

Synthesis and Properties of Vinyltrimethoxysilane–EPDM–Styrene Graft Terpolymer

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Received 22 March 1996; accepted 24 September 1996

ABSTRACT: The graft copolymerizations of vinyltrimethoxysilane (VTMO) and styrene (St) onto ethylene–propylene–diene terpolymer (EPDM) were carried out with benzoyl peroxide (BPO) as an initiator in toluene. The effects of EPDM concentration, mole ratio of VTMO to St, reaction time, reaction temperature, and initiator concentration on the graft copolymerizations were examined. The synthesized VTMO–EPDM–St graft terpolymers (VES) were confirmed by infrared and $^1\text{H-NMR}$ spectroscopies. The molecular weight, thermal stability, light resistance, and weatherability of the graft terpolymer were investigated by gel permeation chromatography, thermogravimetric analysis, and Fade-o-Meter. The number-average molecular weight was 109,000. It was found that the heat resistance and light resistance as well as weatherability of VES are considerably better than those of acrylonitrile–butadiene–styrene terpolymer. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1345–1352, 1998

Key words: graft copolymerization; ethylene–propylene–diene terpolymer (EPDM); vinyltrimethoxysilane–EPDM–styrene graft terpolymer (VES); characterization; light resistance; weatherability; thermal stability; acrylonitrile–butadiene–styrene copolymer (ABS); acrylonitrile–EPDM–styrene copolymer (AES)

INTRODUCTION

The terpolymer of acrylonitrile–butadiene–styrene (ABS) 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 over the years. Among the several attempts to improve the poor performance, the substitution of ethylene–propylene–diene terpolymer (EPDM) for butadiene has been investigated in this laboratory.^{3–15} A typical example is acrylo-

nitrile–EPDM–styrene (AES) copolymer.¹⁶ EPDM has outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component.^{17–24} It has been reported that the graft copolymers containing EPDM include poly (EPDM-*g*-styrene), poly (EPDM-*g*-acrylonitrile), and AES copolymer.^{25–34}

The aim of this study is to improve heat resistance, light resistance, and weatherability of ABS resin by using EPDM in place of butadiene rubber (BR) and vinyltrimethoxysilane (VTMO)^{35,36} in place of acrylonitrile. VTMO and styrene (St) were grafted onto EPDM under argon atmosphere in the presence of benzoyl peroxide (BPO) as the initiator and toluene as the solvent. The effects of various factors, such as mole ratio of VTMO to St, EPDM content, reaction temperature, initiator concentration, and reaction time in the graft copolymerizations were studied. The thermal stabil-

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Contract grant sponsor: Ministry of Education, Korea (Research Fund for Advanced Materials in 1995).

Journal of Applied Polymer Science, Vol. 67, 1345–1352 (1998)

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CCC 0021-8995/98/081345-08

Table I Graft Copolymerization Conditions Used in This Study

Condition	Description
Mole ratio of [VTMO]/[St]	0.5, 1.0, 1.5, 2.0
EPDM concentration (%)	5, 10, 15, 20
Reaction temperature (°C)	60, 70, 80, 90
Initiator concentration (based on monomers + EPDM) (wt %)	0.5, 1.0, 2.5, 5.0, 10.0
Reaction time (h)	24, 48, 72, 96, 120

ity, light resistance, and weatherability of the synthesized graft terpolymer were also determined.

EXPERIMENTAL

Materials

VTMO (Aldrich Chemical Co.; USA) was purified by vacuum distillation, and St (Junsei Chemical Co., Japan) was washed twice with 5% aqueous NaOH and three times with water, then dried with Na₂SO₄ and distilled under nitrogen at reduced pressure. BPO (Hayashi Chemical Co., Japan) was purified by recrystallization from methanol. EPDM, having ethylidene norbornene (ENB) as a termonomer [Aldrich; ethylene/propylene = 50/42 by mol %, ENB = 8 by mol %, ML50, $M_n = 50,500$; $M_w = 102,000$ ($M_w/M_n = 2.02$)], was used as received. ABS (Japan Synthetic Rubber Co., Japan; JSR 10 grade) and AES (Japan Synthetic Rubber Co.; JSR 110 grade) were used for comparison. *n*-Hexane, acetone, toluene, and tetrahydrofuran (THF) were distilled prior to use.

