

Synthesis and Properties of Methacrylonitrile–EPDM–2-Vinylnaphthalene Graft Terpolymer

SEUNG WOOK LEE, DUCK JEI PARK, CHANG SIK HA, and WON JEI CHO*

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

SYNOPSIS

The graft terpolymer of methacrylonitrile (MAN) and 2-vinylnaphthalene (2-VN) onto ethylene–propylene–diene terpolymer (EPDM) was synthesized in toluene using benzoyl peroxide (BPO) as an initiator. The effects of EPDM content, mole ratio of 2-VN to MAN, reaction time, reaction temperature, and initiator concentration on the graft copolymerization were examined. The synthesized graft terpolymer was identified by IR and $^1\text{H-NMR}$ spectroscopies. The light resistance, thermal stability, molecular weight, and tensile properties of the graft terpolymer were investigated by Fade-o-meter, thermogravimetric analysis, gel permeation chromatography (GPC), and a universal tensile machine (UTM). It was found that the light resistance and heat resistance as well as the tensile strength of the graft terpolymer are considerably better than those of the acrylonitrile–butadiene–styrene (ABS) terpolymer. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The acrylonitrile–butadiene–styrene (ABS) terpolymer 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 several attempts to improve this poor performance, the substitution of ethylene–propylene–diene terpolymer (EPDM) for butadiene has been widely investigated in many laboratories.^{3–11,16} EPDM has outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component.^{12–15}

The aim of the present study is to improve the heat resistance, light resistance, and weatherability of ABS resin by using EPDM in place of the butadiene rubber (BR) component, and 2-vinylnaphthalene (2-VN) in place of styrene. Because of the high light resistance of EPDM and the high glass-

transition temperature (T_g) of poly(2-vinylnaphthalene) [P(2VN)], it is expected that the graft terpolymer will have a good thermal stability.¹⁶ Graft copolymerizations were carried out under an argon atmosphere in the presence of benzoyl peroxide (BPO) as an initiator and toluene as a solvent. The effects of various factors, such as EPDM content, mole ratio of 2-VN to MAN, reaction time, reaction temperature, and initiator concentration in the graft copolymerizations were studied. The light resistance, thermal stability, and tensile properties of the graft terpolymer are also discussed.

EXPERIMENTAL

Materials

Methacrylonitrile (MAN) (Aldrich Chemical Co., USA) and 2-Vinylnaphthalene (2-VN) (Aldrich) were purified by standard procedures. BPO (Hayashi Chemical Co., Japan) was purified by recrystallization from methanol. EPDM, having ethylidene norbornene as a termonomer (Aldrich; ethylene/propylene = 50/42 by mol %, ML 50), was used as received. *n*-Hexane, acetone, methyl ethyl ketone

* To whom correspondence should be addressed.

(MEK), tetrahydrofuran (THF), and toluene were distilled before use.

Synthesis of Methacrylonitrile-EPDM-2-Vinylnaphthalene Graft Terpolymer (MEV₂N)

The grafting reactions were carried out in a 1-L separable flask equipped with a modified Hopkins cooler, thermometer, and argon gas inlet. A given amount of EPDM was dissolved by 100 ml of toluene in the flask. A mixture of 2-VN and MAN at the given mole ratio was dissolved in 50 mL of toluene; 0.12 g of BPO was then added. After stirring, 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, and the precipitate was filtered and dried *in vacuo*.

Separation of Graft Terpolymer

In the synthesis, the products obtained consisted of ungrafted EPDM, MEV₂N, several copolymers, and unbound homopolymers. Each separation step was done by the soxhlet extraction method.

