Syntheses and Properties of *N*-Vinylpyrrolidione-*g*-EPDM and Its Modified Polymer

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ABSTRACT: The graft copolymerizations of *N*-vinylpyrrolidione(NVP) onto ethylene– propylene–diene terpolymer (EPDM) were carried out with benzoyl peroxide (BPO) as an initiator in toluene. The synthesized EPDM-*g*-NVP (ENVP) was characterized by infrared (IR) spectroscopy and gel permeation chromatography (GPC). The effects of initiator and monomer concentrations, reaction time, and temperature were investigated in the graft copolymerization. The highest graft efficiency was obtained at 0.04 mol of NVP, 2 g of EPDM, 2 wt % of BPO and 80°C for 72 h. Modified ENVP (MENVP) was obtained by the reaction of ENVP and KOH in MeOH. Properties of EPDM, ENVP, and MENVP were investigated by a thermogravimetric analyzer (TGA), an instron tensile tester, a Fade-*O*-Meter, and a UV spectrophotometer. Tensile strength and light resistance of ENVP were better than those of MENVP. The dyeability of polymers was increased in following order: MENVP > ENVP > EPDM. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1177–1184, 1999

Key words: graft polymerization; ethylene-propylene-diene terpolymer (EPDM); *N*-vinylpyrrolidione(NVP); EPDM-*g*-NVP (ENVP); modified ENVP (MENVP); graft efficiency; thermal stability; tensile strength; light resistance; dyeability

INTRODUCTION

It has been reported that ethylene-propylenediene terpolymer (EPDM) has good resistances to heat, light, oxygen, and ozone, because it has low contents of the nonconjugated diene component.¹⁻⁴ But it has also poor dyeability and adhesion due to nonpolar properties. The concept of molecular design is applying to the modification of weak points of materials. As an example, acrylonitrile-EPDM-styrene (AES), with excellent light and weather resistance, was prepared using EPDM in place of butadiene in acrylonitrile– butadiene–styrene (ABS), which has a low resistance of light and weather. We have synthesized the high-performance graft polymers containing EPDM to overcome demerits such as poor heat and light resistance of ABS.^{5–16}

The aim of this work is to improve dyeability of EPDM by the synthesis of a new graft copolymer, EPDM-g-NVP (ENVP) and its modification. In this study, ENVP was synthesized by the graft copolymerization of N-vinylpyrrolidione (NVP) onto EPDM using benzoyl peroxide (BPO) as an initiator in toluene, and the modified ENVP (MENVP) was prepared by the reaction of ENVP and potassium hydroxide (KOH) in methanol. The synthesized ENVP and MENVP were identified by IR spectra. The effects of initiator, monomer concentrations, reaction time, and temperature were examined in the graft copolymerization of N-vinylpyrrolidione (NVP) onto EPDM. The

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Scheme 1 Synthetic procedure of ENVP and MENVP.

dyeability, tensile strength, thermal stability, and light resistance of ENVP and MENVP were also investigated.

EXPERIMENTAL

Material

N-Vinylpyrrolidione (Aldrich Co., Milwaukee, WI) was purified by the standard procedure. Benzoyl peroxide (BPO) (Hayashi Chemical Co., Japan) was recrystallized from methanol. Ethylene–propylene–diene terpolymer (EPDM), having ethylidene norbornene as a termonomer (Aldrich Co.; ethylene/propylene = 50/42 by mol %, ML50, M_n = 50,500, M_w = 102,000) was used as received. Toluene, methanol, *n*-hexane, ether, and tetrahydrofuran (THF) were distilled prior to use. Potassium hydroxide (KOH; Shinyo Pure Chemical Co., Korea) and other chemicals were used as received.

TABLE I.Graft Copolymerization ConditionsUsed in This Study.