Synthesis of VTMO-EPDM-St Graft Terpolymer (VES)

A given amount of EPDM (4.45 g) was dissolved in 250 mL toluene in a 1-L separable flask provided with a modified Hopkins cooler, a thermometer, and gas inlet.³ After dissolution, a mixture of VTMO and St with BPO was added to the flask. Taking a copolymerization of 1.0 mole ratio of VTMO to St and 5.0 wt % (based on total mixture) of BPO as an example, a solution of 14.8 g (0.1 mol) VTMO, 10.4 g (0.1 mol) St, and 1 g (5.0 wt %) BPO in 50 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 I). After a predetermined period of reaction, the contents

were poured into methanol with stirring and the precipitate was filtered and dried *in vacuo*.

Separation of Graft Terpolymer

In the synthesis, the products obtained consisted of ungrafted EPDM, VES, and several copolymers, such as poly(VTMO-*co*-St), poly(EPDM-*g*-St), and poly(EPDM-*g*-VTMO). Each separation step was done by the Soxhlet extraction method.

The nongrafted EPDM was extracted by using *n*-hexane. The VES was isolated from mixtures of several copolymers, such as poly(VTMO-*co*-St), poly(EPDM-*g*-St), and poly(EPDM-*g*-VTMO), using acetone and toluene/*n*-hexane (50/50 by vol) mixed solvent. Details of isolation procedure of the graft terpolymer are schematically shown in Figure 1.

The total conversion (%), grafting ratio (%),

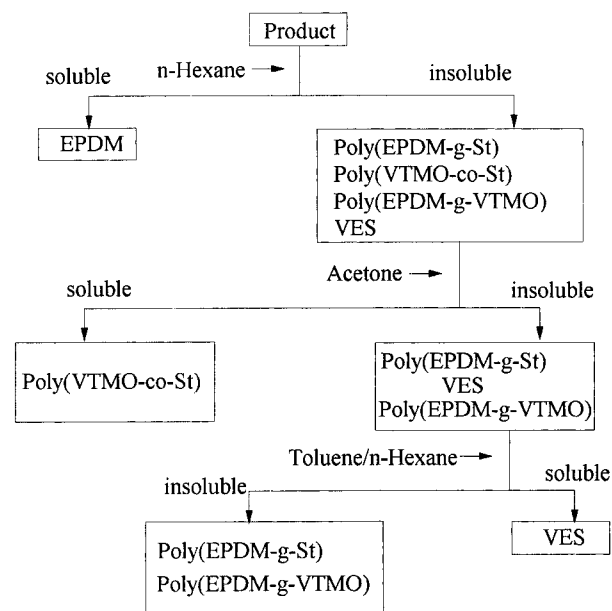


Figure 1 Block diagram of graft terpolymer (VES) isolation procedure.

and grafting efficiency (%) were estimated from the following equation³⁷:

$$\begin{aligned} \text{Total conversion (\%)} \\ = \frac{\text{total weight of polymer formed}}{\text{weight of monomer charged}} \times 100 \quad (1) \end{aligned}$$

$$\begin{aligned} \text{Grafting ratio (\%)} \\ = \frac{\text{weight of polymer in grafts}}{\text{weight of substrate}} \times 100 \quad (2) \end{aligned}$$

$$\begin{aligned} \text{Grafting efficiency (\%)} \\ = \frac{\text{weight of polymer in grafts}}{\text{total weight of polymer formed}} \times 100 \quad (3) \end{aligned}$$

Measurements

Structure Identification

The infrared (IR) spectrum of the graft terpolymer was recorded on a Perkin-Elmer 1330 spectrometer. The ¹H-NMR spectrum of the graft terpolymer was obtained by a JEOL GSX-270 NMR instrument. The measurement was done using CDCl₃ as a solvent, and TMS as an internal reference.

