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SYNTHESIS AND PROPERTIES OF MALEIC ANHYDRIDE-EPDM-STYRENE GRAFT TERPOLYMER

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Key Words: Graft copolymerization; Maleic anhydride-EPDM-styrene graft terpolymer (MAES); Ethylene-propylene-diene terpolymer (EPDM); Characterization; Light resistance; Thermal stability; Acrylonitrile-butadiene-styrene copolymer (ABS); Acrylonitrile-EPDM-styrene copolymer (AES)

ABSTRACT

A graft terpolymer of maleic anhydride (MAH) and styrene (St) on ethylene-propylene-diene terpolymer (EPDM) was obtained using azobisisobutyronitrile (AIBN) as an initiator in toluene. The effects of EPDM concentration, mole ratio of St to MAH, reaction time, reaction temperature, initiator concentration, and solvent on the graft copolymerizations were examined. The synthesized maleic anhydride-EPDM-styrene graft terpolymers (MAES) were identified by IR spectra. It was found that the thermal stability of the MAES was not good when compared to that of acrylonitrile-butadiene-styrene copolymer (ABS), but the light resistance and weatherability of MAES were superior to those of ABS.

INTRODUCTION

Acrylonitrile–butadiene–styrene (ABS) copolymer is one of the most commonly used engineering plastics. ABS has several outstanding properties including high impact strength and rigidity. In combination with these properties, the ease of fabrication makes ABS well suited for the manufacture of various industrial and home goods including automotive parts. But the poor heat resistance and weatherability limit the outdoor use of the material and its blends [1, 2]. Among several attempts to improve the poor performance, the substitution of ethylene-propylene-diene terpolymer (EPDM) for butadiene has been widely investigated [3–10]. A typical example is acrylonitrile–EPDM–styrene (AES) copolymer [11]. It is known that EPDM has outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component [12–19].

The aim of this study is to improve the light resistance and weatherability of ABS resin using EPDM in place of butadiene rubber (BR) and maleic anhydride (MAH) in place of acrylonitrile (AN). MAH and styrene (St) were grafted onto EPDM under argon atmosphere in the presence of AIBN as an initiator. The effects of EPDM concentration, mole ratio of St to MAH, reaction time, reaction temperature, initiator concentration, and solvent were investigated in graft copolymerizations. The thermal stability, light resistance, and weatherability of the graft terpolymer were analyzed.

EXPERIMENTAL

Materials

Maleic anhydride and styrene (Junsei Chemical) were purified by standard procedures. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Ethylene–propylene–diene terpolymer (EPDM), with ethylidene norbornene as a termonomer [Aldrich Chemical:ethylene/propylene = 50/42 mol%, ML50, M_n = 50,500 ($\overline{M}_w/\overline{M}_n$ = 2.02)], 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, acetone, toluene, and tetrahydrofuran (THF) were distilled prior to use.

Synthesis of Maleic Anhydride–EPDM–Styrene Graft Terpolymer (MAES)

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 [3]. After dissolution, a mixture of MAH and styrene (St) with AIBN was added to the flask. Taking a copolymerization of 1.0 of a mole ratio of St to MAH and 0.5 wt% of AIBN as an example, a solution of 5.8 g (0.056 mol) St, 5.5 g (0.056 mol) MAH, and 0.06 g (0.5 wt%) AIBN 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. After a chosen reaction period, the contents were poured into methanol with stirring, the precipitate was filtered, and then dried in a vacuum oven until it reached constant weight. The nongrafted EPDM was extracted by using *n*-hexane. The maleic anhydride-EPDM-styrene graft terpolymer was isolated from a mixture of several copolymers and a homopolymer such as poly(St-*co*-MAH) and polystyrene (PS) using acetone.

The total conversion (%), grafting ratio (%) and grafting efficiency (%) were estimated from the following equations [20]:

$$\text{Total conversion (\%)} = \frac{\text{weight of monomers (MAH + St) reacted onto EPDM}}{\text{weight of monomer charged}} \times 100$$

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

$$\text{Grafting efficiency (\%)} = \frac{\text{weight of polymer in grafts}}{\text{weight of monomers (MAH + St) reacted onto EPDM}} \times 100$$

Measurements

IR and ^{1}H-NMR Spectroscopy

The infrared spectrum of the graft copolymer was recorded on a Perkin-Elmer 1330. ^{1}H-NMR spectra were obtained in tetrahydrofuran-d_8 on a Varian Unity Plus 300 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.