The MEV₂N was isolated from mixtures of several copolymers and homopolymers, such as poly(2-VN-co-MAN), poly(EPDM-g-2-VN), poly(EPDM-g-MAN), poly(methacrylonitrile) [P(MAN)], and poly(2-vinylnaphthalene) [P(2-VN)] using acetone and THF/*n*-hexane (50/50 by volume) mixed solvent. 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.¹⁷

Table I Graft Copolymerization Conditions Used in This Study

Condition	Description
EPDM Concentration (wt %)	5, 10, 15, 20
Mole Ratio of [2-VN]/[MAN]	0.5, 0.75, 1.0, 1.5, 2.0
Reaction Time (h)	24, 48, 60, 72
Reaction Temperature (°C)	60, 70, 80, 90
Initiator Concentration (wt %)	0.5, 2.5, 5, 7.5, 10.0

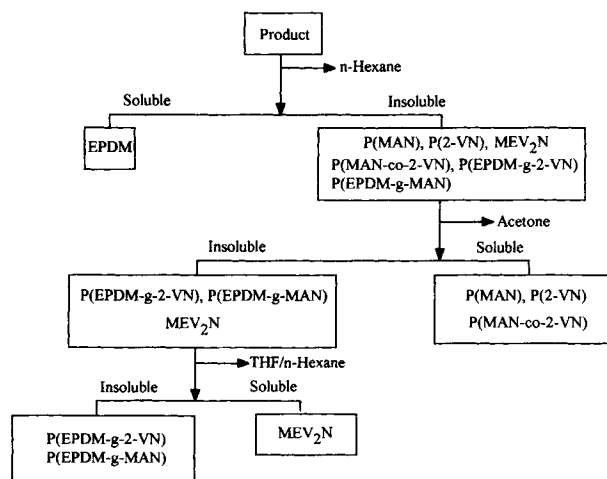


Figure 1 Block diagram of isolation process for graft terpolymers (MEV₂N).

Grafting ratio (%)

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

Grafting efficiency (%)

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

IR and ¹H-NMR Measurements

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 instrument. The measurement was done using CDCl₃ as a solvent, and TMS as an internal reference.

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 under nitrogen.

Gel Permeation Chromatography (GPC)

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

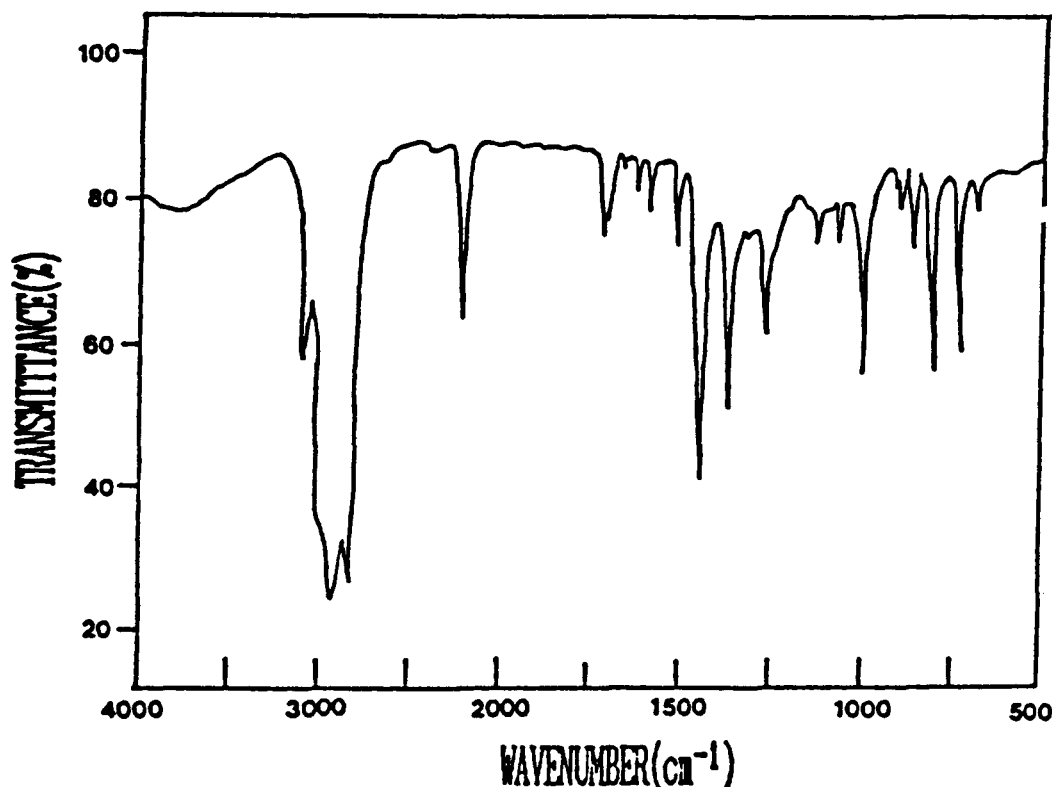


Figure 2 IR spectrum of MEV₂N (THF film).

