Synthesis and Properties of Acrylonitrile-EPDM-4-Chlorostyrene Graft Copolymer

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SYNOPSIS

Graft copolymerization of acrylonitrile (AN) and 4-chlorostyrene (4-Clst) onto ethylene–propylene–diene terpolymer (EPDM) was carried out using benzoyl peroxide as initiator. The effects of EPDM content, initiator concentration, solvent, mole ratio of 4-Clst to AN, reaction time, and reaction temperature on the graft copolymerization were examined. It was found that the light resistance, weatherability, and thermal stability of the acrylonitrile–EPDM–4-chlorostyrene graft copolymer were considerably better than those of acrylonitrile–butadiene–styrene copolymer.

INTRODUCTION

Acrylonitrile–butadiene–styrene (ABS) copolymer is one of the most commonly used engineering plastics. However, its poor heat resistance and weatherability limit the outdoor use of the material and its blends.[1,2] Among the several attempts to improve the poor performance, the substitution of ethylene–propylene–diene terpolymer (EPDM) for butadiene has been widely investigated.[3–8] A typical example is acrylonitrile–EPDM–styrene (AES) copolymer. It has been known that EPDM has outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component.[9,10]

The aim of this study is to improve heat resistance and weatherability of ABS resin by replacing BR and styrene by EPDM and 4-chlorostyrene (4-Clst), respectively. 4-Chlorostyrene was selected because of its chlorine atom, which might be expected to improve thermal stability of ABS. Acrylonitrile (AN) and 4-Clst were grafted onto EPDM under argon atmosphere in the presence of benzoyl peroxide (BPO) as an initiator. The effects of EPDM content, initiator concentration, solvent, mole ratio of 4-Clst to AN, reaction time, and reaction temperature were investigated in the graft copolymerizations. The light resistance, weatherability, ther-

mal stability, and tensile properties of the graft copolymer 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), having ethylidene norbornene as a termonomer (Aldrich Chemical; ethylene/propylene = 50/50 by mol %, ML 50), was used as received. 4-Chlorostyrene (4-Clst) monomer was prepared by dehydration of 4-chlorophenylmethyl carbinol, as described previously.[11] n-Hexane, dimetyl formamide (DMF), acetone, toluene, cyclohexane, ethyl acetate, and tetrahydrofuran (THF) were distilled prior to use.

Preparation of Materials

Synthesis of Acrylonitrile–EPDM–4-Chlorostyrene Graft Copolymer (AECS)

A given amount of EPDM was dissolved in 72.5 mL of n-hexane. A mixture of AN and 4-clst at a given mole ratio was diluted with 25 mL of n-hexane and then added with 0.12 g of BPO in a 1-liter separable flask equipped with a modified Hopkins cooler (specially designed for this work).[12] The flask was sealed

Table I   Graft Copolymerization Conditions Used in This Study

Condition	Description
Mole ratio ([4-Clst]/[AN])	0.40, 0.80, 1.20, 1.60, 2.00, 2.40
Solvent system	HE (n-hexane/ethyl acetate, 50/50[a]) CE (cyclohexane/ethyl acetate, 50/50) TE (tetrahydrofuran/ethyl acetate, 50/50) T (THF)
Polymerization time (hr)	10, 20, 30, 40, 60
Reaction temperature (°C)	60, 70, 80, 90
Initiator concentration (moles/liter) × 10^4	2.48, 4.95, 9.91, 19.82
EPDM concentration (%)	5, 10, 15, 20

[a] By vol. %.

after charging with argon and the reaction was carried out under various experimental conditions (see Table I).

After a chosen period of reaction, the contents was poured into methanol with stirring; the precipitate was filtered and dried in a vacuum oven until kept at a constant weight. The nongrafted EPDM was extracted using n-hexane. The acrylonitrile–EPDM–4-chlorostyrene graft copolymer (AECS) was isolated from a mixture of several copolymers and homopolymers such as poly(EPDM-graft-AN), poly(EPDM-graft-4-Clst), and poly(4-Clst-co-AN) using DMF and acetone. The isolation procedure is shown schematically in Figure 1.

