Synthesis and Properties of 2-Vinylnaphthalene–EPDM–Methyl Methacrylate Graft Copolymer

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SYNOPSIS

A graft copolymer of 2-vinylnaphthalene (2-VN) and methyl methacrylate (MMA) onto ethylene–propylene–diene terpolymer (EPDM) was synthesized in tetrahydrofuran using benzoyl peroxide. The effects of EPDM content, mol ratio of 2-VN to MMA, reaction time, reaction temperature, and initiator concentration in the graft copolymerization were examined. The light resistance, thermal stability, and the tensile properties of the graft copolymer were investigated by using Fade-o-Meter, thermogravimetric analyzer, and tensile tester. It was found that the light resistance and the heat resistance as well as the tensile strength of the graft copolymer are considerably better than those of the acrylonitrile–butadiene–styrene (ABS) copolymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The 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 several attempts to improve the poor performance, the substitution of ethylene–propylene–diene terpolymer (EPDM) for butadiene has been widely investigated.[3–9] 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.[10–13]

The aim of this study was to improve the heat resistance and weatherability of the ABS resin using EPDM in place of butadiene, 2-vinylnaphthalene (2-VN) in place of styrene, and methyl methacrylate (MMA) in place of acrylonitrile (AN), respectively. Because of the high glass transition temperature of

2-VN, it is expected to impart thermal stability to the resultant copolymer, hence resulting in improved heat resistance.[11] MMA was selected because of its good toughness and light resistance.[12] Graft copolymerizations were carried out under argon atmosphere in the presence of benzoyl peroxide (BPO) as the initiator and tetrahydrofuran (THF) as the solvent. The effects of various factors such as EPDM content, mol ratio of 2-VN to MMA, reaction time, reaction temperature, and initiator concentration in the graft copolymerizations were studied. The light resistance, the thermal stability, and tensile properties of the graft copolymer are also discussed.

EXPERIMENTAL

Materials

2-Vinylnaphthalene (2-VN) (Aldrich Chemical Co.) and methyl methacrylate (MMA) (Junsei Chemical) were freed of inhibitors by washing successively with 5% aqueous sodium hydroxide, drying over anhydrous $CaCl_2$, and distilling under vacuum. Benzoyl peroxide (BPO) (Hayashi Chemical Co.) was purified by recrystallization from methanol. Ethylene–propylene–diene terpolymer (EPDM), having ethylidene norbornene as a termonomer (Aldrich; ethylene/propylene = 50/42 by mol %, ML50), was used as received. n-Hexane, acetone, methyl ethyl

ketone (MEK), toluene, and tetrahydrofuran (THF) were distilled prior to use.

Synthesis of 2-Vinylnaphthalene–EPDM–Methyl Methacrylate Graft Copolymer (VEM)

The grafting reactions were carried out in a 1 L separable flask equipped with a modified-Hopkins cooler, a thermometer, and an argon gas inlet. A given amount of EPDM was dissolved in 100 mL of THF in the flask. A mixture of 2-VN and MMA at a given mol ratio was dissolved in 50 mL of THF and then added with 0.12 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 Copolymer

In the synthesis, the products obtained consist of ungrafted EPDM, VEM, and several copolymers and unbound homopolymers. The nongrafted EPDM was separated from the rest of the products by extraction using petroleum ether. The VEM was isolated from a mixture of several copolymers and homopolymers such as poly(2-VN-co-MMA), poly(EPDM-g-2-VN), poly(EPDM-g-MMA), poly(methyl methacrylate) (PMMA), poly(2-vinylnaphthalene) (P2VN)) using MEK/acetone (50/50 by vol), and toluene/n-hexane (50/50 by vol) mixed solvents. Details of isolation procedures of the graft copolymer 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[14]:

