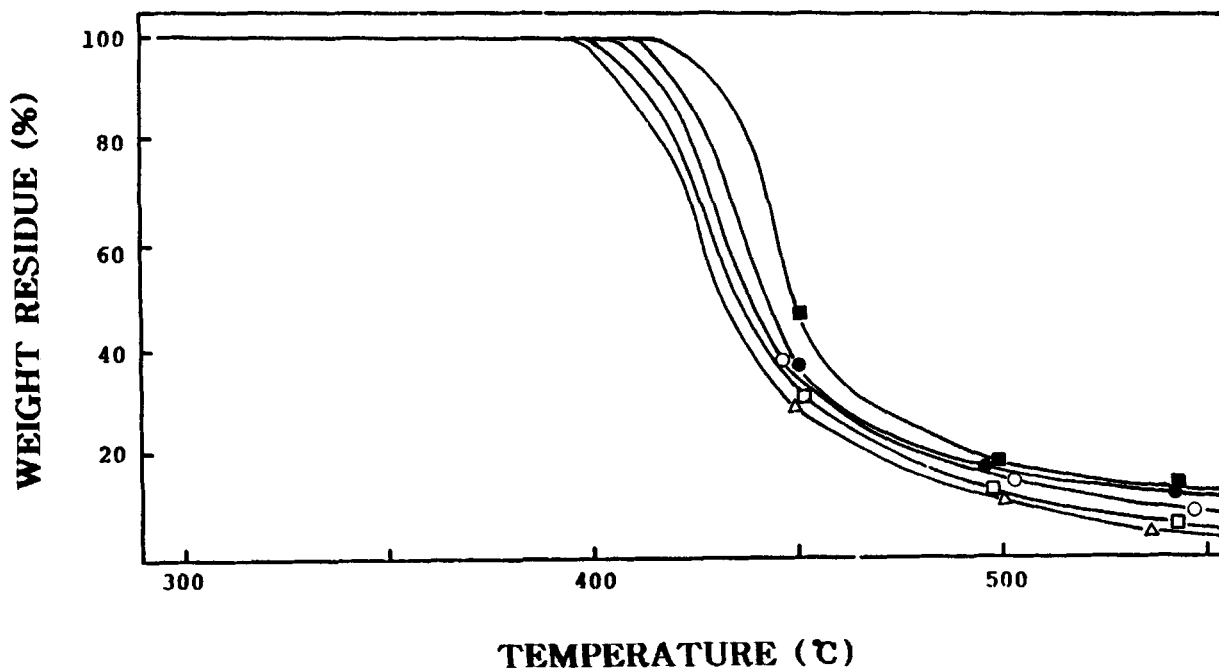
Figure 7   Effect of mole ratio of *N*VC to AN in graft copolymerization on the TGA curves: Heating rate: 10°C/min in nitrogen. △, [*N*VC]/[AN] = 0.5; □, [*N*VC]/[AN] = 0.75; ○, [*N*VC]/[AN] = 1.0; ●, [*N*VC]/[AN] = 1.5; ■, [*N*VC]/[AN] = 2.0.
