# Synthesis and Properties of Methyl Methacrylate–EPDM–Styrene Graft Terpolymer

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

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

SYNOPSIS

The graft copolymerizations of methyl methacrylate (MMA) 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, mol ratio of St to MMA, reaction time, reaction temperature, and initiator concentration on the graft copolymerizations were examined. The synthesized MMA–EPDM–St graft terpolymers (MES) were identified by IR and $^1$H-NMR spectra. The number-average molecular weight ($M_n$) was 110,000. The thermal stability, tensile strength, light resistance, and weatherability of MES were considerably better than those of the acrylonitrile–butadiene–St (ABS) copolymer. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Acrylonitrile–butadiene–styrene (ABS) copolymer is one of the most commonly used engineering plastics. ABS has several outstanding properties such as high impact strength and rigidity. In combination with these properties, the ease of fabrication makes ABS well suited for 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 the attempts to improve 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 has been 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 was to improve the heat resistance and weatherability of the ABS resin using EPDM in place of butadiene and methyl methacrylate (MMA) in place of acrylonitrile (AN), respectively. MMA was selected because poly(MMA), PMMA, has a good resistance to ultraviolet light degradation, and hence a good weathering resistance.[20,21] MMA 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 EPDM contents, mol ratio of St to MMA, reaction time, reaction temperature, and initiator concentration in the graft copolymerizations were studied. The thermal stability, light resistance, weatherability, and tensile properties of the graft terpolymer were also analyzed.

## EXPERIMENTAL

### Materials

MMA (Junsei Chemical Co.) and St (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, acetone, toluene, and tetrahydrofuran (THF) were distilled prior to use.

* To whom correspondence should be addressed.

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**Table I Graft Copolymerization Conditions Used**

| Condition | Description |
|---|---|
| EPDM concentration (wt %) | 5, 10, 15, 20 |
| Mol ratio of [St]/[MMA] | 0.20, 0.40, 1.00, 2.50, 5.00 |
| Reaction time (h) | 30, 45, 55, 65, 75 |
| Reaction temperature (°C) | 60, 70, 80, 90, 100 |
| Initiator concentration (based on the monomers + EPDM) (wt %) | 0.1, 0.8, 1.6 |

## Synthesis of MES

A given amount of EPDM was dissolved in 200 mL of toluene in a 1-L separable flask provided with a modified Hopkins cooler, a thermometer, and gas inlet.[5] After dissolution, a mixture of MMA and St with BPO was added into the flask. Taking a copolymerization mol ratio of 0.40 of MMA to St and 0.8 wt % of BPO as an example, a solution of 4.0 g (0.04 mol) MMA, 10.4 g (0.1 mol) St, and 0.115 g (0.8 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 I). 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 MES was isolated from a mixture of several homopolymers and copolymers such as polystyrene (PS), PMMA, poly(MMA-*co*-St), poly(EPDM-*g*-MMA), and poly(EPDM-*g*-St) 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 (%), and grafting efficiency (%) were estimated from the following equation[22]:

$$\text{Total conversion (\%)} = \frac{\text{weight of monomers (MMA + St) reacted onto EPDM}}{\text{weight of monomer charged}} \times 100 \quad (1)$$