Table I   Graft Copolymerization Conditions Used in This Study

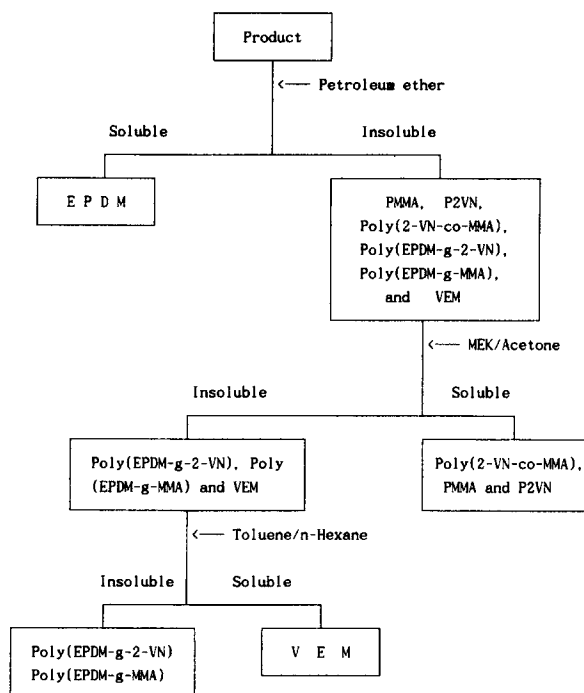| Condition	Description
EPDM content (wt %)	2.0, 3.5, 5.0, 6.5, 8.0
Mol ratio ([2-VN]/[MMA])	0.5, 0.75, 1.0, 1.5, 2.0
Polymerization time (h)	10, 20, 30, 40, 60, 90
Reaction temperature (°C)	60, 70, 80, 90
BPO content [$(M/L) \times 10^4$]	2.48, 4.95, 9.81, 19.82

Figure 1   Block diagram of graft copolymer (VEM) isolation procedure (notations are described in the text).

Grafting ratio (%)

$$= \frac{\text{weight of polymer in grafts}}{\text{weight of substance}} \times 100 \quad (1)$$

Grafting efficiency (%)

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

Measurements

IR and ^{1}H-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 JEOL GSX-270 NMR spectrophotometer.

Gel Permeation Chromatography (GPC)

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

Thermogravimetric Analysis (TGA)

Thermal stabilities of polymers were examined with a Shimadzu-DT 30A TGA instrument at a scanning of 10°C/min under nitrogen.
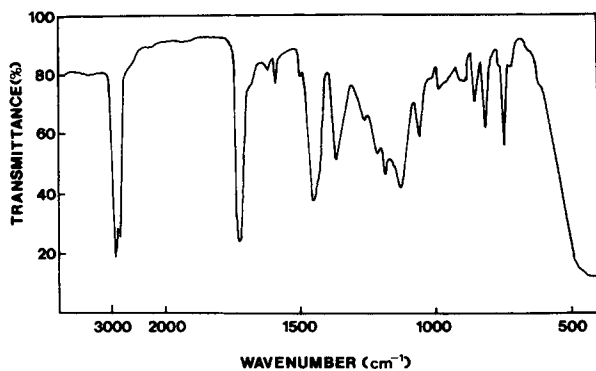
Figure 2   IR spectrum of VEM graft copolymer.

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 toluene 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 cm^2, with a thickness of 35 μm. The color difference (ΔE) of the films after exposing to UV was calculated using the Hunter–Schofiled equation.[13]

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

Characterization

Figure 2 shows the IR spectrum of the graft copolymer, VEM. The IR spectra of VEM exhibited characteristic absorption bands at 3000 cm^{-1} (stretching vibration of the aromatic C—H bond), 2900 cm^{-1} (stretching vibration of the aliphatic C—H bond), 1725 cm^{-1} (stretching vibration of the C=O bond), 1465 cm^{-1} (scissoring of CH$_2$), 1375 cm^{-1} (bending of CH$_3$), 1135 cm^{-1} (stretching of C—O), and 900–650 cm^{-1} (out-of-plane rotational vibration of aromatic C—H). The graft copolymer was also characterized by its ^{1}H-NMR

spectra. The VEM spectra showed multiple peaks at 0.8, 1.0–2.5, and 7.2–7.8 ppm, which are due to the methyl protons of the polymer backbone chain, the methine and methylene protons, and the naphthalene protons of the 2-VN unit, respectively.

It should be pointed out that more detailed studies should be carried out on the accurate characterization of the terpolymer compositions such as mol percentages of 2-VN and MMA in the graft terpolymer, even though the determination of a terpolymer composition is not easy at present. For reference, however, elemental analysis (Carlo Erba 1108) for a typical VEM with 0.75 feed mol ratio of 2-VN to MMA gives the results as follows:

ANAL: C, 84.55%; H, 12.13%; O, 3.22%.

In this case, the grafted VEM was synthesized with 0.12 g of BPO at 60°C for 40 h. The weight-average molecular weight of the typical VEM was determined as 222,000 ($M_w/M_n = 2.47$).