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)

The thermal stabilities of terpolymers were examined with a Shimadzu DT 30A TGA instrument at a scanning rate of 15°C/min in nitrogen.

Light Resistance

The light resistance was determined using a Fade-o-Meter (Atlas) (at 60°C and 65% relative humidity) and color difference meter (NP-101DP). The film specimens were cast from THF solutions (ca. 3 wt %) on a nonyellowing urethane-coated hiding paper. The films were dried slowly at room temperature and then kept under vacuum until they reached constant weight. The cross-sectional area of the films was 3 × 5 cm² and thickness was 35 μm. The color difference (ΔE) of the samples after exposing to UV was calculated using the Hunter-Schofield equation.⁴

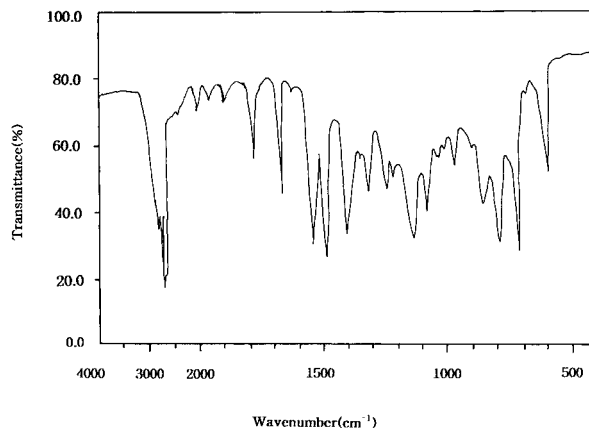


Figure 2 IR spectrum of VES (chloroform film).

Weatherability

The weather resistance (ASTM G53) was measured at 60°C, using a Q panel ultraviolet (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 exposing to UV and moisture was compared using the same methodology as that to test light resistance. The weatherability was measured at 100% relative humidity (UV irradiation for 12 h and condensation for 12 daytime h).

RESULTS AND DISCUSSION

Characterization of VES

The structure of VES was identified by IR spectrophotometry (Perkin-Elmer 1330). The IR spectra of VES exhibited characteristic absorption bands at 3,025 cm⁻¹ (stretching vibration of aromatic C—H bond), 2,920 cm⁻¹ (stretching vibration of aliphatic C—H bond), 1,720 cm⁻¹ (stretching vibration of C=O bond), 1,465 cm⁻¹ (scissoring of CH₂), 1,375 cm⁻¹ (bending of CH₃), 1,000–1,100 cm⁻¹ (stretching vibration of —Si—O—C—), and 760 cm⁻¹ (out-of-plane rotational vibration of aromatic C—H bond) (Fig. 2). The graft copolymer was also characterized by its ¹H-NMR spectra. The VES spectra showed multiple peaks at 0.9 ppm, 1.0–2.3 ppm, and 7.2–7.3 ppm, which are due to the methyl protons of the polymer backbone chain, methylene protons, and the phenyl protons of the St unit, respectively. In this case,

Table II Effect of Mole Ratio of VTMO and St on the Graft Copolymerization of VTMO and St onto EPDM

Mole Ratio [VTMO]/[St]	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
0.5	41	146	54
1.0	38	142	52
1.5	31	139	52
2.0	24	128	49

EPDM, 15%; solvent, toluene; reaction temperature, 70°C; reaction time, 48 h; BPO, 5.0 wt %.

the grafted VES was synthesized with 5.0 wt % of BPO at 70°C for 48 h. The number-average molecular weight (M_n) of the typical VES was determined as 109,000 ($M_w/M_n = 1.61$).