The structure of AECS was identified by IR spectrophotometry (Perkin-Elmer 1330). The IR spectra of AECS exhibited characteristic absorption bands at 3020 cm^{-1} (stretching vibration of aromatic C—H bond), 2920 cm^{-1} (stretching vibration of aliphatic C—H bond), 2240 cm^{-1} (stretching vibration of C≡N group), 1485 cm^{-1} (scissoring of CH$_2$), 1090 cm^{-1} (stretching vibration of C—Cl), and 820 cm^{-1} (out-of-plane rotational vibration of aliphatic C—H).

The total conversion, grafting ratio, and grafting efficiency of AECS were estimated by using the following equations[13]:

Total conversion (%)

$$= \frac{\text{total weight of crude product}}{\text{weight of monomer charged}} \times 100 \quad (1)$$

Grafting ratio (%)

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

Grafting efficiency (%)

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

Measurements

Thermogravimetric Analysis (TGA)

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

Weatherability

The weather resistance (ASTM G53) was measured at 60°C, using a Q panel UV B313 Weathering Tester coupled with a UV lamp of 315–280 nm in wavelength. 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
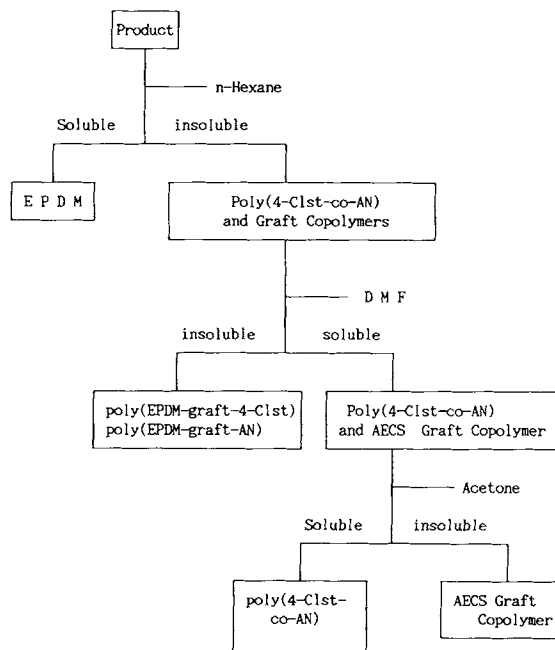
Figure 1 Block diagram of graft copolymer isolation process (notations are described in text).

they reached constant weight. The cross-sectional area of the films was 3 × 5 cm², and 35 μm thick. The color difference (ΔE) of the samples after exposing to UV and moisture was calculated using the Hunter-Schofield equation.[14] A color difference meter (ND-101DP, Japan) was used for measurements of the color difference.

Light Resistance

The light resistance was determined using Fade-o-Meter (Atlas) (at 60°C and 65% relative humidity) and color difference meter (ND-101 DP). The film specimens were prepared by the same method as described in the measurement of weather resistance, except their dimensions. The cross-sectional area of the films was 5 × 10 cm², with a thickness of 35 μm. The color difference (ΔE) of the films after exposing to UV was compared by the same method as applied to test weatherability.

Tensile Properties

The tensile tests were performed using a 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 adjusted at 25 mm.

RESULTS AND DISCUSSION

Reaction Conditions

Effect of EPDM Content

Figure 2 shows the effect of EPDM content on the graft copolymerization. The reaction was performed at 60°C for 40 h in tetrahydrofuran (THF) with a mole ratio of 4-Clst to AN of 1.6. The grafting efficiency increases with EPDM content. For convenience, however, the EPDM content was fixed at 15% to investigate several other effects on the graft copolymerizations, unless otherwise specified.