Effect of Variables on Grafting

Effect of Reaction Time

The effect of reaction time on the graft copolymerization is shown in Figure 3. The graft copolymerization was carried out in THF at 60°C with con-
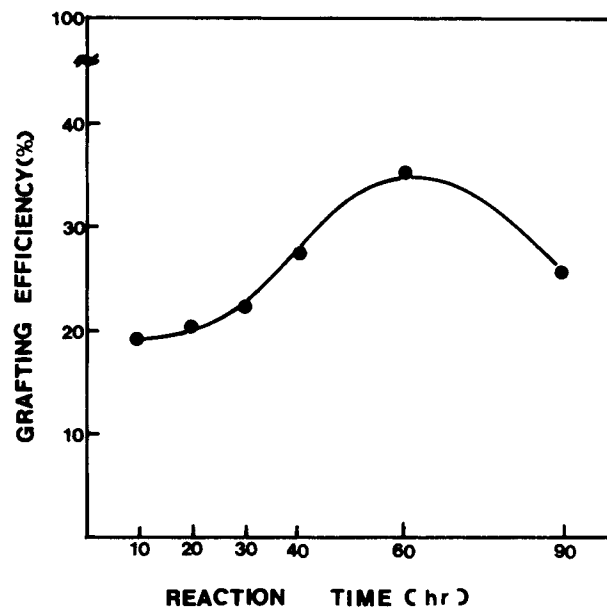

Figure 3   Plot of grafting efficiency vs. reaction time: [2-VN]/[MMA], 0.75; reaction temp, 60°C; solvent, THF; BPO, 0.12 g.

Table II   Effect of Mol Ratio of 2-VN to MMA on the Graft Copolymerization of MMA and 2-VN onto EPDM and the Molecular Weight Characteristics: Reaction Time: 40 h, Reaction Temp: 60°C; Solvent: THF, BPO: 0.12 g

Exp. No.	Mol Ratio of 2-VN to MMA	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)	M_n	M_w	M_w/M_n
VEM (0.5)	0.5	36.7	74.9	30.5	149,000	321,000	2.15
VEM (0.75)	0.75	36.1	69.6	27.9	90,000	222,000	2.47
VEM (1.0)	1.0	35.4	65.8	26.2	81,000	142,000	1.75
VEM (1.5)	1.5	34.3	62.9	24.8	59,000	104,000	1.76
VEM (2.0)	2.0	33.6	61.3	24.1	59,000	101,000	1.71

stant concentrations of EPDM and BPO. The mol ratio of 2-VN to MMA was fixed at 0.75. The grafting efficiency increased up to 60 h and then decreased. The decrease in grafting efficiency after 60 h 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.[8,15]

Effect of Mol Ratio

Table II shows the effect of mol ratio of 2-VN to MMA on the graft copolymerization onto EPDM. The reaction was carried out in THF with 0.12 g of BPO at 60°C for 40 h.

As can be seen, the grafting efficiency decreases with increase in the mol ratio of 2-VN to MMA. The grafting efficiency is highest at 30.5% at the mol ratio of 2-VN to MMA of 0.5. This effect may be explained by the difference in reactivity between 2-VN and MMA; r_1(2-VN) and r_2(MMA) were reported as 1.0 and 0.4, respectively, for the copolymerization at 60°C,[16] meaning that MMA has a much lower tendency to homopolymerize than does 2-VN. Table II also lists the molecular weight characteristics of the graft copolymers having various mol ratios in feed. It is seen that the molecular weights of the graft copolymers become smaller as the grafting efficiency is lower. A similar tendency has been shown in our previous work[11] for the graft copolymerization of AN and 4-chlorostyrene onto EPDM.

Effect of Reaction Temperature

The effect of reaction temperature on the graft copolymerization is shown in Figure 4. The grafting was carried out at 60, 70, 80, and 90°C, keeping all the variables constant. The mol ratio of 2-VN and MMA was fixed at 0.75. On increasing the temperature, the grafting efficiency passes through a max-

imum at 80°C. The increase in grafting efficiency with increasing temperature up to 80°C may be due to the decomposition rate of BPO as a function of temperature, since BPO will decompose faster at higher temperatures with a sacrifice in molar mass.[17,18] However, the exact reason is not clear why the grafting efficiency decreases with further increasing temperature.