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 (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 3×5 cm^2 and the thickness was 35 μm. The color difference (ΔE) of the samples after exposure to UV was calculated using the Hunter-Schofield equation [4].

Weatherability

The weather resistance (ASTM G53) was measured at 60°C 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 was applied to test light resistance.

RESULTS AND DISCUSSION

Identification of Terpolymer

The structure of MAES was identified by IR and ^{1}H-NMR spectra. The IR spectra of MAES exhibited characteristic absorption bands at 3025 cm^{-1} (stretching vibration of aromatic C—H), 2920 cm^{-1} (stretching vibration of aliphatic C—H bond), 1770 and 1730 cm^{-1} in anhydride of maleic anhydride, 1465 cm^{-1} (scissoring of CH_2), 1375 cm^{-1} in CH_3 of EPDM moiety, and 760 cm^{-1} (out-of-plane bending vibration of aromatic C—H bond) (Fig. 1).

The ^{1}H-NMR spectrum of MAES showed the methyl protons of a polymer backbone chain at 0.8, the methine proton at 1.0, methylene protons in EPDM at 2.2, methine proton in the maleic anhydride unit at 3.59, and aromatic protons in the St unit at 7.02 ppm. Elemental analysis (Carlo Erba 1108) for a typical MAES with a 1.0 feed mole ratio of MAH to St gives the following results: C, 67.98; H, 7.93; O, 24.09%. In this case the grafted MAES was synthesized with 0.5 wt% of AIBN at 60°C for 16 hours. The weight-average molecular weight of the typical MAES was determined as 157,000 ($\overline{M}_w\overline{M}_n$ = 1.54).

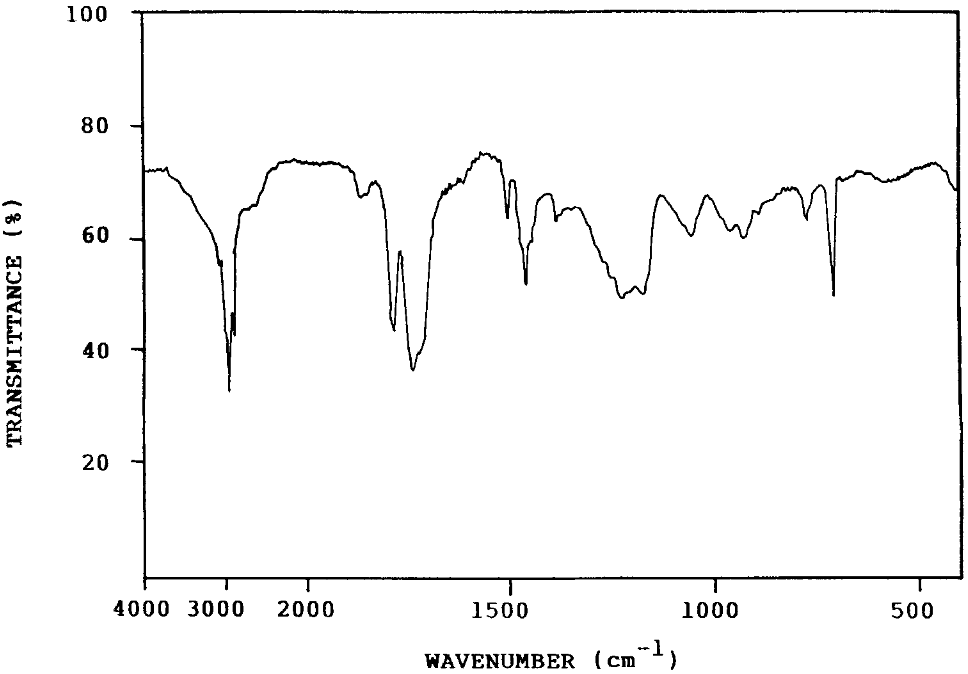

FIG. 1. IR spectrum of maleic anhydride-EPDM-styrene graft terpolymer (MAES).