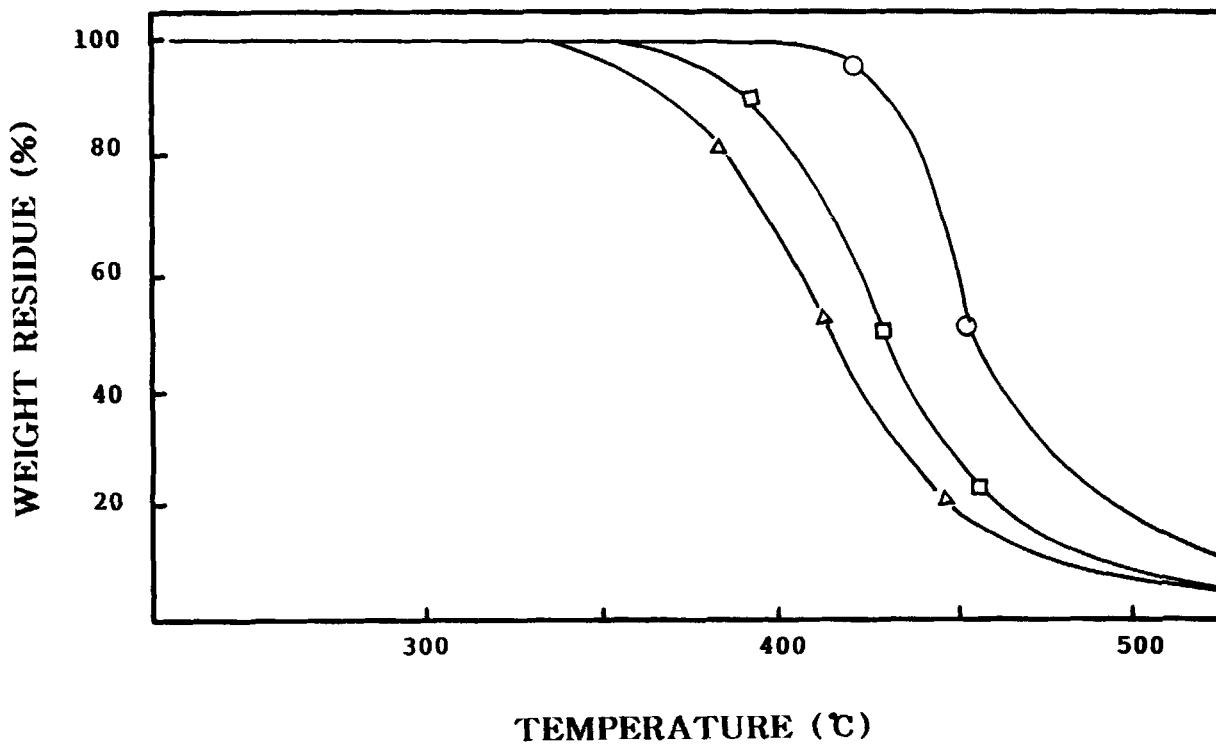
Figure 8   TGA curves of ABS, AES, and AEVC: Heating rate: 10°C/min in nitrogen. △, ABS; □, AES; ○, AEVC.
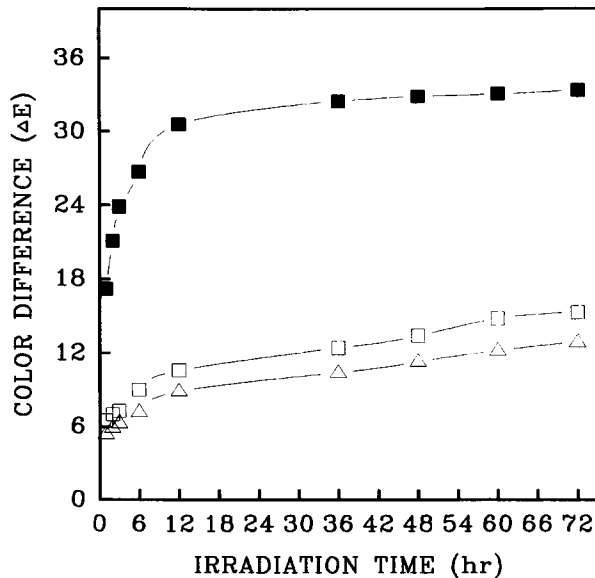
Figure 9 Plot of color difference vs. irradiation time for various samples (by Fade-o-Meter). △, EPDM; □, ABS; ■, AEVC.