Effect of Initiator Concentration

The effect of initiator concentration on the graft copolymerization is shown in Figure 3. The reaction conditions were the same as those described earlier. The grafting efficiency decreases with initiator concentrations. The result is expected since the homopolymer is formed more readily than the graft copolymer as initiator concentration increases.
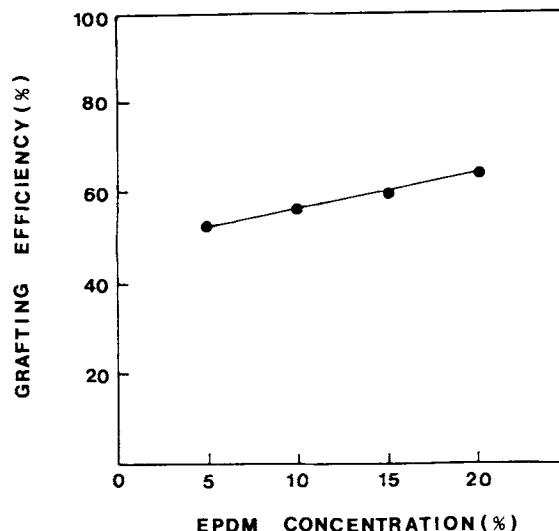

Figure 2 Plot of grafting efficiency vs. EPDM content: [4-Clst]/[AN], 1.60; reaction time, 40 h; reaction temp., 60°C; solvent, THF, BPO 0.12 g.

Effect of Mole Ratio

Figure 4 shows the effect of mole ratio of 4-Clst to AN on the graft copolymerization onto EPDM. The reaction was carried out in THF with 0.06 g of BPO as an initiator at 60°C for 90 h.

It can be seen that the grafting efficiency increases with increasing mole ratio of 4-Clst to AN up to 1.6 and thereafter it decreases. This effect may be explained by considering the difference in reactivity between 4-Clst and AN; kp/kt of (AN) at 25°C and that of 4-Clst at 30°C were reported as 3.4×10^{-6} and 1.16×10^{-6}, respectively.[15] This implies that the propagation rate of AN is 1.7 times faster than that of 4-Clst. In other words about 1.6 times of moles of 4-Clst compared to that of AN is needed to keep the reaction of 4-Clst and AN at equimolar conditions in the graft copolymerization of 4-Clst and AN onto EPDM.

Effect of Reaction Time

The effect of reaction time on the graft copolymerization is shown in Figure 5. The grafting was carried out at constant EPDM concentration (15%) and BPO content (0.06 g) at 60°C. The mole ratio of 4-Clst to AN was fixed at 1.6. The grafting efficiency increased with reaction time up to 40 h and then leveled off. This may be caused by the decrease of the unreacted monomer concentrations as well as the increase of viscosity of the reaction mass along the reaction path.
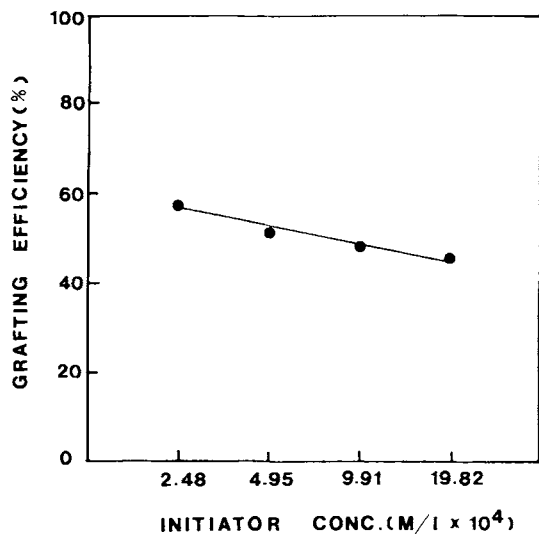
Figure 3   Plot of grafting efficiency vs. initiator concentration: [4-Clst]/[AN], 1.60; reaction time, 40 h; reaction temp., 60°C; solvent, THF, BPO 0.12 g.

served as 73, 60, 64, and 70% for T (THF), HE [n-hexane/ethyl acetate (50/50 by volume)], CE [cyclohexane/ethyl acetate (50/50 by volume)], and TE [tetrahydrofuran/ethyl acetate (50/50 by volume)], respectively. These results come from the difference in solvent power of each solvent–polymer pair;[18,19] i.e., n-hexane and cyclohexane are good solvents for EPDM but poor solvents for AECS or other copolymers and homopolymers obtained as by-products such as poly(4-Clst-co-AN), respectively, whereas ethyl acetate is a poor solvent for EPDM but a good solvent for AECS or other by-products. Thus, it was found that, since tetrahydrofuran dissolves the polymers more readily than any other solvents used, like cyclohexane or n-hexane, the grafting efficiency was the highest when tetrahydrofuran was used as a solvent. Odian et al. reported similar results of solvent effect on graft copolymerizations of styrene onto nylon, polyethylene, and polypropylene.[20-22]