Effect of Reaction Conditions on the Graft Copolymerization of Maleic Anhydride and Styrene onto EPDM

Effect of EPDM Contents

Figure 2 shows the effect of EPDM content on graft copolymerization. In this case the reaction was carried out at 60°C for 16 hours in toluene at a mole ratio of St to MAH of 1.0. The grafting efficiency increased with an increase in the 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 active centers [21] and, thus, the higher degree of homopolymerization of PS. Composition of St and MAH units in the side chain of the graft terpolymer were 37.6 (wt%) of St units and 38.9 (wt%) of MAH units from analysis of the ^{1}H-NMR spectrum of MAES.

Effect of Mole Ratio

The effect of the mole ratio of St to MAH on the graft copolymerization of EPDM is shown in Table 1. The reaction was carried out in toluene with AIBN (0.5 wt%) as an initiator at 60°C for 16 hours. It can be seen that the grafting efficiency increased with an increasing mole ratio of St to MAH up to 0.5 but thereafter decreased slightly with any further increase of the mole ratio of St to MAH. This result was attributed to the formed 1:1 charge complex of St and MAH that was grafted onto EPDM in the graft terpolymerization.

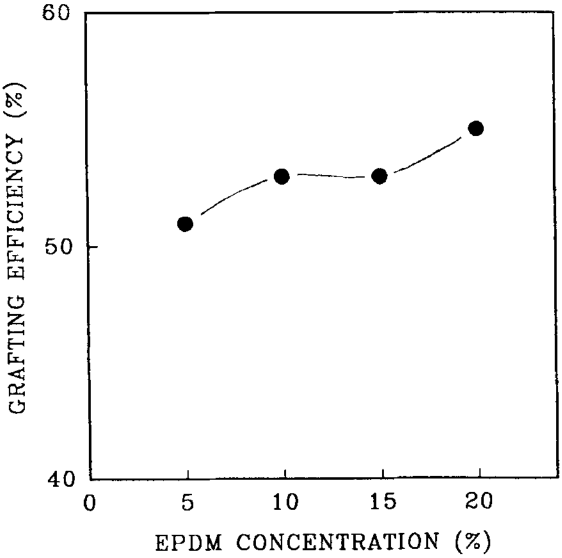

FIG. 2. Plot of grafting efficiency vs EPDM concentration: [St]/[MAH], 1.0; reaction temperature, 60°C; solvent, toluene; reaction time, 16 hours; AIBN, 0.5 wt%.

TABLE 1. Effect of Mole Ratio of St and MAH on the Graft Copolymerization of St and MAH onto EPDM: EPDM, 15%; Solvent, Toluene; Reaction Temperature, 60°C; Reaction Time, 16 Hours; AIBN, 0.5 wt%

Mole ratio [St]/[MAH]	Total conversion, %	Grafting ratio, %	Grafting efficiency, %
0.3	53	369	53
0.5	78	331	52
1.0	96	329	53
2.0	71	345	37

Effect of Reaction Time

Figure 3 shows the effect of reaction time on the grafting process. In this case the mole ratio of St to MAH was 1.0 and the reaction took place at 60°C. The grafting efficiency gradually increased with reaction time up to 16 hours and then leveled off. With an 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 with reaction time is observed [10].

Effect of Reaction Temperature

The effect of reaction temperature on graft copolymerization is shown in Fig. 4. The grafting was carried out at 50, 60, 70, and 80°C while all the variables were