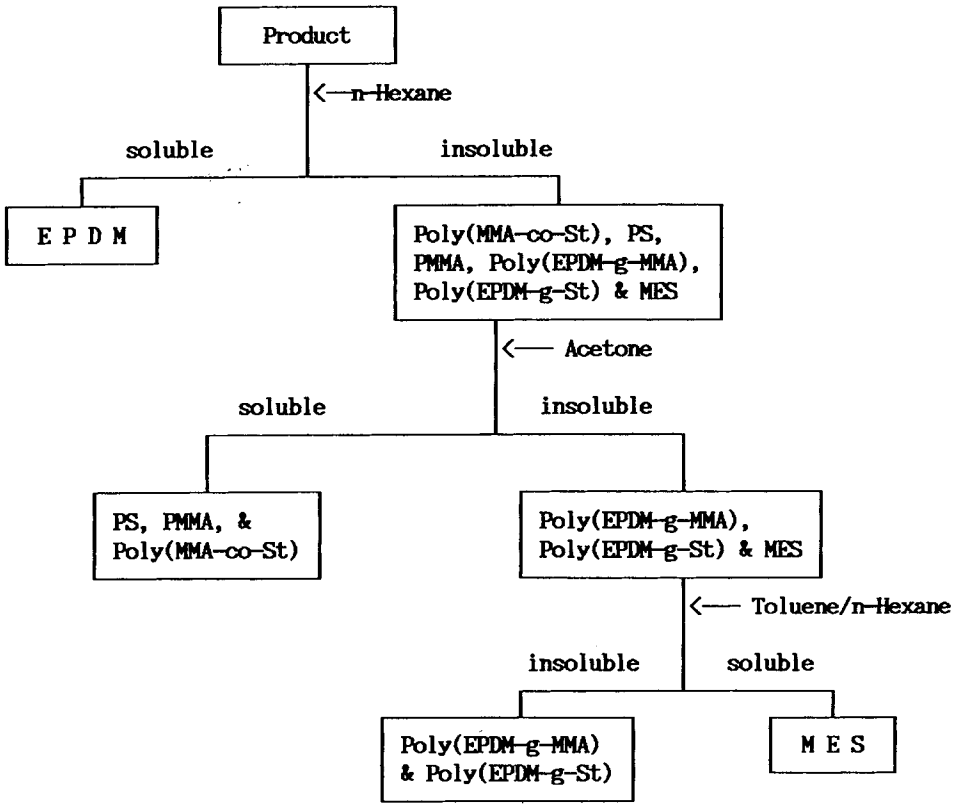


**Figure 1** Block diagram of graft terpolymer (MES) isolation process (notations are described in the text).

grafting ratio (%)

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

grafting efficiency (%)

$$= \frac{\text{weight of polymer in grafts}}{\text{weight of monomers (MMA + St) reacted onto EPDM}} \times 100. \quad (3)$$

### Measurements

#### *IR and $^1$H-NMR Spectroscopy*

The IR spectrum of the graft terpolymer was recorded on a 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 PS 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 D 638-84. The crosshead speed was 5 mm/min, and the initial gauge length was adjusted at 25 mm.

#### *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-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 $3 \times 5$ cm$^2$ and thickness was 35 $\mu$m. The color difference ($\Delta E$) of the samples after exposing to UV was calculated using the Hunter-Schofield equation.[6]

#### *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 $\Delta E$ of the samples after exposing to UV and moisture was compared by the same method as applied to test light resistance.

## RESULTS AND DISCUSSION

### Characterization

The structure of MES was identified by IR spectrophotometry (Perkin-Elmer 1330). The IR spectra of MES 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); 1720 cm$^{-1}$ (stretching vibration of C=O bond); 1465 cm$^{-1}$ (scissoring of $CH_2$); 1375 cm$^{-1}$ (bending of $CH_3$); and 760 cm$^{-1}$ (out-of-plane rotational vibration of aromatic C—H bond) (Fig. 2). The graft terpolymer was also characterized by its $^1$H-NMR spectra. The MES spectra showed multiple peaks at 0.8, 1.0–2.5, and 7.2–7.4 ppm, which are due to the methyl protons of the polymer backbone chain, the methine and methylene protons, and the phenyl protons of the St unit, respectively.

Elemental analysis (Carlo Erba 1108) for a typical MES with 0.40 feed mol ratio of MMA to St gives the results as follows:

ANAL: C, 83.82%; H, 11.64%; 0, 4.14%.

In this case, the grafted MES was synthesized with 0.8 wt % of BPO at 70°C for 55 h. The weight-average molecular weight of the typical MES was determined as 165,000 ($M_w/M_n$ = 1.50).

### Effect of Reaction Conditions on Graft Copolymerizations of MA and St onto EPDM

#### *Effect of EPDM Contents*

The effect of EPDM contents on the graft copolymerization is shown in Figure 3. The grafting efficiency gradually increases with EPDM contents. This result is probably caused by the increasing diene contents of the graft site in EPDM as EPDM contents increase. A slight Trommsdorff effect was observed due to the systematic variation of viscosity, when EPDM contents became higher. On the other hand, it seems that the lower the concentration of