Effect of Reaction Temperature

The highest grafting efficiency was observed at 70°C within our experimental temperature ranges, as shown in Figure 6. It may be related to the decomposition rate of BPO as a function of temperature.[16,17]

Effect of Solvent

Table II shows the effect of solvent on the graft copolymerization. The grafting efficiencies were ob-

Viscosity

The inherent viscosity, as a measure of molecular weight, was obtained using Cannon-Fenske viscometer and is summarized in Table III. It is seen that the inherent viscosity of AECS strongly depends on the concentration of EPDM. For a given EPDM concentration (15%), the AECS synthesized with tetrahydrofuran as a solvent shows the highest inherent viscosity, which is closely related to the
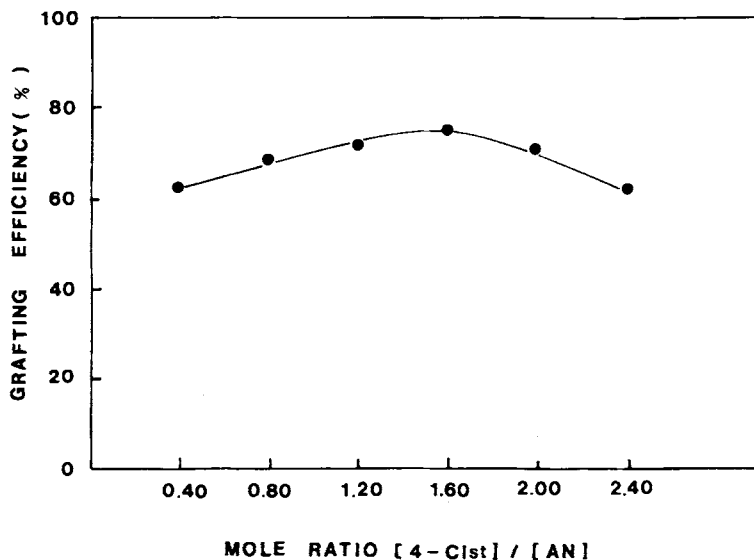

Figure 4   Plot of grafting efficiency vs. mole ratio of [4-Clst] to [AN]: reaction time, 40 h; reaction temp., 60°C; solvent, THF, BPO 0.12 g.
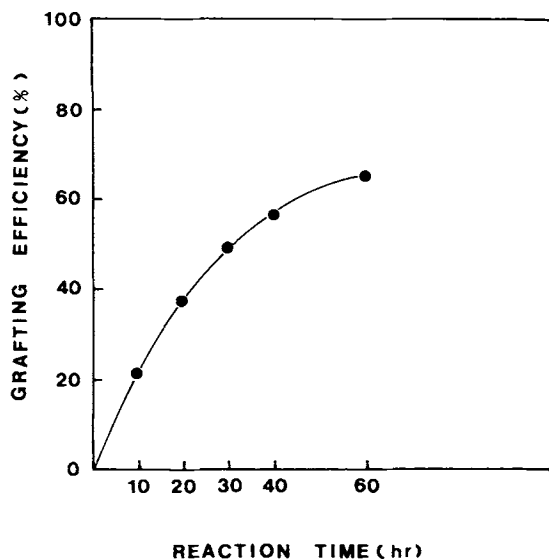
Figure 5 Plot of grafting efficiency vs. reaction time [4-Clst]/[AN], 1.60; solvent, THF; reaction temp., 60°C; BPO 0.12 g.

grafting efficiency, as described in the previous section.

