

## Maleic anhydride-2-Vinylnaphthalene과 EPDM으로 된 새로운 엔지니어링 플라스틱의 합성과 물성

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### Synthesis and Properties of the Newly Designed Engineering Plastic from Maleic anhydride-2-Vinylnaphthalene with EPDM

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**요약** : 여러가지 용매 존재하에서 benzoyl peroxide(BPO)를 개시제로 사용하여 ethylene-propylene-diene terpolymer(EPDM)에 maleic anhydride(MAH)와 2-vinylnaphthalene(2-VN)을 주어진 온도에서 그래프트 공중합하였다. 합성한 MAH-EPDM-2-VN(MAEV2) 그래프트 공중합체는 IR 분광법으로 확인하였다. 그래프트 공중합시 MAH에 대한 2-VN의 몰비, 용매, 중합 시간, 중합 온도, 개시제 농도, 그리고 EPDM 농도등의 영향을 조사하였다. 그래프트 효율은 MAH에 대한 2-VN의 몰비값이 1.0일 때, 중합 온도는 70°C 그리고 용매는 toluene일 때 가장 좋은 값을 나타내었다. EPDM 농도 변화에 따른 그래프트 효율은 EPDM의 함량이 증가할수록 증가하였다. MAEV2와 ABS의 열분해 온도는 각각 424°C와 373°C이었다. MAEV2의 내열성과 내광성은 ABS 보다 우수하였다.

**Abstract** : The graft copolymerizations of maleic anhydride(MAH) and 2-vinylnaphthalene(2-VN) onto ethylene-propylene-diene terpolymer(EPDM) were carried out with benzoyl peroxide(BPO) as an initiator in several solvents at given temperatures. The synthesized graft copolymer, [(MAEV2)], was identified by IR spectroscopy. The effects of mole ratio of 2-VN to MAH, solvents, reaction time, reaction temperature, initiator concentration and EPDM concentration on graft copolymerization were examined. The maximum grafting efficiency was obtained at 1 : 1 mole ratio of 2-VN to MAH, 70°C and in toluene. It was observed that grafting efficiency increased with increasing EPDM concentration. Decomposition temperatures of MAEV2 and ABS were 424°C and 330°C, respectively. The thermal stability and light resistance of MAEV2 were better than those of ABS.

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## 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 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.<sup>1-3</sup>

Among the several attempts to improve the poor performance, the substitution of ethylene-propylene-diene terpolymer (EPDM) for butadiene has been widely investigated.<sup>4-10</sup> 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.<sup>11,12</sup>

The aim of this study is to improve heat resistance and weatherability of ABS resin using EPDM in place of butadiene rubber (BR), maleic anhydride (MAH) in place of acrylonitrile (AN) and 2-vinylnaphthalene (2-VN) in place of styrene, respectively. MAH and 2-VN were selected because of their polarity and high glass transition temperature, respectively. It might be expected that the end-use properties of the materials consisting of the two components could be improved to a large extent. MAH and 2-VN were grafted onto EPDM under argon atmosphere in the presence of benzoyl peroxide (BPO) as an initiator. The effects of mole ratio of 2-VN to MAH, solvent, reaction time, reaction temperature, initiator concentration, and EPDM content were investigated in the graft copolymerizations. The thermal stability and light resistance of the graft copolymer, MAH-EPDM-2-VN (MAEV2), were analyzed.

## EXPERIMENTAL

### Materials

Maleic anhydride (MAH) (Junsei Chemical) and

2-vinylnaphthalene (2-VN) (Aldrich Chemical) were purified by standard procedures. Benzoyl peroxide (BPO) (Hayashi Chemical) was recrystallized from methanol. Ethylene-propylene-diene terpolymer (EPDM) having ethylidene norbornene as a comonomer (Aldrich Chemical; ethylene/propylene = 50/50 by mol, ML 50) was used as received. Benzene, toluene, and tetrahydrofuran (THF) were distilled prior to use.

### Synthesis of Maleic Anhydride-EPDM-2-Vinylnaphthalene Graft Copolymer (MAEV2)

A given amount of EPDM (5g) was dissolved in 156ml of toluene placed in a 1 liter separable flask provided with a modified Hopkins cooler (specially designed for this work),<sup>13</sup> a thermometer, a glass tube for bubbling a gas. After dissolution, a mixture of 15g of 2-VN and 10g of MAH with 0.24g of BPO in 100ml of toluene were added in the flask. The flask was sealed after charging with argon and the reaction was carried out under various experimental conditions (see Table 1).