Effect of Reaction Conditions on the Graft Copolymerizations of VTMO and St onto EPDM

Effect of Mole Ratio

The effect of mole ratio of VTMO to St on the graft copolymerization onto EPDM is shown in Table II. The reaction was carried out in toluene with

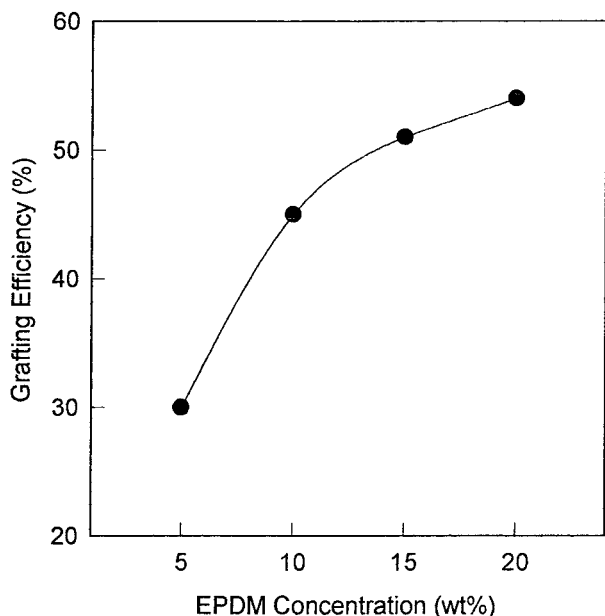


Figure 3 Plot of grafting efficiency versus EPDM concentration: [VTMO]/[St], 1.0; reaction temperature, 70°C; solvent, toluene; reaction time, 48 h; BPO, 5.0 wt %.

BPO (5.0 wt %) as an initiator at 70°C for 48 h. As can be seen, the grafting efficiency increases with decrease in the mole ratio of VTMO to St. The grafting efficiency is highest at 54% when the mole ratio of VTMO to St was 0.5.

Effect of EPDM Content

The effect of EPDM content on the graft copolymerization is shown in Figure 3. The grafting efficiency increased with EPDM content. This result is probably caused by the increasing diene contents of graft site in EPDM as EPDM content increase. The lower the concentration of EPDM, the fewer active centers,²² and thus the higher degree of copolymerization of poly(VTMO-co-St). For convenience, however, the EPDM content was fixed at 15% to investigate several other effects on the graft copolymerizations, unless otherwise specified. The reaction was carried out at 70°C for 48 h in toluene with a mole ratio of VTMO to St of 1.0.

Effect of Reaction Temperature

Figure 4 shows the effect of reaction temperature on the graft copolymerization. The reaction was performed in toluene with 5.0 wt % of BPO and 1.0 mole ratio of VTMO to St for 48 h. On increas-

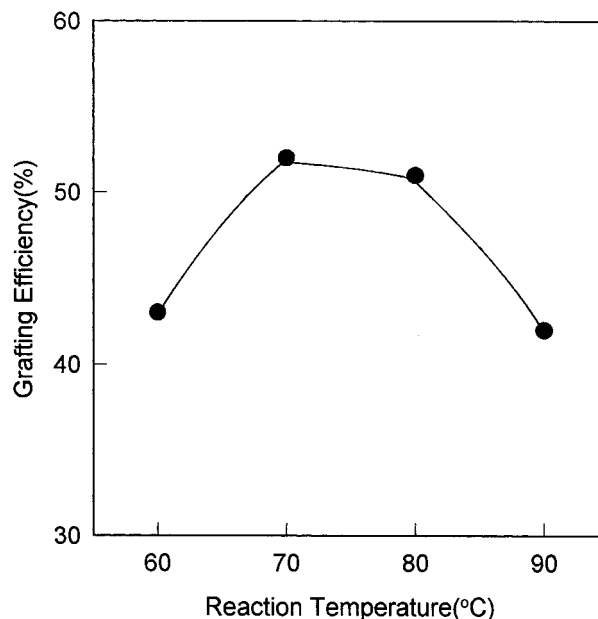


Figure 4 Plot of grafting efficiency versus reaction temperature: [VTMO]/[St], 1.0; EPDM, 15%; reaction time, 48 h; solvent, toluene; BPO, 5.0 wt %.