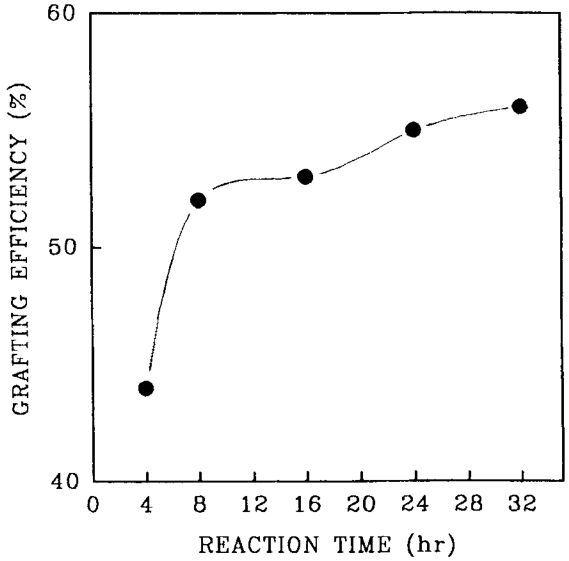

FIG. 3. Plot of grafting efficiency vs reaction time: [St]/[MAH], 1.0; EPDM, 15%; reaction temperature, 60°C; solvent, toluene; AIBN, 0.5 wt%.

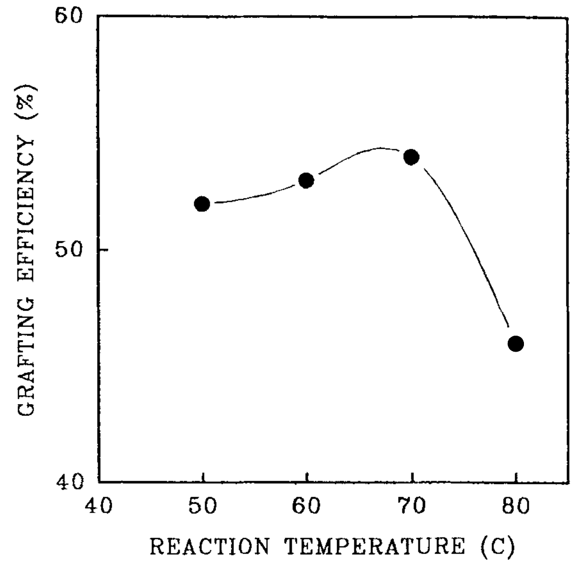

FIG. 4. Plot of grafting efficiency vs reaction temperature: [St]/[MAH], 1.0; EPDM, 15%; reaction time, 16 hours; solvent, toluene; AIBN, 0.5 wt%.

kept constant. The mole ratio of St and MAH was fixed at 1.0. On increasing the temperature, grafting efficiency passes through a maximum at 70°C. 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, grafting efficiency increases initially but then decreases with any further increase in temperature. A similar observation was made by Porejko et al. [22, 23] for the grafting of maleic anhydride onto LDPE.

Effect of Initiator Concentration

Figure 5 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 St to MAH at 60°C for 16 hours. The grafting efficiency increased with increasing initiator concentration up to 0.3 wt% but thereafter 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 [24].

Effect of Solvent

Table 2 shows the effect of solvent on graft copolymerization. The grafting efficiency is highest at 53% when toluene was used as the solvent whereas the grafting efficiency decreased with increasing THF in the toluene-THF mixed solvents. These results come from the difference in solvent power of each solvent-polymer pair [25, 26]; i.e., THF is a good solvent for EPDM but a poor solvent for

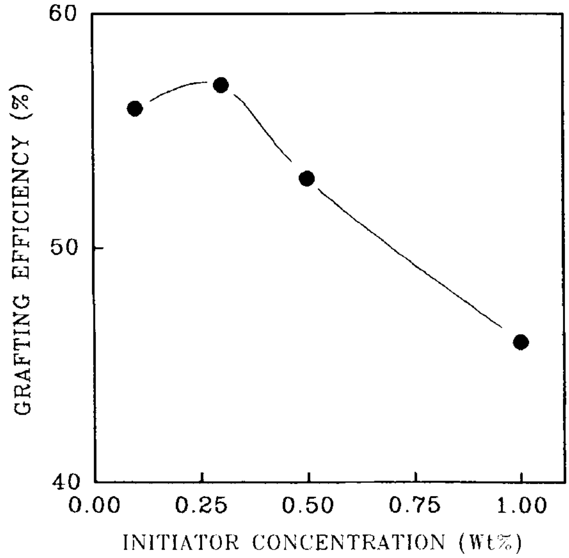

FIG. 5. Plot of grafting efficiency vs initiator concentration: [St]/[MAH], 1.0; EPDM, 15%; reaction temperature, 60°C; solvent, toluene; reaction time, 16 hours. The initiator concentration is based on the monomers + EPDM.