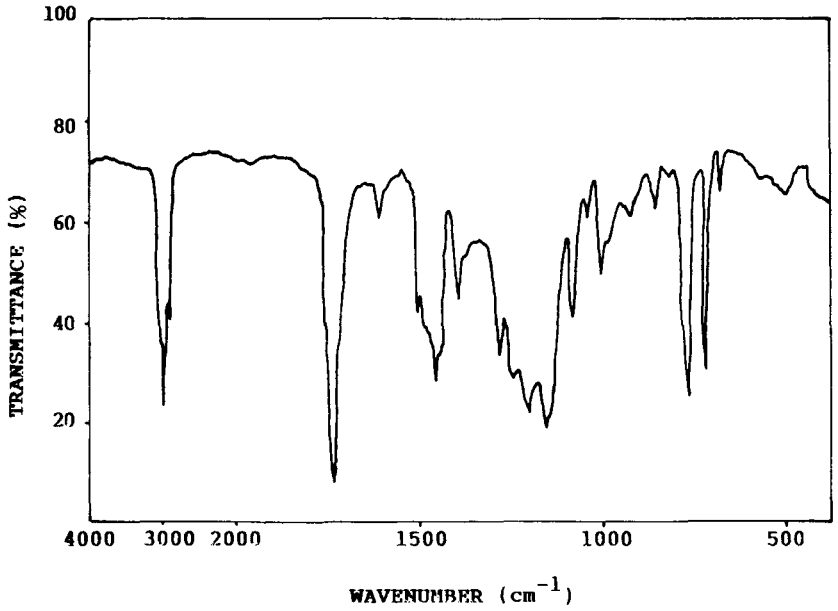


**Figure 2** IR spectrum of methyl methacrylate–EPDM–tyrene (MES) graft terpolymer.

EPDM, the fewer active centers[17] and, thus, the higher degree of homopolymerizations of PS and PMMA. 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 55 h in toluene with a mol ratio of MMA to St of 0.40.

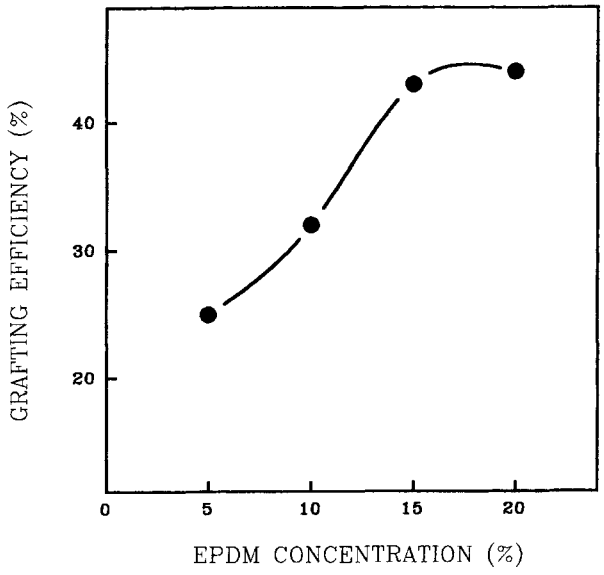


**Figure 3** Plot of grafting efficiency vs. EPDM concentration: [St]/[MMA], 0.40; reaction temp., 70°C; solvent, toluene; reaction time, 55 h; BPO, 0.8 wt %.

### *Effect of Mol Ratio*

Table II shows the effect of mol ratio of MMA to St on the graft copolymerization onto EPDM. The reaction was carried out in toluene with BPO (0.8 wt %) as an initiator at 70°C for 55 h. As can be seen, the grafting efficiency increases with a decrease in the mol ratio of St to MMA. The grafting efficiency is highest at 47% at the mol ratio of St to MMA of 0.20.

### *Effect of Reaction Time*

The effect of reaction time on the grafting process is shown in Figure 4. In this case, the mol ratio of St to MMA was 0.40 and the reaction was made at

**Table II Effect of Mol Ratio of St and MMA on the Graft Copolymerization of MMA and St onto EPDM**

| Mole Ratio [St]/[MMA] | Total Conversion (%) | Grafting Ratio (%) | Grafting Efficiency (%) |
|---|---|---|---|
| 0.20 | 84 | 195 | 47 |
| 0.40 | 72 | 146 | 43 |
| 1.00 | 62 | 121 | 39 |
| 2.50 | 51 | 96 | 32 |
| 5.00 | 52 | 92 | 30 |

EPDM, 15%; solvent, toluene; reaction temp., 70°C; reaction time, 55 h; BPO, 0.8 wt %.

70°C. The grafting efficiency linearly increased with reaction time up to 65 h and thereafter gradually increased. With increase in reaction time, the radicals have more time for reaction and as a result increases in grafting efficiency was observed. After some time all the initiator was used. As a result no further change in grafting efficiency was observed with an increase in reaction time. A similar tendency has been shown in our previous work[6] for the graft copolymerization of AN and MMA onto EPDM.