Condition	Description		
EPDM weight (g)	2		
NVP concentration (mol)	0.02, 0.03, 0.04, 0.05		
Initiator concentration (wt %)	1, 2, 3, 4		
Reaction time (h)	24, 48, 72, 96		
Reaction temperature (°C)	60, 70, 80, 90		

Synthesis of ENVP

EPDM of 5 g was dissolved in 150 mL toluene in a 250-mL flask equipped with a stirrer, a thermometer, and a nitrogen gas inlet. The 2 wt % of BPO was added into the flask, and then the solution of a given amount of NVP dissolved in 50 mL toluene was put into EPDM solution. The graft polymerization scheme and the experimental conditions were shown in Scheme 1 and Table I, respectively.

After a predetermined period of reaction, the contents were poured into excess methanol under stirring. The precipitate was collected by filtration and then dried in a vacuum oven. The ENVP was isolated from the reaction mixture by exctraction in a soxhlet apparatus using n-hexane. The isolation procedure of ENVP was schematically shown in Figure 1.

Total conversion (%), grafting ratio (%), and grafting efficiency (%) were estimated from the following equation; 14,22,23



Figure 1 Block diagram of isolation procedure for the graft copolymer (ENVP).

 $Total \ conversion \ (\%)$

$$= \frac{\text{total weight of polymer formed}}{\text{weight of monomer charged}} \times 100$$

Grafting ratio (%)

$$= \frac{\text{weight of polymer in grafts}}{\text{weight of substrate}} \times 100$$

Grafting efficiency (%)

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

Modification¹⁷ of ENVP

A given amount of ENVP was dissolved in 20 mL of THF. The flask was sealed after charging with nitrogen and then dropped with KOH in MeOH. The reaction was carried out at 50°C for 24 h. After reaction, the contents were poured into water. The precipitate was filtered and dried in vacuum to a constant weight. The modification of ENVP was shown in Scheme 1.

Measurements

Infrared Spectroscopy (IR)

The IR spectra of ENVP and MENVP were obtained with a Jasco FT/IR-5300 spectrophotometer by using a KBr pellet for analysis.

Gel Permeation Chromatography (GPC)

The average number (M_n) and weight (M_w) molecular weight of ENVP was determined by GPC (Waters 410), which was calibrated using polystyrene as the standard and THF as the eluent.

Thermal Stability

The thermal stabilities of EPDM, ENVP, and MENVP were examined with a Shimadzu DT 30A TGA instrument at a scanning rate of 15°/min under nitrogen.

Tensile Property

The tensile tests were performed by the Instron Tensile Tester (Model 4204). The samples were prepared according to the procedure of ASTM D638-84. 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 a Color Difference Meter (NP-101 DP). The film specimens were casted from a mixed solvent of benzene and *m*-cresol (80/20 by vol) on a nonyellowing urethane-coated hiding paper. The films were slowly dried at room temperature and kept under vacuum until they reached constant weight. The color difference (ΔE) of the samples after exposure to UV light was calculated using the Hunter-Schofield equation.^{6,18}

Elemental Analysis

Elemental analyses were performed by an elemental analyzer (EA ; Carlo Erba Instruments, EA-1180).

Dyeability

The synthesized samples were dyed with C.I. Direct Blue 71 (3-amino-1,5-naphthalenedisulfonic acid) at 80°C for 7 h. The dyed samples were dried in room temperature, and then extracted with 25% aqueous pyridine solution at 90°C. The extracted solution was diluted in 25% aqueous pyridine solution. The absorbance of the dilute solution was measured by UV spectrophotometer (Kontron Unikon 860).

RESULTS AND DISCUSSION

Synthesis of ENVP

Figure 2 shows the IR spectra of EPDM and ENVP. The IR spectra of ENVP exhibited characteristic absorption band at 1670 cm⁻¹ (C=O streching) due to NVP, and 1460 cm⁻¹ ($-CH_2$) bending) and 1375 cm⁻¹ ($-CH_3$ bending) due to EPDM. Average molecular weight and composition of ENVP were shown in Table II.