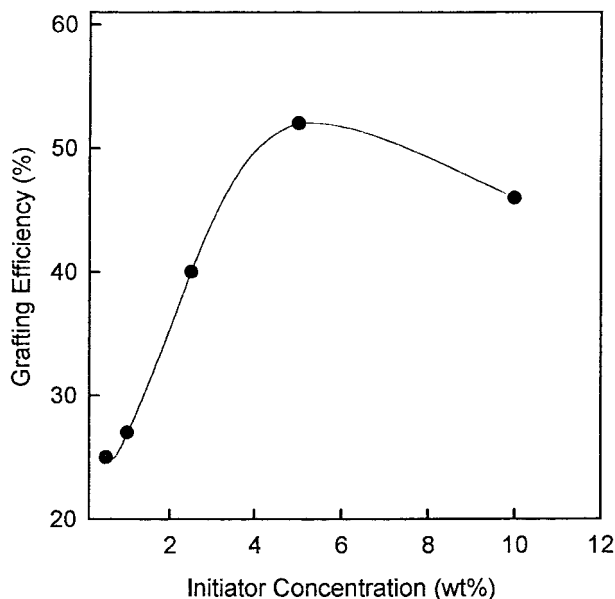


Figure 5 Plot of grafting efficiency versus initiator concentration: [VTMO]/[St], 1.0; EPDM, 15%; reaction temperature, 70°C; solvent, toluene; reaction time, 48 h. Initiator concentration (based on the monomers + EPDM) (wt %).

ing the temperature, the grafting efficiency passes through a maximum at around 70°C. The grafting efficiency depends on the number of active sites available. The increase in temperature is expected to increase the rate of grafting. With increase in temperature, however, the rate of copolymerization also increases.³⁸ As a result, the grafting efficiency increases initially but on further increase in temperature grafting efficiency decreases.

Effect of Initiator Concentration

Figure 5 shows the effect of initiator concentration on the graft copolymerization. In this case, the reaction was carried out in toluene with 1.0 mole ratio of VTMO to St at 70°C for 48 h. The grafting efficiency increased with increasing initiator concentration up to 5.0 wt % but thereafter decreased slightly with further increasing initiator concentration. The decrease in the grafting efficiency at higher initiator concentration is expected because the homopolymer is formed more readily than the graft copolymer as initiator concentration increases. A similar observation was made in Voek's work.³⁹

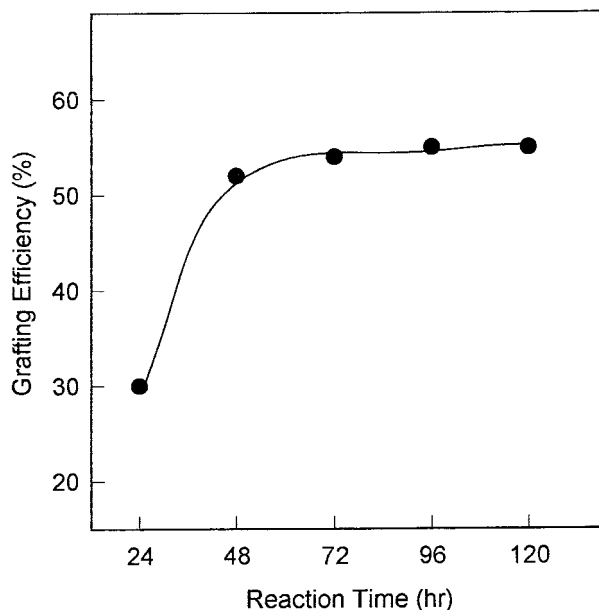


Figure 6 Plot of grafting efficiency versus reaction time: [VTMO]/[St], 1.0; EPDM, 15%; reaction temperature, 70°C; solvent, toluene; BPO, 5.0 wt %.