After a predetermined period of reaction, the contents were poured into methanol under stirring, the precipitate was filtered and dried in a vacuum oven. The nongrafted EPDM was extracted using n-hexane. The maleic anhydride-EPDM-2-vinylnaphthalene (MAEV2) graft polymer was isolated from a mixture of several copolymers and homopolymers obtained as by product, such as poly(MAH-co-2-VN), poly(EPDM-g-2-VN), and

**Table 1.** Graft Copolymerization Conditions Used in This Study

Condition	Description
Mole ratio of [2-VN]/[MAH]	0.50, 1.00, 1.58, 2.00
Solvent System	Tetrahydrofuran (THF) Benzene Toluene
Polymerization Time (hr)	48, 60, 72, 96
Reaction Temperature (°C)	50, 60, 70, 80
EPDM Concentration (%)	14, 25, 33, 40
BPO Concentration (%)	3.75, 7.5, 11.25

poly(EPDM-g-MAH) using THF, toluene and acetone. Details of isolation procedure of graft copolymers synthesized are schematically shown in Fig. 1.

The total conversion, grafting ratio, and grafting efficiency of MAEV2 were estimated by using the following equation.<sup>14</sup>

- i) Total conversion(%) = 
$$\frac{\text{total weight of crude product}}{\text{weight of monomer charged}} \times 100$$
- ii) Grafting ratio(%) = 
$$\frac{\text{weight of polymer in grafts}}{\text{weight of substrate}} \times 100$$
- iii) Grafting efficiency(%) = 
$$\frac{\text{weight of polymer in grafts}}{\text{total weight of polymer formed}} \times 100$$

**Measurements**

**Structure Identification :** The chemical structure

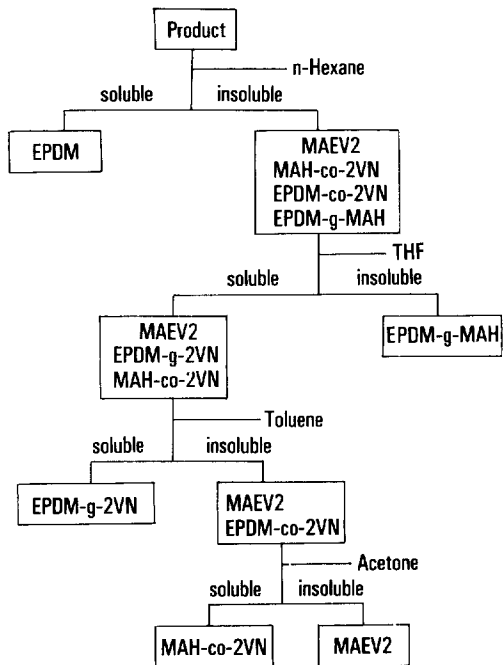


Fig. 1. Block diagram of graft copolymer(MAEV2) isolation process(Notations are described in the Text.)

of polymers was identified by IR spectrophotometry(Perkin Elmer 1330).

**Thermogravimetric Analysis(TGA) :** Thermal stability was examined with a Shimadzu DT 30A TGA instrument at a scanning rate of 15°C/min.

**Light Resistance :** The light resistance was determined using Fade-o-Meter(Atlas)(at 60°C and 65% relative humidity) and 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 and then kept under vacuum until they reached constant weight. The cross-sectional area of the films was 3×5cm<sup>2</sup> and thickness was 35µm. The color difference(ΔE) of the samples after exposing to UV was calculated using the Hunter-Schofield equation.<sup>15</sup>

**RESULTS AND DISCUSSION**

**Identification of Polymers**

The isolation procedure of the graft copolymers obtained is shown schematically in Fig. 1 and identified by IR spectra.

Fig. 2 shows IR spectra of EPDM.

The IR spectra of EPDM exhibited characteristic absorption bands at 2900cm<sup>-1</sup>(stretching vibration of aliphatic C-H bond), 1465cm<sup>-1</sup>(scissoring of CH<sub>2</sub>) and 1375cm<sup>-1</sup>(bending of CH<sub>3</sub>). (Fig. 2)

IR spectra of MAEV2 is shown in Fig. 3.

The structure of MAEV2 was identified by IR spectra and exhibited characteristic absorption bands at 3025cm<sup>-1</sup>(stretching vibration of aromatic C-H bond), 2920cm<sup>-1</sup>(stretching vibration of aliphatic C-H bond), 1850, 1770, 1730cm<sup>-1</sup>(stret-

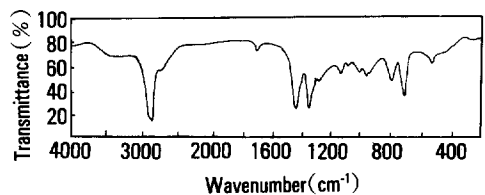


Fig. 2. IR spectrum of ethylene-propylene-diene terpolymer(EPDM).(Chloroform film)