### *Effect of Reaction Temperature*

Figure 5 shows the effect of reaction temperature on the graft copolymerization. The reaction was performed in toluene with 0.8 wt % of BPO and 0.40 mol ratio of St to MMA for 55 h. On increasing the temperature, grafting efficiency passes through a maximum at 80°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 an increase in temperature, however, the rate of homopolymerization also increases.[23] As a result, the grafting efficiency increases initially, but on further increase in temperature, grafting efficiency decreases. A similar observation was made by Porejko et al.[24] for the grafting of maleic anhydride onto low-density polyethylene.

### *Effect of Initiator Concentration*

The effect of initiator concentration on the graft copolymerization is shown in Figure 6. In this case,

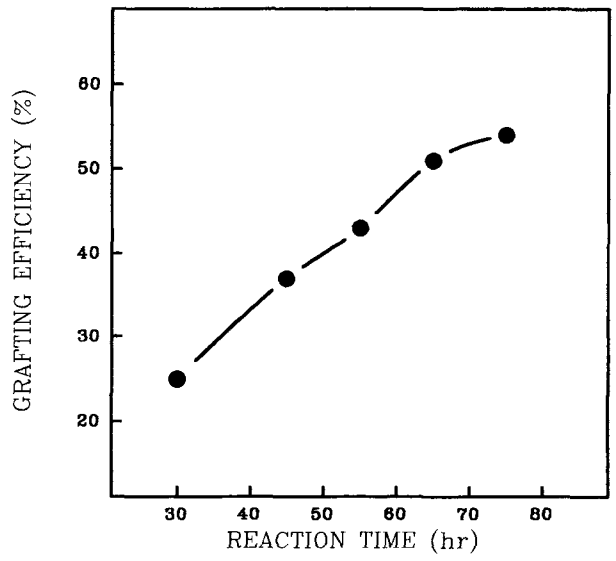


**Figure 4** Plot of grafting efficiency vs. reaction time: [St]/[MMA], 0.40; EPDM, 15%; reaction temp., 70°C; solvent, toluene; BPO, 0.8 wt %.

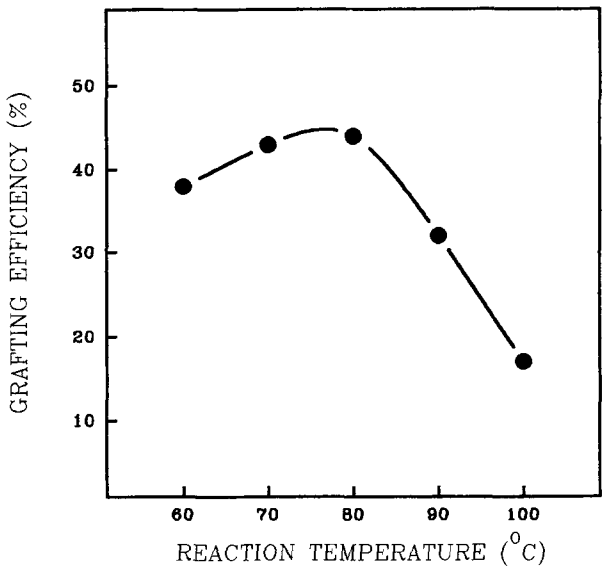


**Figure 5** Plot of grafting efficiency vs. reaction temperature: [St]/[MMA], 0.40; EPDM, 15%; reaction time, 55 h; solvent, toluene; BPO, 0.8 wt %.

the reaction was carried out in toluene with a 0.40 mol ratio of St to MMA at 70°C for 55 h. The grafting efficiency decreased with 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.[25]