Light Resistance and Weatherability

The light resistance and weatherability were measured with a color difference meter (ND-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 in a dark room and then kept under vacuum until they reached constant weight. The cross-sectional area of the films was $5 \times 10 \text{ cm}^2$ with a thickness of $35 \mu\text{m}$. The color difference (ΔE), after exposure to UV, was evaluated by the Hunter-Schofield equation.¹⁸ The light resistance was measured at room temperature without humidity (UV irradiation for all times). The weather resistance (ASTM G53) was measured at 60°C by 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 applied to light resistance. The weatherability was measured at 100% relative humidity (UV irradiation for 12 h and condensation for 12 daytime hours).

Tensile Properties

The tensile tests were performed using an Instron Tensile Tester (Model 4204). The samples were prepared following the procedure of ASTM D638-84. The crosshead speed was 5 mm/min, and initial gauge length was adjusted to 25 mm.

RESULTS AND DISCUSSION

Characterization of Terpolymer

Figure 2 shows the IR spectrum of the graft terpolymer. The characteristic absorption bands of MEV₂N appeared at 3010 cm^{-1} (stretching vibration of aromatic C—H bond), 2900 cm^{-1} (stretching vibration of aliphatic C—H bond), 2240 cm^{-1} (stretching vibration of C≡N bond), 1460 cm^{-1} (scissoring of CH₂), $1375\text{--}1300 \text{ cm}^{-1}$ (asymmetric and symmetric deformation of CH₃), $900\text{--}650 \text{ cm}^{-1}$ (out-of-plane rotational vibration of aromatic C—H).

The graft terpolymer was also characterized by its ¹H-NMR spectrum. The MEV₂N spectrum showed the methyl group in EPDM at 1.0 ppm,

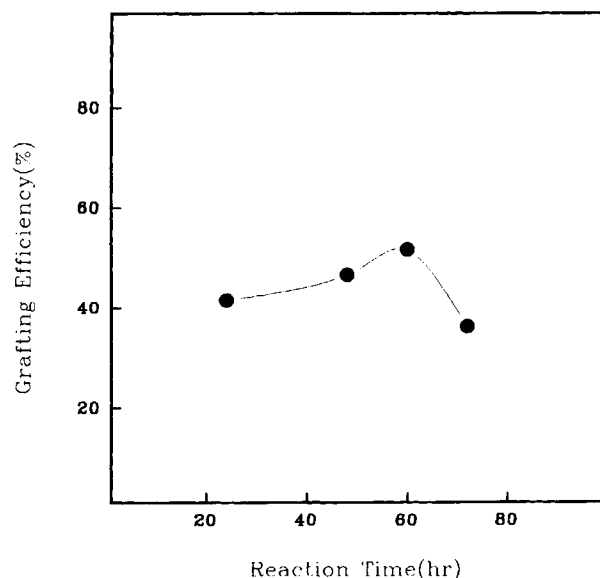


Figure 3 Plot of grafting efficiency vs. reaction time: [2-VN]/[MMA], 1.0; reaction temp., 70°C; solvent, THF; BPO 5 wt %.