Effect of Reaction Conditions

Effect of Monomer Concentration

Figure 3 shows the effect of the monomer concentration on the graft copolymerization. The graft polymerizations were carried out in toluene with a 2 g of EPDM and 3 wt % BPO at 70°C for 48 h using several concentrations of VP such as 0.02, 0.03, 0.04, and 0.05 mol. The grafting efficiency passes through a maximum at 0.04 mol. The de-



Figure 2 IR spectra of ENVP and EPDM.

crease in the grafting efficiency at a higher monomer concentration is ascribed to the fact that the formation of the homopolymer is easier than that of the graft polymer as the monomer concentration increases.

Effect of Initiator Concentration

The effect of initiator concentration on the graft copolymerization is shown in Figure 4. In this case, the reaction was carried out in toluene with a 2 g of EPDM and a 0.04 mol of NVP using several initiator concentration at 70°C for 48 h. The grafting efficiency was increased up to 2 wt % of the initiator but slightly decreased at 3 wt %, and rapidly decreased at 4 wt %. The phenomenon is caused by the fact that the homopolymer is more favorably formed than the graft copolymer⁸ at a high concentration of the initiator.

Effect of Reaction Time

The effect of reaction time on the grafting process is shown in Figure 5. The graft polymerizations were conducted with 2 g of EPDM and 0.04 mol of NVP, and 2 wt % of BPO for several reaction times at 70°C. The grafting efficiency is the maximum at 72 h, and thereafter it was decreased.

Effect of Reaction Temperature

Figure 6 shows the effect of the reaction temperature on the graft copolymerization. The reaction

Sample	Average Molecular Weight ^a			Composition (%) ^b		
	$M_n \ (imes 10^3)$	$M_w \ (imes 10^3)$	M_w/M_n	С	Н	N
ENVP2 ^c	71	312	4.37	69.89	7.45	0.26
ENVP3	53	333	6.18	82.46	13.90	0.62
ENVP4	41	326	7.91	74.91	7.85	0.27
ENVP5	65	332	5.07	78.42	13.36	0.50

Table II. Average Molecular Weight and Composition of ENVP.

^a The number (M_n) and weight (M_m) average molecular weights of the polymers determined by GPC in DMF.

^b The value obtained by elemental analysis.

^c The number denotes the feed concentration ($\times 10^{-2}$ mol) of NVP in graft polymerization.



Figure 3 Plot of grafting efficiency, grafting ratio, and total conversion vs. monomer concentration.

was performed in toluene with 2 g of EPDM, 2 wt % of BPO, and 0.04 mol of NVP at 70°C. The 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; however, the rate of homopolymerization was also increased.¹⁹ As a result, the grafting efficiency was increased initially, but in further increasing the temperature, the grafting efficiency was decreased because the formation of the homopolymer is more favorable than that of the graft polymer. A similar observa-



Figure 4 Plot of grafting efficiency as a function of initiator concentration.



Figure 5 Plot of grafting efficiency vs. reaction time.

tion was made by Porejko et al.²⁰ for the grafting of maleic anhydride onto low-density polyethylene.

Modification of ENVP

Figure 7 shows the IR spectra of ENVP and MENVP. MENVP was exhibited by characteristic peaks at 1560 and 1660 cm⁻¹ due to N—H bending and C=O streching, respectively, whereas the unmodified ENVP appeared as a single carbonyl peak at 1670 cm⁻¹. This result means that MENVP prepared by the reaction of ENVP with KOH in methanol has partially been opened, and it has not only -N—C=O in the ring structure of NVP but also -N—H and C=O groups due to ring opening (Scheme 1).



Figure 6 Plot of grafting efficiency vs. reaction temperature.



Figure 7 IR spectra of ENVP and MENVP.

Comparison of Dyeability

ENVP-4 containing 0.27% nitrogen (Table II) is used for the dyeing test. To measure dyeability by UV spectrophotometer, the Direct Blue 71 dyed into the samples was completely extracted with 25% aqueous pyridine solution. The higher absorbency means the higher concentration of dye in the sample by Beer-Lambert law. The dyeability of ENVP and MENVP was compared to that of EPDM, as shown in Figure 8. The dyeabilities of



Figure 8 Dyeabilities of EPDM, ENVP, and MENVP.

polymers were found to be following order: MENVP > ENVP > EPDM.