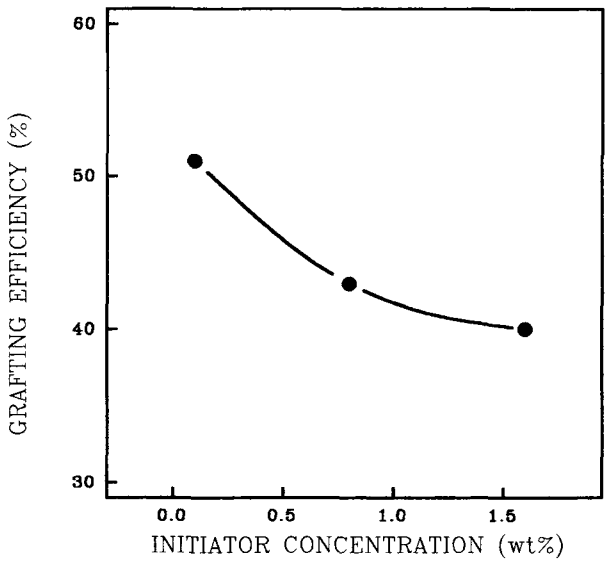


**Figure 6** Plot of grafting efficiency vs. initiator concentration: [St]/[MMA], 0.40; EPDM, 15%; reaction temp., 70°C; solvent, toluene; reaction time, 55 h; initiator concentration (based on the monomers + EPDM) (wt %).

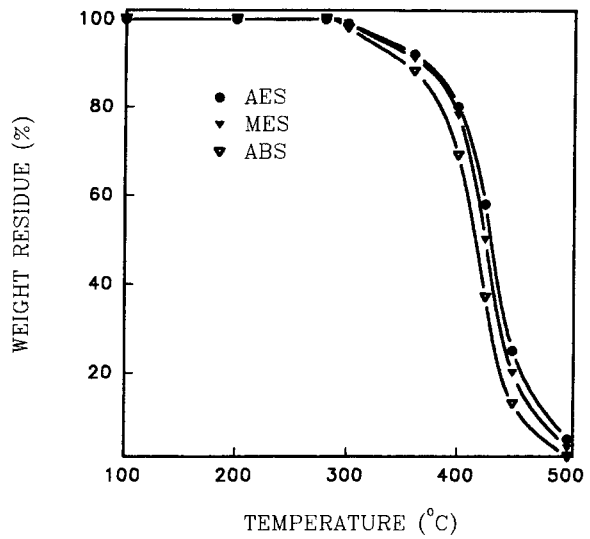


**Figure 7** TGA curves of AES, ABS, and MES: heating rate, 15°C/min in nitrogen: (●) AES; (▽) ABS; (▼) MES.

## Thermal Stability

The TGA curve of a synthesized MES is shown in Figure 7. The thermal data of commercially available ABS and AES were also shown for comparison. In this figure, the grafted MES was synthesized with a 0.40 mol ratio of St to MMA and 0.8 wt % of BPO at 70°C for 55 h. It is clear that the MES shows better thermal stability with better thermal degradation temperature to ABS even though MES does not show better thermal stability than AES. As shown in Figure 7 and Table III, the decomposition temperatures of MES, ABS, and AES were 390, 370, and 390°C, respectively. The residual weight at 450°C of MES is 20% whereas those of ABS and AES are 13 and 25%, respectively.

## Tensile Properties

The tensile properties of MES, AES, and ABS are listed in Table IV. The grafted MES shown in this table was prepared at 70°C for 55 h in toluene with a mol ratio of St to MMA of 0.40. The effect of the reaction conditions on the tensile properties was not significant.

It is pertinent to note the MES has the highest tensile strength as well as the lowest elongation to break in contrast to AES and ABS.

**Table III Decomposition Temperature and Percent Weight Residue of ABS, AES, and MES**

| Material | Initial Decomposition Temperature (°C) | Weight Residue at 450°C (%) |
|---|---|---|
| ABS | 370 | 13 |
| AES | 390 | 25 |
| MES | 390 | 20 |

MES synthesized from graft copolymerization of MMA and St onto EPDM: [St]/[MMA] = 0.40; solvent, toluene; reaction time, 55 h; reaction temp., 70°C; BPO, 0.8 wt %.

**Table IV Comparison of Tensile Properties of ABS, AES and MES**

| Material | Tensile Strength ($kg/cm^2$) | Elongation at Break (%) |
|---|---|---|
| ABS | 295 | 8.4 |
| AES | 311 | 3.7 |
| MES | 390 | 3.5 |

MES synthesized from graft copolymerization of MMA and St onto EPDM: [St]/[MMA] = 0.40; solvent, toluene; reaction time, 55 h; reaction temp., 70°C; BPO, 0.8 wt %.