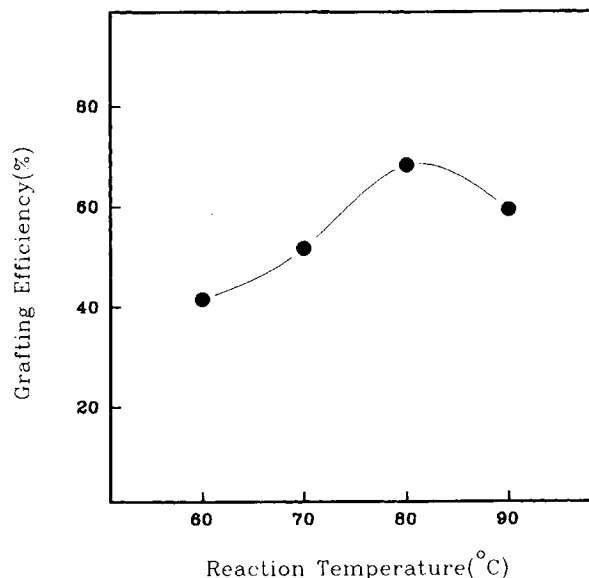


Figure 4 Plot of grafting efficiency vs. reaction temp.: [2-VN]/[MMA], 1.0; reaction time, 60 h; solvent, THF; BPO 5 wt %.

methylene protons at 2.2 ppm, and the naphthalene protons of the 2-VN unit at 7.1 ppm.

Elemental analysis (Carlo Erba 1108) for a typical MEV₂N with a 1.0 feed mole ratio of 2-VN to MAN gives the following results: C, 82%; N, 3%; and H, 15%. In this case, the grafted MEV₂N was synthesized in 5 wt % of BPO at 70°C for 60 h.

Effect of Reaction Conditions

Effect of Reaction Time

The effect of reaction time on graft copolymerization is shown in Figure 3. The graft copolymerization was carried out in toluene at 70°C with constant concentrations of EPDM and BPO.

The mole ratio of 2-VN to MAN was fixed at 1.0. The grafting efficiency increased up to 60 h, and then decreased. The reason for the decrease in grafting efficiency after 60 h may be caused by the formation of homopolymers and copolymers as well as the increase in viscosity of the reaction mass along the reaction path.^{13,19}

Effect of Mole Ratio

Table II shows the effect of the mole ratio of 2-VN to MAN on the graft copolymerization onto EPDM and on molecular weight. The reaction was performed in toluene with 5 wt % of BPO and constant EPDM content at 70°C for 60 h.

As Table II shows, the grafting efficiency decreases with increases in the mole ratio of 2-VN to

Table II Effect of Mole Ratio of 2-VN to MAN on the Graft Copolymerization of 2-VN and MAN onto EPDM and the Molecular Weight Characteristics

Mole Ratio [2-VN]/[MAN]	Total Concentration (%)	Grafting Ratio (%)	Grafting Efficiency (%)	M_n	M_w	M_w/M_n
0.5	56	162	55	156,000	251,000	1.61
0.75	55	187	53	127,000	200,000	1.58
1.0	51	202	52	102,000	155,000	1.52
1.5	49	222	45	94,000	148,000	1.58
2.0	49	175	29	87,000	139,000	1.60

Solvent: toluene; time: 60 h; temp.: 70°C; BPO: 5 wt %.

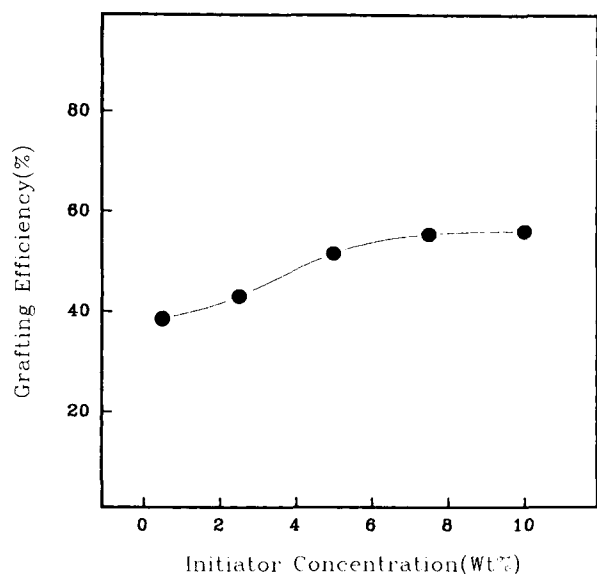


Figure 5 Plot of grafting efficiency vs. initiator conc.: [2-VN]/[MMA], 1.0; reaction temp., 70°C; solvent, THF; reaction time, 60 h.