Effect of Initiator Concentration

Figure 5 shows the effect of the initiator concentration on the graft copolymerization. The grafting was carried out with various concentrations of initiator at 60°C for 40 h. The mol ratio of 2-VN to MMA is the same as described earlier. The grafting efficiency decreases with initiator concentrations. The increase
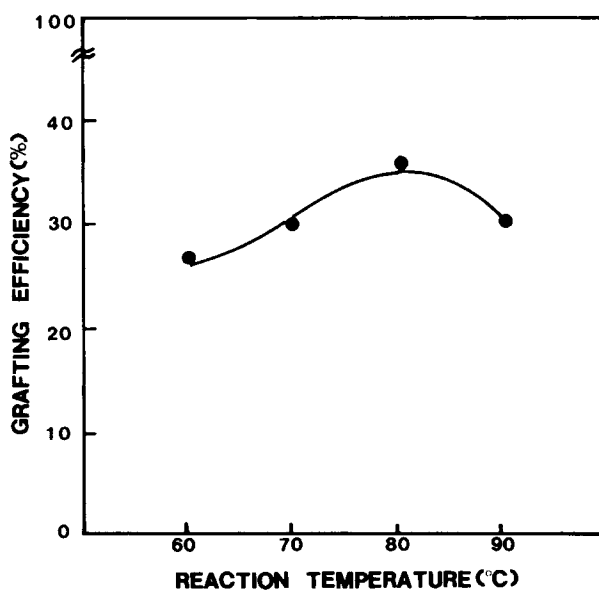

Figure 4   Plot of grafting efficiency vs. reaction temp: [2-VN]/[MMA], 0.75; reaction time, 40 h; solvent, THF; BPO, 0.12 g.
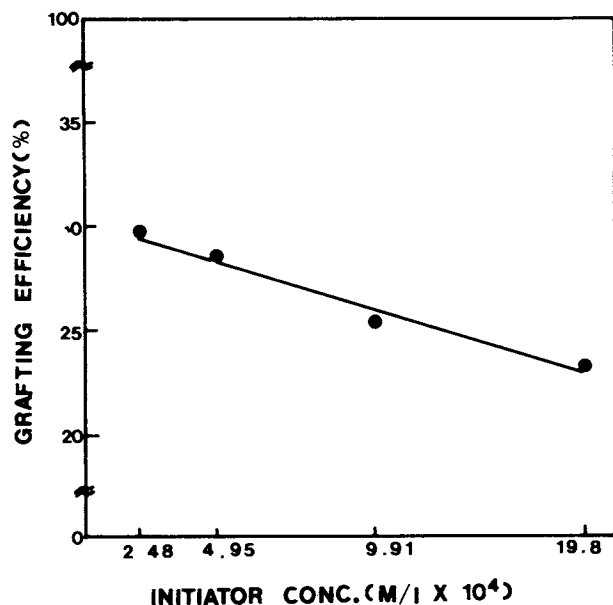
Figure 5 Plot of grafting efficiency vs. initiator conc: [2-VN]/[MMA], 0.75; reaction temp, 60°C; solvent, THF; reaction time, 40 h; BPO, 0.12 g.

Figure 7 Effect of mol ratio of 2-VN to MMA in graft copolymerization of VEM on the TGA curves: heating rate, 10°C/min in nitrogen. (●) [2-VN]/[MMA] = 2.0; (○) [2-VN]/[MMA] = 1.5; (△) [2-VN]/[MMA] = 1.0; (□) [2-VN]/[MMA] = 0.5.

in the initiator concentrations favors the formation of more homopolymers than those of the graft copolymer, and consequently, there is a decrease in grafting efficiency. A similar observation was made in the Voek's work.[19]
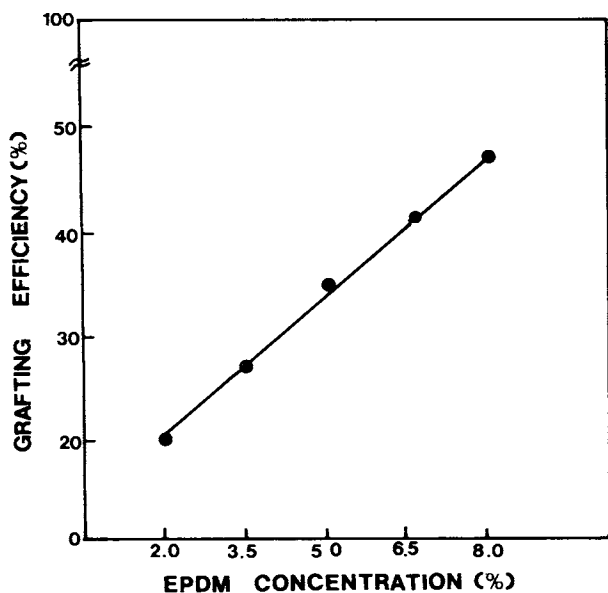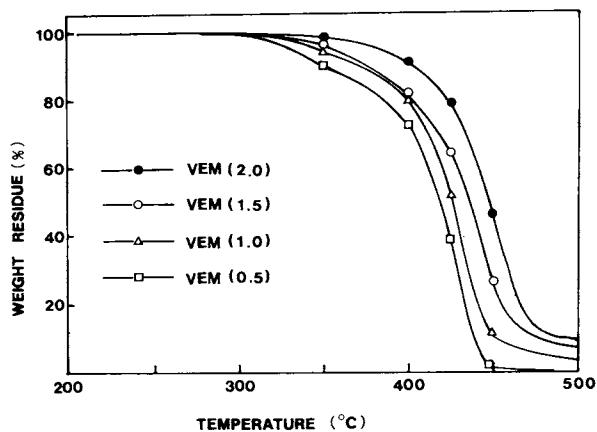
Effect of EPDM Content