MAES or other copolymers and homopolymers obtained as by-products such as poly(styrene-*co*-MAH) and PS, respectively, whereas toluene is a good solvent for both EPDM and MAES. Thus, it was found that since toluene dissolves the polymers more readily than THF, the grafting efficiency was the highest when toluene was used as the solvent. Odian et al. [27-29] reported similar solvent effect results on graft copolymerizations of styrene onto nylon, polyethylene, and polypropylene. The result was also in agreement with our previous results on the AN-EPDM-methyl methacrylate graft terpolymer [4].

TABLE 2. Effect of Solvents on the Graft Copolymerization of St and MAH onto EPDM. EPDM, 15%; [St]/[MAH], 1.0; Reaction Temperature, 60°C; Reaction Time, 16 hours; AIBN, 0.5 wt%

Solvent (toluene/THF)	Total conversion, %	Grafting ratio, %	Grafting efficiency, %
100/0	96	329	53
90/10	97	225	32
50/50	99	227	31
0/100	87	28	5

Thermal Stability

The TGA curve of a synthesized MAES is shown in Fig. 6. The thermal data of commercially available ABS and AES are also shown for comparison. For this figure, the grafted MAES was synthesized with a 1.0 mole ratio of St to MAH and 0.5 wt% of AIBN at 60°C for 16 hours. Unexpectedly, MAES showed inferior thermal stability with the lowest thermal degradation temperature compared to ABS and AES. The decomposition temperatures of MAES, ABS, and AES were 330, 370, and 390°C, respectively. The residual weight at 450°C of MAES is 16% whereas those of ABS and AES are 13 and 25%, respectively.

Light Resistance and Weatherability

There are some experimental techniques for testing the weather resistance of materials [30]. 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 [31-33]. The samples were tested in a Fade-o-Meter for measurements of light resistance for 6, 12, 24, 48, 60, and 72 hours, and in a Weather-o-Meter for the measurements of weatherability for the same time intervals. Figure 7 shows the light resistance of ABS, AES, and MAES. Grafted MAES with a 1.0 mole ratio of St to MAH was synthesized at 60°C for 16 hours in toluene. The ΔE data of commercially available ABS and AES (the same grade as referred to in Fig. 6) are shown for comparison. It should be noted that MAES synthesized in this work shows better light resistance than ABS because of the inclusion of EPDM which has excellent outdoor properties.

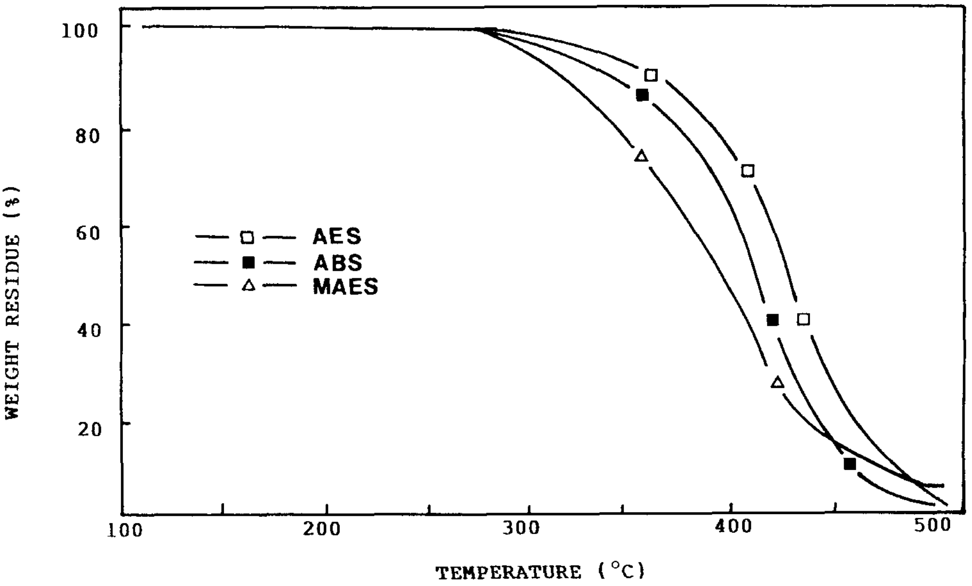

FIG. 6. TGA curves of ABS, AES, and MAES: heating rate, 15°C/min in nitrogen.