Effect of Reaction Time

The effect of reaction time on the grafting process is shown in Figure 6. In this case, the mole ratio of VTMO to St was 1.0 and the reaction took place at 70°C. The grafting efficiency increased with re-

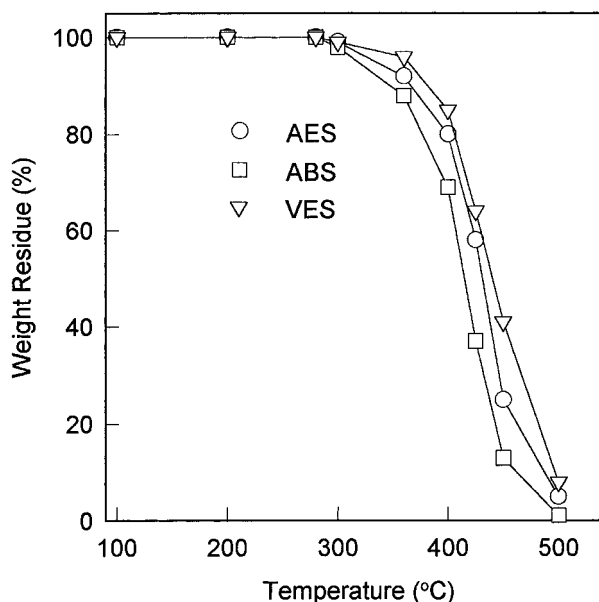


Figure 7 TGA curves of ABS, AES, VES: heating rate, 15°C/min in nitrogen: (□) ABS; (○) AES; (▽) VES.

Table III Decomposition Temperature and Weight Residue of ABS, AES, and VES

Material	Decomposition Temperature (°C)	Weight Residue at 450°C (%)
ABS	370	13
AES	390	25
VES	424	41

VES synthesized from graft copolymerization of VTMO and St onto EPDM: [VTMO]/[St] = 1.0; solvent, toluene; reaction time, 48 h; reaction temp., 70°C; BPO, 5.0 wt %.

action time up to 48 h and then leveled off. With increase in reaction time, the radicals have more time for reaction; as a result, an increase in grafting efficiency was observed. After some time all the initiator is used up, and no further change in grafting efficiency was observed with increase in reaction time.^{9,13}

Thermal Stability

The TGA curve of a synthesized VES is shown in Figure 7. The thermal data for commercially available ABS and AES are also shown for comparison. In this figure, the grafted VES was synthesized with 1.0 mole ratio of VES to St and 5.0 wt % of BPO at 70°C for 48 h. It is clear that the VES shows better thermal stability with highest thermal degradation temperature than ABS and AES.

As shown in Figure 7 and Table III, the decomposition temperatures of VES, ABS, and AES were 424°C, 370°C, and 390°C, respectively. The residual weight at 450°C of VES is 41%, whereas those of ABS and AES are 13 and 25%, respectively.

Light Resistance and Weatherability

The weatherability of polymers is a very important factor to govern other long-term properties. Several primary causes of deterioration of polymers include sunlight, temperature, moisture, and pollutants. There are some experimental techniques to test weather resistivity of materials.⁴⁰ 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 a National