MAN. The grafting efficiency is highest at the 2-VN/MAN mole ratio of 0.5, 56.40%, due to formation of much more homopolymer with increasing monomer ratio. Table II also lists the molecular weight characteristics of the graft terpolymers having various mole ratios in the feed, showing that the molecular weights of the graft terpolymers become smaller as the grafting efficiency is lower. A similar tendency has been shown in our previous work⁷ for the graft copolymerization of MMA and 2-VN onto EPDM.

Effect of Reaction Temperature

The effect of reaction temperature on the graft copolymerization is shown in Figure 4. The reaction was carried out at 60, 70, 80, and 90°C, keeping all factors constant. The mole ratio of 2-VN to MAN was fixed at 1.0. On increasing the temperature, the grafting efficiency passes through a maximum at 80°C. The increase in grafting efficiency with increasing temperature up to 80°C may be due to the decomposition rate of BPO, which decomposes faster at higher temperatures with a sacrifice in molar mass.^{20,21} The exact reason why the grafting efficiency decreases with further increasing temperature, however, is not clear.

Effect of Initiator Concentration

Figure 5 shows the effect of initiator concentration on the graft copolymerization. The grafting was car-

ried out with various concentrations of initiator at 70°C for 60 h. The mole ratio of 2-VN to MAN was the same as described earlier. The grafting efficiency increased with increasing initiator concentrations. General results of this experiment increased to a maximum point and then decreased. In our case, however, the results levelled off somewhat after 5 wt %. It is thought that this is due to expanded grafting sites of EPDM added by increasing initiator concentration. Similar behavior was observed by Huque et al.²²

Effect of EPDM Content

The effect of EPDM content on the graft copolymerization is shown in Figure 6.

The grafting was carried out at 70°C for 60 h with a 2-VN/MAN mole ratio of 1.0. The grafting efficiency increased with increased concentrations of EPDM. With higher EPDM concentrations, 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 and, thus, the higher degree of homopolymerizations of P(2-VN) and P(MAN).

Thermal Stability

The thermal property of the final product was measured up to 550°C by a TGA analyzer under N₂ atmosphere. The thermal stability of MEV₂N com-

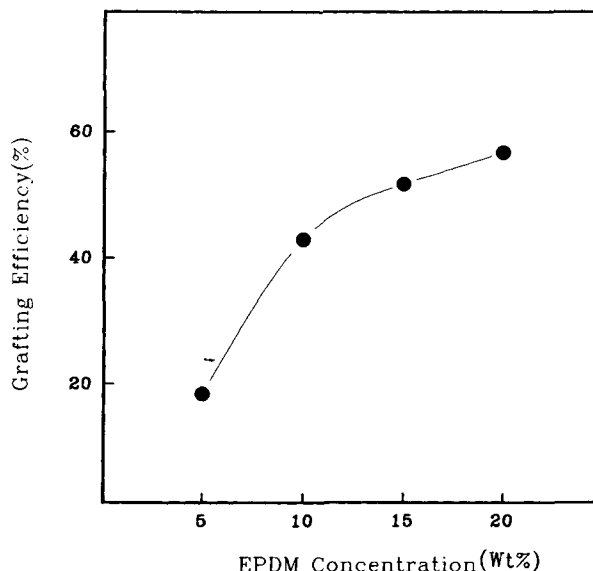


Figure 6 Plot of grafting efficiency vs. EPDM conc.: [2-VN]/[MMA], 1.0; reaction temp., 70°C; solvent, THF; reaction time, 60 h; BPO 5 wt %.

pared to AES (Japan Synthetic Rubber Co., Japan; 110 grade) and ABS (Japan Synthetic Rubber Co.; 10 grade) are shown in Figure 7. For this figure, the grafted MEV_2N was synthesized with a 1.0 mole ratio of 2-VN to MAN and 5 wt % of BPO at 70°C for 60 h. The result shows that the thermal stability of MEV_2N is superior to AES and ABS. The good thermal stability of MEV_2N may be attributed to the synergistic effect of EPDM and 2-VN in the terpolymer because of their inherent good heat resistance.^{23,24}

Table III shows the decomposition temperature and weight residue: the residual weight at 450°C of MEV_2N is 35%, whereas those of other polymers are below 25%. In Figure 7, the curve of MEV_2N has a fairly constant residue weight from 450 to 550°C, but those of the other polymers approach total weight loss.