from 1 to 72 h, and in a Weather-o-Meter for measurements of weatherability for the same time interval. Figure 9 shows the light resistance of EPDM, ABS, and AEVC. The grafted AEVC with 1.00 mole ratio of NVC to AN was synthesized at 70°C for 17 h in toluene. The ΔE data of commercially available ABS (the same grade as referred to in Fig. 8) are also shown for comparison. AEVC synthesized in this work does not show better light resistance than does ABS or EPDM, due to the photoconductive properties of NVC when subjected to UV light.

Similar results were also observed in the weatherability data. The weatherabilities of EPDM, ABS, and AEVC are also shown in Figure 10. AEVC does not show better weatherability than does ABS (see Fig. 9). This result may be caused by the photoconductive properties of NVC when subjected to UV light. AEVS is the same as that referred to in Figure 8. The color difference lines for AEVC in Figures 9 and 10 seem identical. This may be indicative of the inherent strong yellowing properties of NVC by UV light. But for the experimental difficulties, mechanical properties after heat aging would be of considerable interest to correlate the light stability and the thermal stability of the materials obtained in this work. In this connection, TGA data run in air rather than nitrogen would be more pertinent to operating conditions. Further works will be carried out in the near future. The dependence of light resistance and weatherability of AEVC on the reaction conditions was not significant.
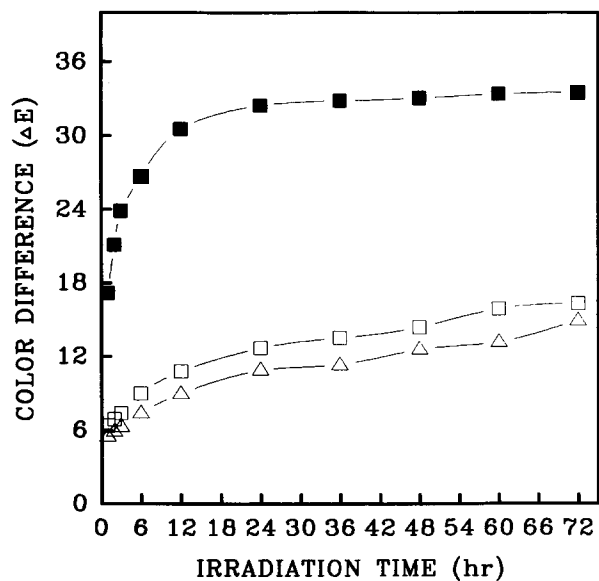
Tensile Properties

Table III shows the tensile properties of AEVC, ABS, and AES. AEVC shown in this table is the same as that referred to in Figure 9. The effect of the reaction conditions on the tensile properties was not significant. It is pertinent to note that the AEVC has the lowest tensile strength. The elongation at break for AEVC (342.2%) seems remarkably higher. It leads to a work to break significantly higher than AES. This result is attributed to the fact that the composition of EPDM in AEVC was high. This result suggests that AEVC can be used as a very tough material, even though the tensile strength is much lower than that of AES or ABS.

CONCLUSION

AEVC graft terpolymer was synthesized with radical initiator by the solution polymerization technique. The dependence of material properties on the various reaction conditions was investigated. The important results are summarized as follows:

1. The grafting efficiency decreased with increasing NVC content relative to that of AN. The grafting efficiency was highest at 21% when the mole ratio of NVC to AN was 0.75.
2. The grafting efficiency showed a maximum at 90°C and was not changed up to 17 h.

Figure 10 Plot of color difference vs. irradiation time for various samples (by Weather-o-Meter). △, EPDM; □, ABS; ■, AEVC.

Table III   Comparison of the Tensile Properties of ABS, AES, and AEVC[a]

Material	Tensile Strength (kg/cm^2)	Elongation at Break (%)
ABS	295	8.4
AES	311	3.7
AEVC	54	342.5

[a] AEVC synthesized from graft copolymerization of NVC and AN onto EPDM: [NVC]/[AN] = 1.00; solvent: toluene; reaction time: 17 h; reaction temp.: 70°C; BPO: 0.21 g.

3. The grafting efficiency decreased with initiator concentrations but increased with EPDM contents.

4. The thermal stability of AEVC was significantly enhanced as compared to ABS and AES.

5. The light resistance and tensile strength of AEVC were poorer than those of ABS.

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