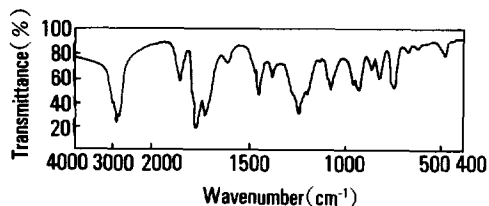


Fig. 3. IR spectrum of MAEV2.(THF film)

Table 2. Effect of Mole Ratio of 2-VN and MAH on the Graft Copolymerization of EPDM ; EPDM : 14%, Solvent : Toluene, Temp. : 70°C, Time : 48hr, BPO : 3.75%

Mole Ratio [2-VN]/[AN]	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
0.50	52	68	26
1.00	48	96	41
1.58	43	95	32
2.00	41	102	32

ching vibration of C=O bond), 1465cm<sup>-1</sup>(scissoring of CH<sub>2</sub>) and 1210, 820cm<sup>-1</sup>(out-of-plane rotational vibration of aliphatic C-H bond).(Fig. 3)

#### Effect of Mole Ratio

Table 2 shows the effect of mole ratio of 2-VN to MAH on the graft copolymerization onto EPDM. The reaction was carried out in toluene with BPO (3.75 wt%) as an initiator at 70°C for 48hr. The mole ratio of 2-VN to MAH is changed from 0.5 to 2.0.

It can be seen that the grafting efficiency was maximum value 41% at the mole ratio 1.0 of 2-VN to MAH and decreased when the mole ratio of 2-VN to MAH is higher than 1.0.

#### Effect of EPDM Contents<sup>16</sup>

Table 3 shows the effect of EPDM contents on the graft copolymerization. The reaction was performed at 70°C for 48hr in toluene with a mole ratio 1.0 of 2-VN to MAH. The grafting efficiency gradually increases with EPDM contents. This result is probably caused by the increasing diene contents of graft site in EPDM as EPDM contents increase.

Table 3. Effect of Weight Percentage of EPDM Concentration on the Graft Copolymerization of 2-VN and MAH onto EPDM ; [2-VN]/[MAH]=1.0, Solvent : Toluene, Time : 48hr, Temp. : 70°C, BPO : 3.75%

EPDM Concentration (%)	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
14	48	96	41
25	57	103	43
33	64	103	50
40	66	83	57

Table 4. Effect of Reaction Temperatures on the Graft Copolymerization of 2-VN and MAH onto EPDM ; EPDM : 14%, [2-VN]/[MAH]=1.0, Solvent : Toluene, Time : 48hr, BPO : 3.75%

Reaction Temp. (°C)	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
50	38	75	28
60	63	126	29
70	48	96	41
80	54	104	27

#### Effect of Reaction Temperature

The effect of reaction temperature on the graft copolymerization is shown in Table 4. The highest grafting efficiency was observed at 70°C within our experimental conditions as shown in Table 4. It may be related to the decomposition rate of BPO as a function of temperature. The grafting was carried out under a constant BPO content(3.75 wt%) and a fixed mole ratio 1.0 of 2-VN to MAH for 48 hr.

#### Effect of Initiator Concentration

Table 5 shows the effect of initiator concentration on the graft copolymerization. The reaction conditions were the same as those described earlier. The grafting efficiency is not significantly changed with increasing initiator concentration. The result is expected since the homopolymer is formed more readily than the graft copolymer as initiator concentration increases. This result is in

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**Table 5.** Effect of Initiator Concentration on the Graft Copolymerization of 2-VN and MAH onto EPDM ; EPDM : 14%, [2-VN]/[MAH]=1.0, Solvent : Toluene, Time : 48hr, Temp. : 70°C

Initiator Concentration (Based on the Monomer + EPDM)(wt %)	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
3.75	48	96	41
7.50	58	126	42
11.75	79	241	44

**Table 6.** Effect of Solvents on the Graft Copolymerization of 2-VN and MAH onto EPDM ; EPDM : 14%, [2-VN]/[MAH]=1.0, Temp. : 70°C, Time : 48hr, BPO : 3.75%

Exp. No.	Solvent	Total Conversion (%)	Grating Ratio (%)	Grafting Efficiency (%)
1	Tetrahydrofuran(THF)	62	93	21
2	Benzene	64	126	29
3	Toluene	48	96	41

accordance with the Voek's work.<sup>17</sup>

#### Effect of Solvent<sup>18-21</sup>

The effect of solvent on the graft copolymerization is shown in Table 6. The total conversions were 62, 64, and 48% for THF, benzene and toluene, respectively. The grafting efficiencies were 21, 29, and 41% for THF, benzene, and toluene, respectively. Thus, it is seen that the grafting efficiency is the highest when toluene was used as a solvent. The result may be ascribed to the fact that toluene dissolves the polymers more readily than any other solvents used, like THF or benzene. Odian et al. reported similar results of solvent effect on graft copolymerizations of styrene onto nylon, polyethylene, and polypropylene.<sup>22</sup>