Light Resistance and Weatherability

The light resistance and weatherability were determined by color change (ΔE) with a National Bureau of Standards unit. The measurements were performed in a color difference meter for various times.

Table III Decomposition Temperature and Weight Residue at 450°C for Various Samples

Samples	Decomposition Temperature (°C)	Weight Residue at 450°C (%)
ABS	370	13
AES	390	25
MEV_2N^a	450	35

^a MEV_2N synthesized from graft copolymerization of 2-VN and MAN onto EPDM. Solvent: toluene; temp.: 70°C; time: 60 h, [2-VN]/[MAN] = 1.0; BPO, 7.5 wt %.

Figure 8 shows the light resistance of EPDM, ABS, and MEV_2N . The MEV_2N is better than ABS but not compared to EPDM upon exposure to UV light. The weatherability of EPDM, ABS, and MEV_2N is shown in Figure 9. It results in similar trends in light resistance but changes to a more yellowish color.

Tensile Properties

Table IV shows the tensile properties of MEV_2N , ABS, and AES used in this test. The effect of re-

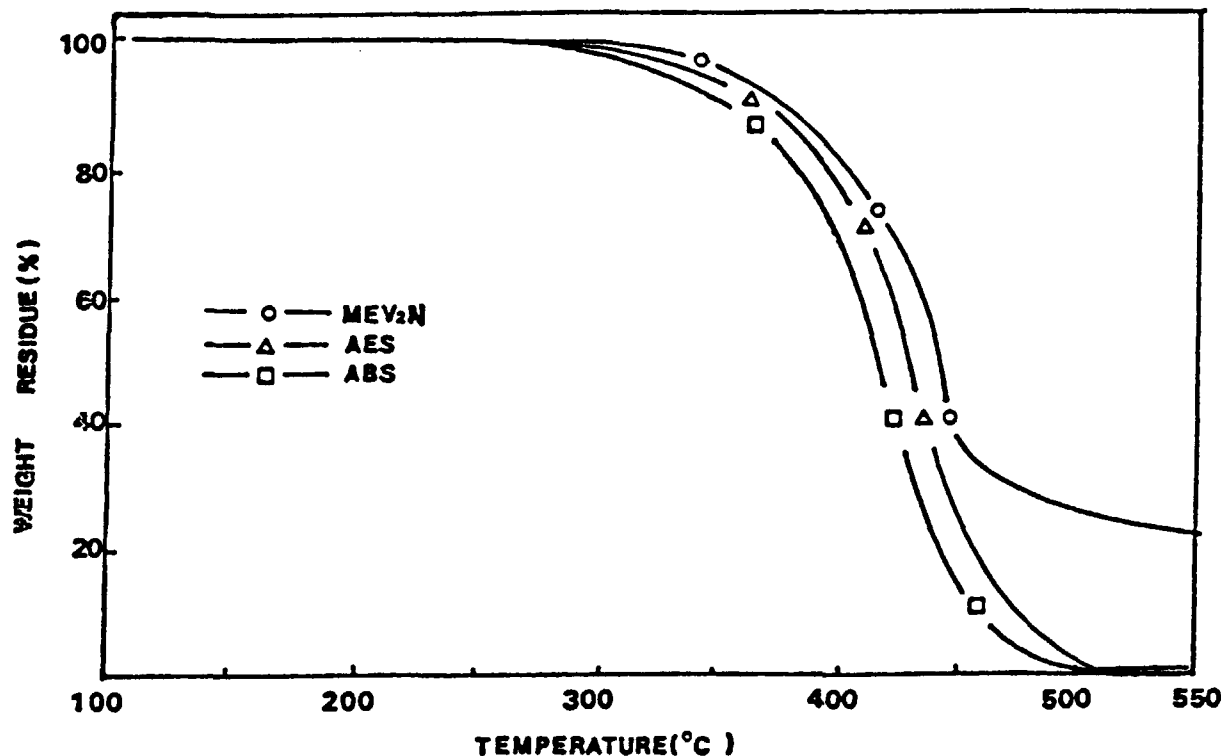