Thermal Stability

The effect of solvent in graft copolymerization on the decomposition temperature is shown in Figure 7. 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. Initial decomposition temperature of ABS is 370°C and those of AECS synthesized in HE, CE, and TE were 393, 405, and 410°C, respectively. Similar behavior was also observed for the final decomposition temperature. It is seen that the heat resistance follows the order AECS(T) > AECS(TE) > AECS(CE) > AECS-(HE) > AES > ABS. This may be due to the difference in solvent power. The grafting efficiency becomes higher in better solvent. The effect of various solvents on the thermal stability follows the order HE < CE < TE < T. It should be pointed out that all of AECSs show superior thermal stability with higher thermal degradation temperature to ABS and AES regardless of the solvents used. The good thermal stability of AECS may be attributed to EPDM unit in the copolymer having high heat resistance.[23,24]

The influence of mole ratio of 4-Clst to AN on the thermal stability should be also noted, as shown in Figure 8. The decomposition temperature increases as the mole ratio increases. The trend is as-

cribed to the role of 4-Clst containing a chlorine atom in the molecule. Tang and Niell[25] and Nara and Matsuyama[26] reported in their separate studies on α-cellulose or epoxy resins that the material having more residues after decomposition has better flammability.

Figure 7 shows that the weight percent of residue at 450°C of AECS is highest as 54% when THF was used as a solvent while that of ABS is only 13%. The superior thermal stability of AECS may be related to the active role of the chlorine atom in 4-Clst unit in the copolymer. It was observed that the effects of other reaction conditions on the thermal stability were not significant in our experimental ranges.

Light Resistance and Weatherability

The weatherability of polymers is a very important factor among other long-term properties. Several primary causes of deterioration of polymers include sunlight, temperature, moisture, and pollutants.[27] There are some experimental techniques to test weather resistivity of materials. We applied two kinds of accelerated weathering tests to compare the weatherability and the light resistance; viz., Fade-o-Meter and Weather-o-Meter.

The light resistance and weatherability were semiquantitatively expressed in terms of color difference (ΔE) with National Beaureau of Standards Unit. The smaller ΔE means better light resistance and weatherability.[28,29] The samples were tested in a Fade-o-Meter for the measurements of light re-
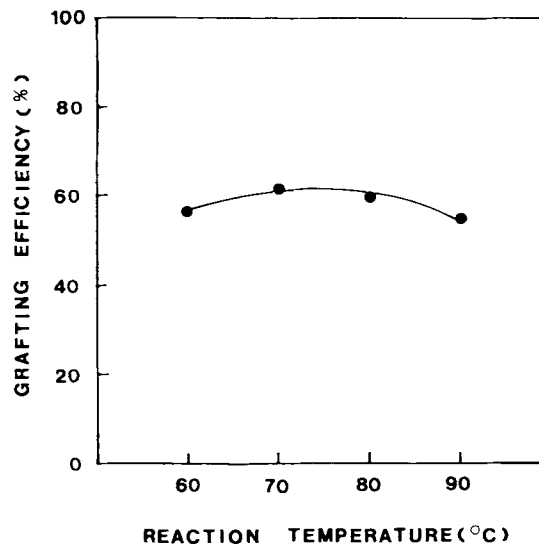

Figure 6 Plot of grafting efficiency vs. reaction temperature: [4-Clst]/[AN], 1.60; reaction time, 40 h; solvent, THF, BPO 0.12 g.

Table II Effect of Solvent on the Graft Copolymerization of 4-Clst and AN onto EPDM[a]

Exp. No.	Solvent	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
AECS (HE)	HE: hexane/ethyl acetate (50 : 50)	45	171	60
AECS (CE)	CE: cyclohexane/ethyl acetate (50 : 50)	50	193	64
AECS (TE)	TE: tetrahydrofuran/ethyl acetate (50 : 50)	55	246	70
AECS (T)	T: tetrahydrofuran	58	287	73

[a] [4-Clst]/[AN] = 1.60; reaction time, 24 h; reaction temp., 60°C; BPO, 0.12 g.

sistance for 5, 10, 20, and 40 h, and in a Weather-o-Meter for the measurements of weatherability for 19, 27, 43, and 62 h.