The fact that dyeabilities for ENVP and MENVP are higher than that of EPDM comes from the formation of hydrogen bonds between





Scheme 2 Hydrogen bond between dyestuff and graft polymer.



Figure 9 Tensile properties of EPDM, ENVP, and MENVP.

the carbonyl and hydroxy group in ENVP or MENVP and the hydroxy or amino group in the dye molecule, as shown in Scheme 2.

This result agrees with the literature²⁴ that the hydroxy, amino, or azo groups in dyestuff can form hydrogen bonds with the carbonyl or carboxyl group of the graft polymers. In the case of EPDM, it does not have hydroxy, amino, or azo



Figure 10 TGA curves of EPDM, ENVP, and MENVP.



Figure 11 Light resistances of EPDM, ENVP, and MENVP.

groups; therefore, it cannot form the hydrogen bond with dyestuff. As can see in Figure 8, dyeability of MENVP was better than that of ENVP. This result may be attributed to the number of hydrogen bonding sites in MENVP.

Tensile Property

The tensile properties of ENVP and MENVP are shown in Figure 9. The tensile strength of ENVP was higher than that of EPDM. This was attributed to the brittle property of poly(*N*-vinyl pyrrolidione)[PVP].²¹ For MENVP, the PVP moiety in the graft polymer disappeared, partially because of the ring opening, and its tensile strength was decreased and elongation was increased.

Thermal Stability

The TGA curves of synthesized ENVP and MENVP, together with EPDM, are shown in Figure 10. In this figure, the decomposition temperatures of the polymers were in the following order: EPDM > ENVP > MENVP. The low thermal stability of ENVP was caused by the taking a large space between its molecular chains due to the bulky pyrrolidione ring in the side chain of ENVP. In the case of MENVP, its flexible side chain (Scheme 1) increases the molecular mobility and makes a lower thermal stability than ENVP.

Light Resistance

ENVP-4 containing 0.27% nitrogen listed in Table II is used in the light-resistance test. Figure 11 shows the light resistance of EPDM, ENVP, and MENVP. The light resistance was semiquantitatively expressed in terms of ΔE with a National Bureau of Standards Unit. A smaller ΔE means better light resistance. It is seen that ENVP synthesized in this work does not show better light resistance than EPDM due to the carbonyl group in the NVP. The color change of MENVP was larger than ENVP. This can be explained by the fact that the oxidation of nitrogen attached to both alkyl carbons in the side chain of MENVP was easier than that of nitrogen directly bonded to the carbonyl group in ENVP (Scheme 1). This means that the loss of electron in a lone pair of electrons on the nitrogen of ENVP due to the electron-withdrawing effect of neighboring carbonyl group was more difficult than that of MENVP.

CONCLUSIONS

ENVP was synthesized by the graft polymerization of NVP onto EPDM using benzoyl peroxide as an initiator in toluene, and the modification of ENVP was prepared by the reaction of ENVP and KOH in MeOH. Properties of EPDM, ENVP, and MENVP were investigated. (a) The important results are summarized as follows: the highest grafting efficiency was observed at 0.04 mol of NVP, 2 wt % of BPO, 72 h, and 80°C, and the NVP contents in the graft polymer were in the range of 1.4-4.1 wt %, depending on the NVP feed concentration. (b) The IR spectrum of ENVP showed characteristic absorption bands at 1670 $\rm cm^{-1}$ (—C==O) due to the NVP unit, and 1460 $\rm cm^{-1}$ $(-CH_2-)$ and 1375 cm⁻¹ $(-CH_3)$ owing to the EPDM moiety, whereas MENVP exhibited two bands at 1560 cm⁻¹ (-NH bending) and 1660 cm^{-1} (μC =O stretching), together with the peaks of EPDM. (c) Tensile strength of ENVP is higher than that of EPDM and MENVP, but the decomposition temperatures of ENVP and MENVP were lower than EPDM. (d) The light resistance of ENVP was better than that of MENVP, and the dyeabilities of the polymers were found to be in the following order: MENVP > ENVP > EPDM.

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