Figure 7 Thermal decomposition of ABS, AES, and MEV_2N ; heating rate = 15°C/min in nitrogen.

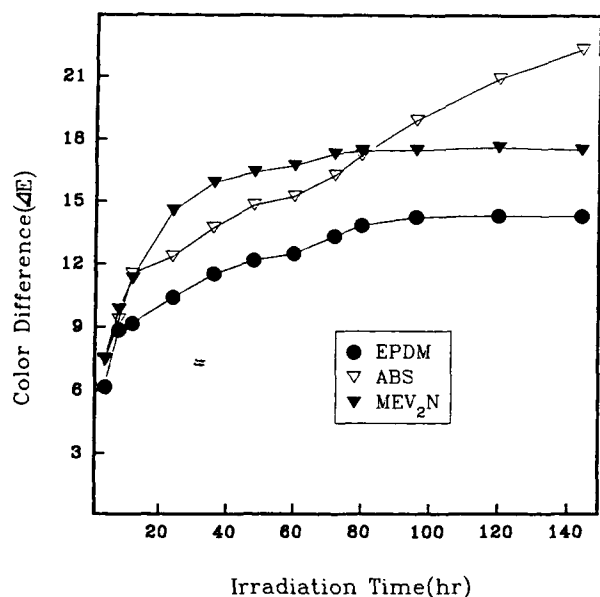


Figure 8 Plot of color difference vs. irradiation time for various samples (light resistance): (●) EPDM; (▽) ABS; (▼) MEV₂N.

action conditions on the tensile properties is not significant. It is noted that MEV₂N has the highest tensile strength of the three.

CONCLUSIONS

Methacrylonitrile-EPDM-2-vinylnaphthalene graft terpolymer was synthesized with radical initiation

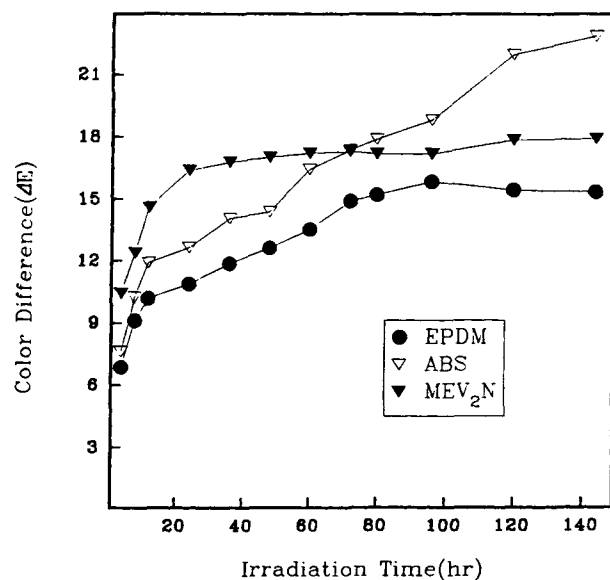


Figure 9 Plot of color difference vs. irradiation time for various samples (weatherability): (●) EPDM; (▽) ABS; (▼) MEV₂N under 100% relative humidity.

Table IV Comparison of Tensile Properties of ABS, AES, and MEV₂N

Samples	Tensile Strength (kg/cm ²)	Elongation at Break (%)
ABS	295	8.4
AES	311	3.7
MEV ₂ N ^a	345	1.8

^a MEV₂N synthesized from graft copolymerization of 2-VN and MAN onto EPDM. Solvent: toluene; temp.: 70°C; time: 60 h; [2-VN]/[MAN] = 1.0; BPO, 7.5 wt %.