Figure 9 shows the light resistance of various samples. The grafted AECS was synthesized in THF with 1.6 mole ratio of 4-Clst to AN at 60°C for 40 h. The ΔE data of commercially available ABS and AES (the same grades as described in the previous section) are also shown for comparison. It should be noted that the AECS shows better light resistance than ABS because of inclusion of EPDM, which has excellent outdoor properties. The dependences of light resistance of AECS on the reaction conditions were not significant, except the mole ratio of 4-Clst

to AN. The effect of mole ratio on the light resistance of the AECS is profound, as shown in Figure 10. The AECS with higher mole ratio revealed poorer light resistance. This may be due to the yellowing properties of chlorine atoms in 4CS by UV or light.[3,30]

Another interesting feature is that AECS shows better weatherability rather than ABS, even though AECS does not show better weatherability than EPDM (see Fig. 11). The weatherability of AECS was comparable to that of AES. This result implies that the incorporation of EPDM is very effective to improve poor weatherability of ABS. The materials are the same as that referred to in Figure 9.

Table III Inherent Viscosities of AECSs

Exp. No.[a]	Samples	η_{inh}[b]	Exp. No.	Samples	η_{inh}[b]
1	AECS (10 h)	0.194	4	AECS (0.40)	0.287
	AECS (20 h)	0.217		AECS (0.80)	0.291
	AECS (30 h)	0.286		AECS (1.20)	0.295
	AECS (40 h)	0.312		AECS (1.60)	0.312
	AECS (60 h)	0.327		AECS (2.00)	0.290
				AECS (2.40)	0.283
2	AECS (HE)	0.233	5	AECS (60°C)	0.312
	AECS (CE)	0.451		AECS (70°C)	0.481
	AECS (TE)	0.469		AECS (80°C)	0.285
	AECS (T)	0.481		AECS (90°C)	0.273
3	AECS (5%)	0.197	6	AECS (2.48)	0.310
	AECS (10%)	0.312		AECS (4.95)	0.312
	AECS (15%)	0.410		AECS (9.91)	0.317
	AECS (20%)	0.540		AECS (19.82)	0.300

[a] Exp. No. 1, effect of reaction time; 2, effect of solvent; 3, effect of EPDM concentration; 4, effect of mole ratio of 4-Clst to AN; 5, effect of reaction temperature; 6, effect of initiator concentration [(moles/liter) $\times$ 10^4].

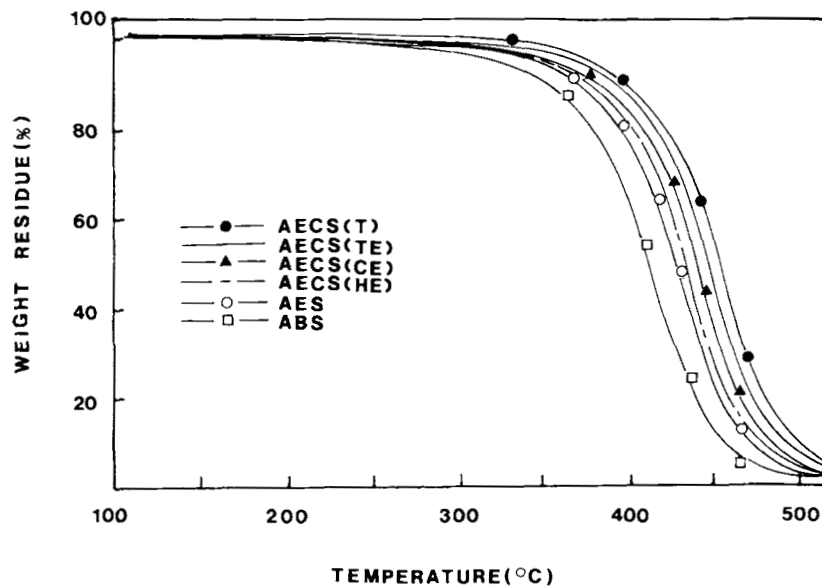[b] η_{inh}: dL/g in THF at 30 $\pm$ 0.05°C.