The effect of EPDM content on the graft copolymerization is shown in Figure 6. The reaction was carried out at 60°C for 40 h with a mol ratio of 2-VN to MMA of 0.75. The grafting efficiency increased with 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[8] and, thus, the higher degree of homopolymerizations of P2VN and PMMA.

Figure 6 Plot of grafting efficiency vs. EPDM concentration: [2-VN]/[MMA], 0.75; reaction temp, 60°C; solvent, THF; reaction time, 40 h; BPO, 0.12 g.
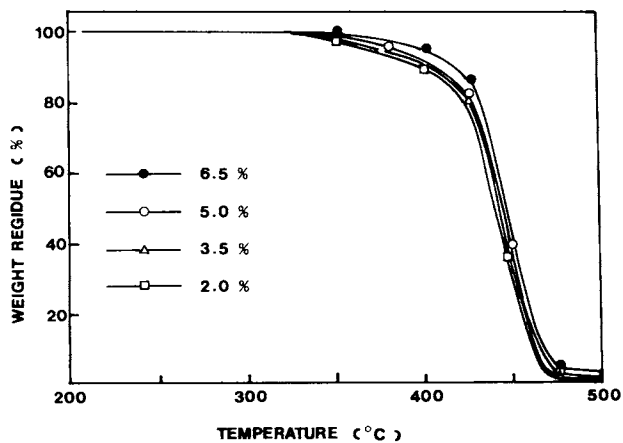

Figure 8 Effect of EPDM content in graft copolymerization of VEM on the TGA curves: heating rate, 10°C/min in nitrogen. (●) 6.5%; (○) 5.0%; (△) 3.5%; (□) 2.0%.
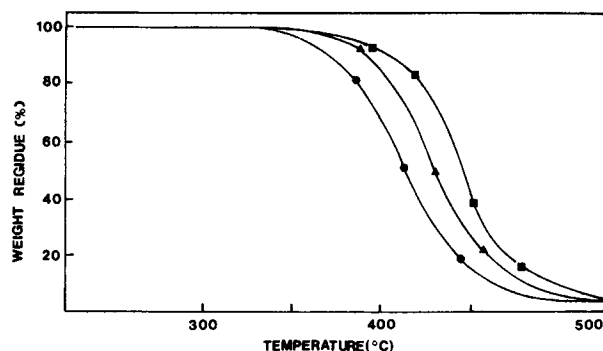
Figure 9 TGA curves of ABS, AES, and VEM: heating rate, 10°C/min in nitrogen. (●) ABS; (▲) AES; (■) VEM.

Thermal Stability

The effect of mol ratio of 2-VN to MMA in the graft copolymerization on the decomposition temperature is shown in Figure 7. In 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 VEM increased in the order of VEM (0.5) < VEM (1.0) < VEM (1.5) < VEM (2.0), meaning that the VEM with higher 2-VN content showed higher thermal stabilities.

The influence of EPDM content on the thermal stability of VEM should be also noted, as shown in Figure 8. The grafting reaction conditions were same as those referred to in Figure 6. The thermal stability of VEM increased with the rising concentration of EPDM.