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

In the graft copolymerization of 2-VN and MAN onto EPDM, the grafting efficiency increased with decreasing mole ratio, and the maximum was at 0.5. The effect of initiator on the graft copolymerization showed that the behavior leveled off at 5 wt %. In the effect of reaction temperature, the grafting efficiency increased up to 80°C and then decreased with further increasing temperature. The effect of reaction time increased up to 60 h and then decreased. The grafting efficiency of the graft terpolymer increased with increasing EPDM concentrations. The thermal decomposition temperature of MEV₂N was considerably enhanced when compared to ABS. The light resistance and weatherability of MEV₂N were better than those of ABS. The molecular weight of MEV₂N was about 150,000 M_n and 250,000 M_w , and M_w/M_n was about 1.6.

This work was supported by the Ministry of Education, Korea (Research Fund for Advanced Materials, 1994).

REFERENCES

1. K. J. Saunders, *Organic Polymer Chemistry*, Chapman and Hall, London, 1977.
2. A. K. Mukerjee and B. D. Gupta, *J. Macromol. Sci., Chem.*, **A19**(7), 1069 (1983).
3. D. I. Kang, C. S. Ha, and W. J. Cho, *Eur. Polym. J.*, **29**(3), 562 (1992).
4. D. J. Park, N. J. Lee, C. S. Ha, and W. J. Cho, *J. Appl. Polym. Sci.*, **44**, 727 (1992).
5. Y. O. Bae, C. S. Ha, and W. J. Cho, *Eur. Polym. J.*, **27**(2), 121 (1991).
6. S. K. Choi, C. S. Ha, and W. J. Cho, *J. Kor. Inst. Rubber Ind.*, **24**, 265 (1989).

7. J. Y. Park, D. J. Park, C. S. Ha, and W. J. Cho, *J. Appl. Polym. Sci.*, **51**, 1303 (1994).
8. C. S. Ha, S. K. Choi, and W. J. Cho, *J. Appl. Polym. Sci.*, **45**, 2159 (1992).
9. D. J. Park, Y. O. Bae, C. S. Ha, and W. J. Cho, *Polymer (Korea)*, **16**(2), 235 (1992).
10. D. J. Park, C. S. Ha, and W. J. Cho, *J. Macromol. Sci.*, **A30**(12), 949 (1993).
11. D. J. Park, C. S. Ha, and W. J. Cho, *J. Appl. Polym. Sci.*, to appear.
12. C. L. Meredith, R. E. Barret, and W. H. Bishop, U.S. Pat. 3,538,190 1970.
13. K. S. J. Srinivasan, N. Radhakrishnan, and M. Kuttalmpillai, *J. Appl. Polym. Sci.*, **37**, 1551 (1989).
14. R. D. Allen, *J. Elastom. Plast.*, **15**, 19 (1983).
15. H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, *Encyclopedia of Polymer Science and Engineering*, 2nd Ed., Wiley, New York, Vol. 6, p. 522, 1986.
16. D. J. Park, W. J. Cho, *Polymer (Korea)*, **15**(1), 1 (1990).
17. A. Dipak and K. Raval, *J. Appl. Polym. Sci.*, **35**, 2201 (1988).
18. F. Schofield, *Nat'l. Paint, Varnish, Lacquer Assoc. Sci. Soc., Circular*, 644 (1943).
19. H. Raval, Y. R. Sing, M. H. Mehta, and S. Devii, *Polym. Int.*, **24**, 99 (1991).
20. J. Bandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd Ed., Wiley, New York, 1975.
21. M. Becher and H. Mark, *Angew. Chem.*, **73**, 641 (1961).
22. M. M. Huque, M. Habibuddowla, A. J. Mahmood, and M. A. Jabber, *J. Polym. Sci., Polym. Chem. Edn.*, **18**, 1447 (1980).
23. R. H. McCable, *Rubber Age*, **96**, 396 (1964).
24. B. L. Treherne, *Elastomerics*, **D25**, 24 (1982).

Received December 19, 1994

Accepted March 7, 1995