Figure 7   Effect of solvent in graft copolymerization of AECS on the TGA curves; heating rate, 15°C/min in air. (— ● —; AECS(T), ——; AECS(TE), — ▲ —; AECS(CE), — – —; AECS(HE), — ○ —; AES, — □ — ABS).

Tensile Properties

The tensile properties of AECS, ABS, and AES are listed in Table IV. The grafted AECS shown in this table is prepared in THF with mole ratio of 4-Clst to AN at 1.60 at 60°C for 40 h. The effect of the reaction conditions on the tensile properties was not significant. It is pertinent to note that the AECS has similar tensile strength of ABS even though it has lower tensile strength than that of AES.

Conclusions

Acrylonitrile–EPDM–4-chlorostyrene graft copolymer (AECS) was synthesized with radical initiator
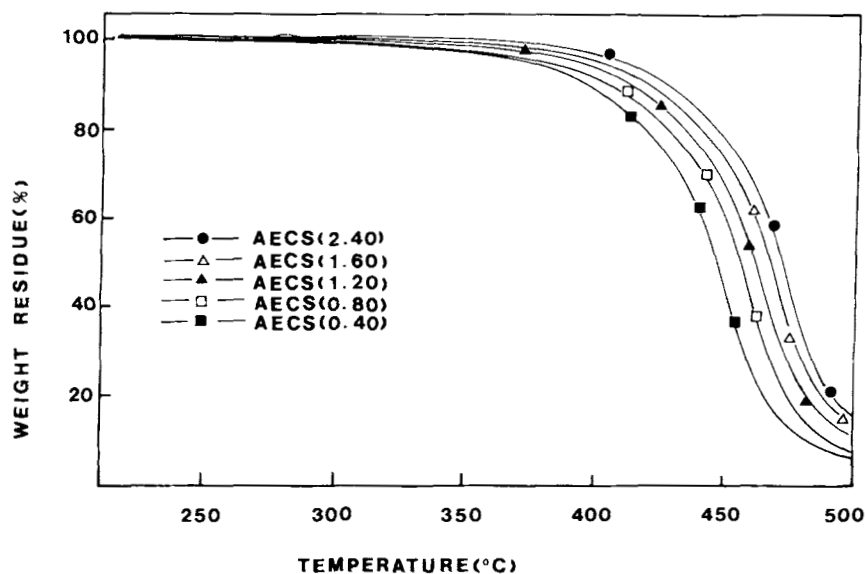

Figure 8   Effect of mole ratio of 4-Clst to AN in graft copolymerization of AECS on the TGA curves; heating rate, 15°C/min in air. [— ● —; AECS(2.40), — △ —; AECS(1.60), — ▲ —; AECS(1.20), — □ —; AECS(0.80); — ■ —; AECS(0.40)].
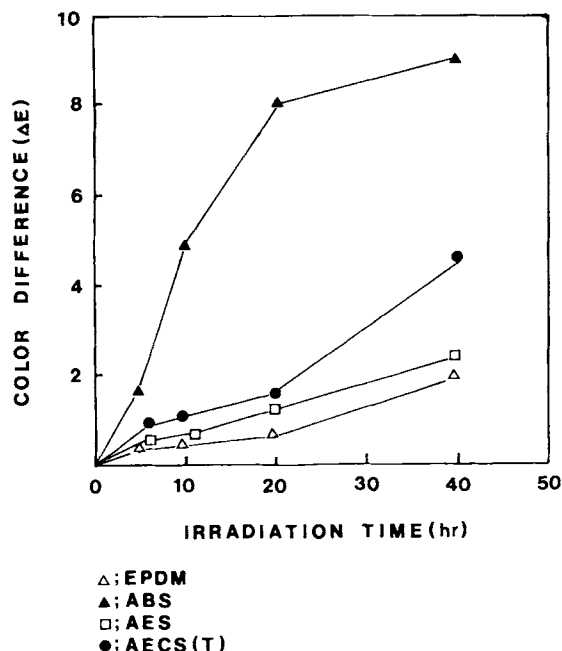
Figure 9 Plot of color difference vs. irradiation time for various samples. (by Fade-o-Meter) [△, EPDM; ▲, ABS; □, AES; ●, AECS(T)].