Figure 9 shows TGA curves of ABS, AES, and VEM. 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 VEM was synthesized with 0.75 mol ratio of 2-VN to MMA and 0.12 g of BPO at 60°C for 40 h. It is clear that the VEM shows much better thermal stability with the highest thermal degradation temperature compared to ABS and AES. As shown in Figure 9, the residual weight at 450°C of VEM is 45%, whereas those of other polymers are below 26%.[†] The good thermal stability of VEM may be

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[†] When discussing the thermal stability of a material in the context of engineering applications such as automotive parts, the present datum of a residual weight of 45% at 450°C of VEM, using a dynamic TGA experiment under nitrogen, is not yet satisfactory, even though the VEM shows much better thermal stability with the highest thermal degradation temperature compared to ABS and AES. It should be noted that isothermal TGA experiments should be performed as a function of time in air and nitrogen and measure molecular weights or melt flow as a function of time, in order to evaluate the thermal stability of the VEM more meaningfully.

attributed to the synergestic effect of the EPDM and 2-VN component in the copolymer because of their inherent high heat resistances.[20,21]

Light Resistance

The light resistance was semiquantitatively expressed in terms of color difference (ΔE) with the National Bureau of Standards Unit.[11–13] The samples were tested in a Fade-o-Meter for 4, 8, 12, and 16 h. Figure 10 shows the light resistance of EPDM, ABS, AES, and VEM. The VEM as well as ABS and AES are the same as those referred to in Figure 9. It is seen that VEM synthesized in this work does not show better light resistance than does AES or EPDM, due to the inherent yellowing properties of 2-VN when subjected to UV light. It should be noted, however, that the VEM shows better light resistance than does ABS because of the inclusion of EPDM, which has excellent outdoor properties.

Tensile Properties

Table III shows the tensile properties of VEM, ABS, and AES. The grafted VEM shown in this table is the same as that referred to in Figures 9 and 10. The effect of the reaction conditions on the tensile
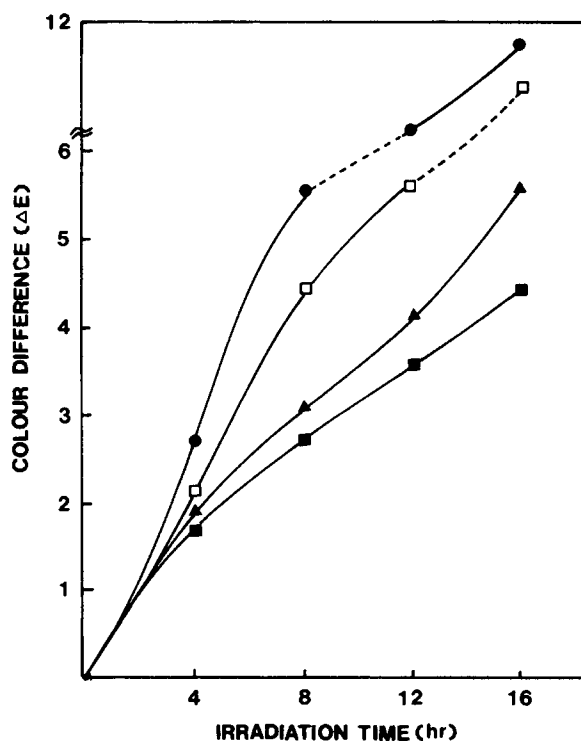

Figure 10 Plot of color difference vs. irradiation time for various samples (by Fade-o-Meter): (●) ABS; (□) VEM; (▲) AES; (■) EPDM.

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

Materials	Tensile Strength (kg/cm^2)	Elongation at Break (%)
ABS	295	8.4
AES	311	3.7
VEM	345	1.8

[a] VEM synthesized from graft copolymerization of 2-VN and MMA onto EPDM: [2-VN]/[MMA] = 0.75, solvent: THF, reaction time: 40 h; BPO: 0.12 g.

properties was not significant. It is pertinent to note that the VEM has the highest tensile strength in contrast to ABS and AES.

CONCLUSIONS

2-Vinylnaphthalene–EPDM–methyl methacrylate (VEM) graft copolymer was synthesized with a radical initiator by the 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 VEM, the grafting efficiency decreased with increasing 2-VN content relative to that of MMA. The grafting efficiency was highest at 35% when the mol ratio of 2-VN to MMA was 0.5.

2. The grafting efficiency showed a maximum at 80°C.

3. The grafting efficiency of VEM increased up to 60 h but decreased with further increasing reaction time.

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

5. The thermal stability and the tensile strength of VEM were significantly enhanced as compared to ABS and AES.

6. The light resistance of VEM was better than that of ABS.

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