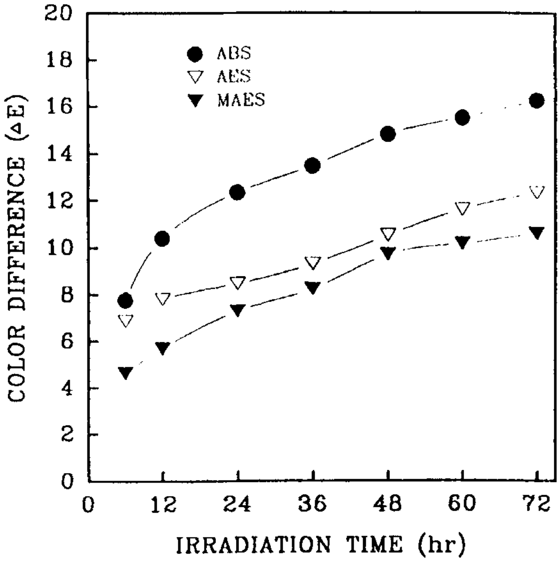

FIG. 7. Plot of color difference vs irradiation time for various samples (by Fade-o-Meter).

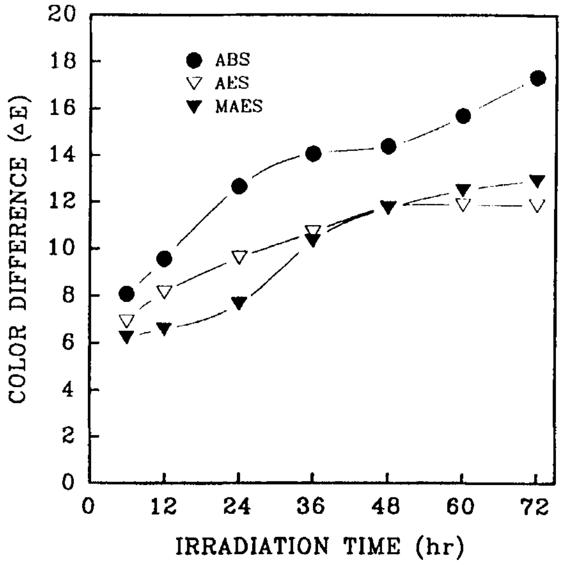

FIG. 8. Plot of color difference vs irradiation time for various samples (by Weather-o-Meter).

Another interesting feature is that MAES shows better weatherability than does ABS, even though MAES does not show better weatherability than does AES (see Fig. 8). In this case the MAES is the same as that referred to in Fig. 7. This result implies that the incorporation of EPDM is very effective for improving the poor weatherability of ABS. The dependence of light resistance and weatherability of MAES on the reaction conditions was not significant.

CONCLUSIONS

Maleic anhydride-EPDM-styrene graft terpolymer (MAES) was synthesized with azobisisobutyronitrile (AIBN) 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 maleic anhydride and styrene onto EPDM, the grafting efficiency increased with EPDM content.
2. The grafting efficiency was similar at mole ratios of St to MAH from 0.3 to 1.0 when toluene was used as the solvent.
3. The effect of reaction time on grafting efficiency increased with increasing reaction time.
4. The grafting efficiency of the graft terpolymer increased up to 70°C but decreased with any further increase in temperature.
5. The effect of initiator concentration on grafting efficiency increased up to 0.3 wt% and then decreased.
6. The thermal stability of MAES was inferior to that of ABS but the light resistance and the weatherability of MAES were superior to those of ABS.

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