△;EPDM
▲;ABS
□;AES
●;AECS(T)

○ ; EPDM
● ; A B S
△ ; A E S
▲ ; AECS (T)
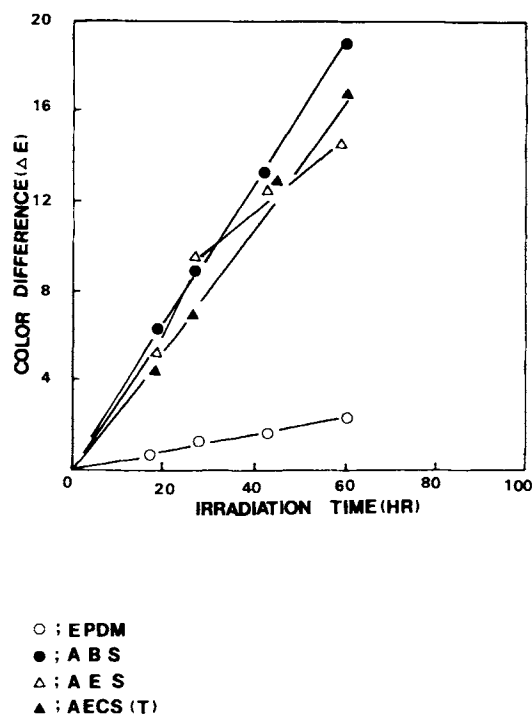
Figure 11 Plot of color difference vs. irradiation time for various samples (by Weather-o-Meter) [○, EPDM; ●, ABS; △, AES; ▲, AECS(T)].

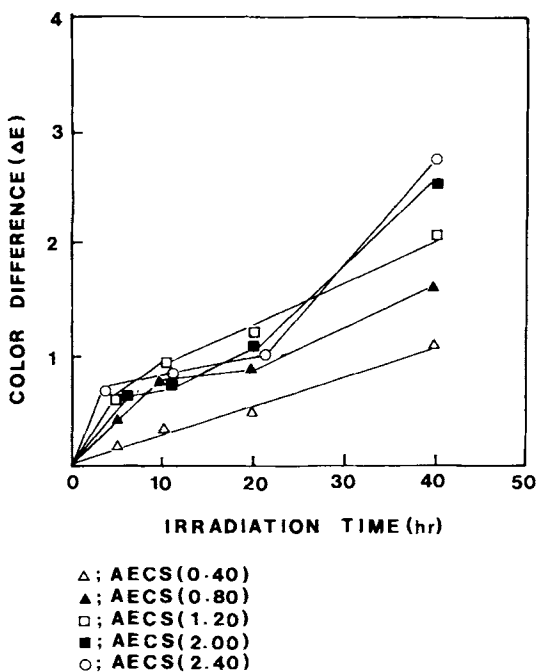△ ; AECS(0.40)
▲ ; AECS(0.80)
□ ; AECS(1.20)
■ ; AECS(2.00)
○ ; AECS(2.40)

Figure 10 Effect of mole ratio on the plot of color difference vs. irradiation time (by Weather-o-Meter) [△, AECS(0.40); ▲, AECS(0.80); □, AECS(1.20); ■, AECS(2.00); ○, AECS(2.40)].

by solution polymerization technique. The dependence of material properties on the various reaction conditions were investigated. The important results are summarized as follows:

1. In the graft copolymerization of AECS, the grafting efficiency increased with increasing 4-Clst content relative to that of AN.
2. The grafting efficiency of AECS increased up to 40 h but leveled off.
3. The grafting efficiency was highest at 70°C when tetrahydrofuran was used as solvent.

Table IV Comparison of Tensile Properties of ABS, AES, and AECS[a]

Materials	Tensile Strength (kg/cm^2)	Elongation at Break (%)
ABS	295	8.4
AES	311	3.7
AECS	293	1.8

[a] AECS synthesized from graft copolymerization of 4-Clst and AN onto EPDM: [4-Clst]/[AN] = 1.60; solvent, THF; time, 40 h; BPO, 0.12 g.

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

5. The light resistance and weatherability of AECS were better than those of ABS.

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