## Light Resistance and Weatherability

There are some experimental techniques to test weather resistivity of materials.[26] 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 $\Delta E$ with a National Bureau of Standards Unit. The smaller $\Delta E$ means better light resistance and weatherability.[27-29] The samples were tested in a Fade-o-Meter for the measurements of light resistance for 6, 12, 24, 36, 48, 60, and 72 h, and in a Weather-o-Meter for the measurements of weatherability for the same time interval. Figure 8 shows the light resistance of EPDM, ABS, and MES. The grafted MES with a 0.40 mol ratio of St to MMA was synthesized at 70°C for 55 h in toluene. The $\Delta E$ data of commercially available ABS (the same grade as referred to in Fig. 7) is also shown for comparison. It should be noted that MES synthesized in this work shows better light resistance than ABS because of the inclusion of EPDM, which has excellent outdoor properties.

Similar results were also observed in the weatherability data. The weatherability of EPDM, ABS, and MES are also shown in Figure 9. MES shows better weatherability than does ABS (see Fig. 9). This result implies that the incorporation of EPDM is very effective to improve poor weatherability of ABS. The MES is the same as that referred to in Figure 8. The dependence of light resistance and

weatherability of MES on the reaction conditions was not significant.

## CONCLUSIONS

MES was synthesized with BPO 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. In the graft copolymerization of MMA and St onto EPDM, the grafting efficiency was increased with increasing EPDM contents.
2. The grafting efficiency was highest at the mol ratio of St to MMA of 0.20 when toluene was used as a solvent.
3. The grafting efficiency was increased with increasing reaction time up to 65 h and then levelled off.
4. The grafting efficiency of the graft terpolymer was increased up to 80°C but decreased with further increased in temperature.
5. The grafting efficiency was increased with decreasing initiator concentration.
6. The thermal stability and tensile strength of MES were somewhat enhanced as compared to ABS and AES.
7. The light resistance and the weatherability of MES were better than those of ABS.

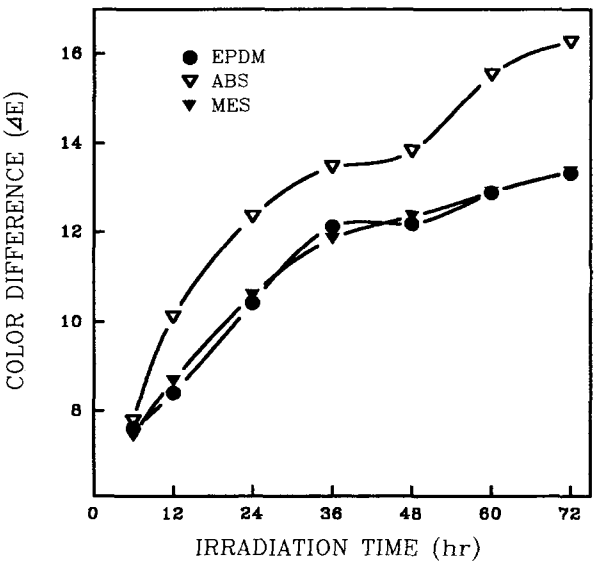


**Figure 8** Plots of color difference vs. irradiation time for various samples (by Fade-o-Meter): (●) EPDM; (▽) ABS; (▼) MES.

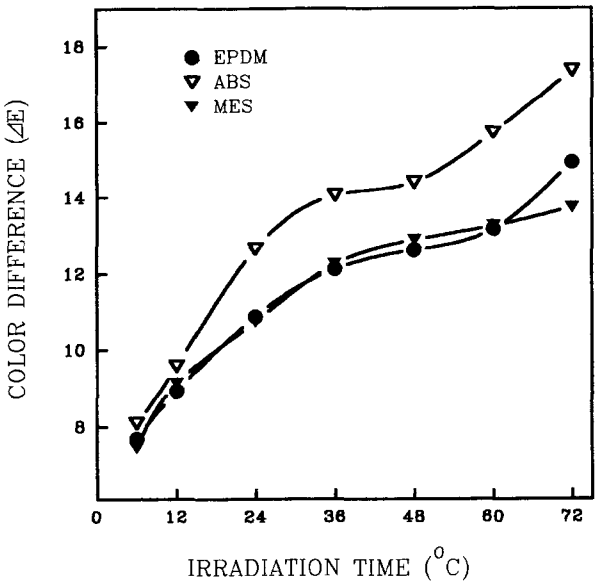


**Figure 9** Plots of color difference vs. irradiation time for various samples (by Weather-o-Meter): (●) EPDM; (▽) ABS; (▼) MES.

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