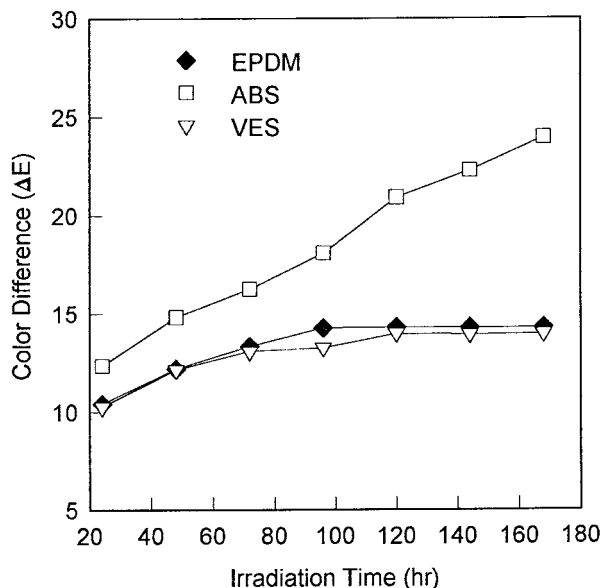


Figure 8 Plots of color difference versus irradiation time for samples (by Fade-o-Meter): (◆) EPDM; (□) ABS; (▽) VES.

Bureau of Standards Unit. The smaller ΔE means better light resistance and weatherability.⁴¹⁻⁴³ The samples were tested in a Fade-o-Meter for the measurement of light resistance for 24, 48, 72, 120, 144, and 168 h, and in a Weather-o-Meter for the measurement of weatherability for the same time intervals. Figure 8 shows the light re-

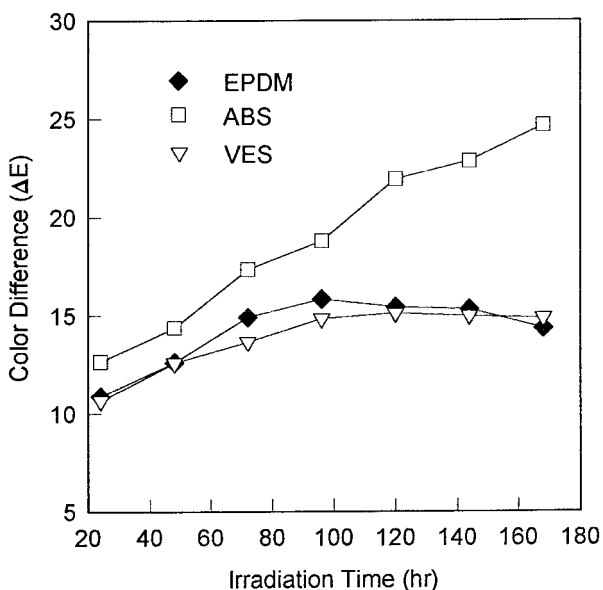


Figure 9 Plots of color difference versus irradiation time for samples (by Weather-o-Meter): (◆) EPDM; (□) ABS; (▽) VES.

sistance of EPDM, ABS, and VES. The grafted VES with 1.0 mole ratio of VES to St was synthesized at 70°C for 48 h in toluene. The ΔE data of commercially available ABS (the same grade as referred to in Fig. 7) is also shown for comparison. It should be noted that the VES synthesized in this work shows better light resistance than ABS because of the inclusion of EPDM, which has excellent outdoor properties.

Similar results were observed in the weatherability data. The weatherability of EPDM, ABS, and VES are also shown in Figure 9. VES shows better weatherability than ABS (see Fig. 9). This result implies that the incorporation of EPDM is very effective in improving the poor weatherability of ABS. The VES is the same as that referred to in Figure 8. The dependence of light resistance and weatherability of VES on the reaction conditions was not significant.

CONCLUSIONS

VES was synthesized with BPO by 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 VTMO and St onto EPDM, the grafting efficiency was increased with increasing EPDM content.
2. The grafting efficiency was highest at the mole ratio of VTMO to St of 0.50 when toluene was used as solvent.
3. The effect of reaction time on the grafting efficiency was increased with increasing the reaction time to 48 h, and then it leveled off.
4. The grafting efficiency of the graft terpolymer was increased up to 70°C but decreased with further increase in temperature.
5. The effect of initiator concentration on the grafting efficiency was increased with increasing initiator concentration up to 5.0 wt %, and then it leveled off.
6. The thermal stability of VES was significantly enhanced as compared with ABS and AES.
7. The light resistance and weatherability of VES were better than those of ABS.

This work was supported by the Ministry of Education, Korea (Research Fund for Advanced Materials in 1995).

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