#### Effect of Reaction Time

Table 7 shows the effect of reaction time of 2-VN to MAH on the graft copolymerization onto EPDM. The grafting was carried out at constant

**Table 7.** Effect of Reaction Time on the Graft Copolymerization of 2-VN and MAH onto EPDM ; EPDM : 14%, [2-VN]/[MAH]=1.0, Solvent : Toluene, Temp. : 70°C, Time : 48hr, BPO : 3.75%

Reaction Time (hr)	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
48	48	96	41
60	53	95	43
72	58	115	48
96	59	110	50

**Table 8.** Decomposition Temperature and Weight Residue at 450°C for Several Samples

Samples*	Decomposition Temperature(°C)	Weight Residue at 450°C(%)
ABS	370	13
AES	390	25
MAEV2	424	41

\* MAEV2 synthesized from the graft copolymerization of 2-VN and MAH onto EPDM ; [2-VN]/[MAH]=1.0, Solvent : Toluene, Temp. : 70°C, Time : 48hr, BPO : 3.75%

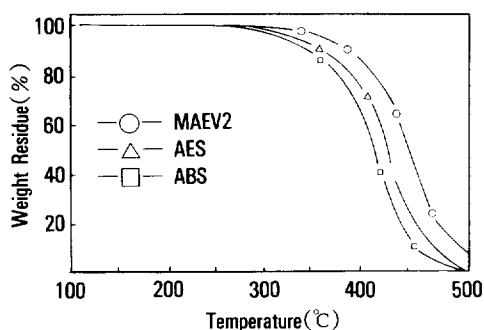
EPDM concentration(14%) and BPO content(3.75 wt%) at 70°C. The mole ratio of 2-VN to MAH was fixed at 1.0. The grafting efficiency increased with reaction time up to 72hr and then levelled off. This may be caused by the decrease of the unreacted monomer concentration as well as the increase of viscosity of the reaction mass along the reaction path.

#### Thermal Stability

TGA curves and the decomposition temperature of synthesized MAEV2 are shown in Fig. 4 and Table 8. 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. MAEV2 showed superior thermal stability. As shown in Fig. 4 and Table 8, the decomposition temperatures of MAEV2, AES and ABS were 424, 390 and 370°C, respectively. It was observed that the decomposition temperature of MAEV2 was hi-

**Table 9.** Color Difference Determined by Fade-o-Meter for Several Samples

Sample	$\Delta E$						
	6hr	12hr	24hr	36hr	48hr	60hr	72hr
EPDM	7.62	8.41	10.42	12.13	12.19	12.90	13.34
ABS	7.77	10.11	12.35	13.47	14.82	15.52	16.26
MAEV2	10.21	10.52	11.71	13.90	13.98	14.41	14.64



**Fig. 4.** TG curves of ABS, AES and MAEV2 : heat rate = 15°C/min in air.

gher by 54°C than that of ABS. The good thermal stability of MAEV2 may be attributed to the synergistic effect of EPDM unit and 2-VN component in the copolymer because of their high heat resistances.<sup>23</sup>

#### Light Resistance

The light resistance was semiquantitatively expressed in terms of color difference ( $\Delta E$ ) with National Bureau of Standards Unit. The smaller  $\Delta E$  means better light resistance.<sup>24-26</sup> The samples were tested in a Fade-o-Meter for 6, 12, 24, 36, 48, 60, and 72hr. Table 9 shows the light resistance of EPDM, ABS and MAEV2. The grafted MAEV2 was synthesized in toluene with 1.0 mole ratio of 2-VN to MAH at 70°C for 48hr. The  $\Delta E$  data of commercially available EPDM and ABS (the same grades as referred to in Fig. 8) are also shown for comparison. It should be noted that MAEV2 shows better light resistance than ABS against long exposure to UV light, even though the MAEV2 shows poor light resistance when exposed initially to UV light in the Fade-o-Meter.

## CONCLUSION

Maleic anhydride-EPDM-2-vinylnaphthalene graft copolymer (MAEV2) was synthesized by solution polymerization with radical initiator.

1. In the graft copolymerization of MAEV2, the grafting efficiency was the highest when the mole ratio of 2-VN to MAH was 1.0 and reaction temperature was 70°C.

2. The grafting efficiency increased with EPDM content.

3. The effect of solvent on the grafting efficiency was increased in the order of toluene > benzene > THF; The effect of reaction time was increased up to 72hr and then levelled off.

4. The effect of initiator on the grafting efficiency was negligible.

5. The thermal decomposition temperature of MAEV2 was significantly enhanced as compared to ABS. Namely, the thermal decomposition temperature of MAEV2 was higher by 54°C than that of ABS.

6. The light resistance of MAEV2 was better than that of ABS.

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