

Syntheses and Properties of Graft Polymers of *N*-Substituted Acrylamides onto EPDM

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ABSTRACT: The graft polymerizations of *N*-isopropylacrylamide (NIPAM) or *N*-phenylacrylamide (NPAM) onto ethylene-propylene-diene terpolymer (EPDM) were carried out with benzoyl peroxide (BPO) as an initiator in toluene or THF. The structures of synthesized graft polymers, EPDM-*g*-*N*-isopropylacrylamide (ENIPAM) and EPDM-*g*-*N*-phenylacrylamide (ENPAM), were identified by infrared (IR) spectroscopy. The effects of monomer concentration, reaction time, and initiator concentration were investigated on the graft polymerization. The highest graft efficiency of NIPAM was obtained at 0.75 mol/L of NIPAM, 4 g of EPDM, 3 wt % of BPO, and 70°C for 48 h and that of NPAM did not much change up to 0.75 mol/L of NPAM, 4 g of EPDM, 3 wt % of BPO, and 70°C for 72 h. The thermal decomposition temperatures, wettabilities, and tensile strengths of ENIPAM and ENPAM all decreased with an increasing concentration of NIPAM and NPAM moiety in the corresponding polymers, respectively. The morphologies of ENIPAM and ENPAM after irradiation showed many gel particles as compared with those of ENIPAM and ENPAM before irradiation. The UV light and ⁶⁰Co γ -ray resistances of ENIPAM and ENPAM were worse than those of EPDM due to carbonyl group in NIPAM and NPAM. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3259–3267, 1999

Key words: graft polymerization; ethylene-propylene-diene terpolymer (EPDM); EPDM-*g*-*N*-isopropylacrylamide (ENIPAM); EPDM-*g*-*N*-phenylacrylamide (ENPAM); graft efficiency; thermal stability; morphology; wettability; light resistance; tensile property; ⁶⁰Co γ -ray resistance

INTRODUCTION

It has been reported that ethylene-propylene-diene terpolymer (EPDM) has good resistances to heat, light, oxygen, and ozone, because it has low contents of nonconjugated diene component.^{1–4} But it also has poor wettability and adhesion due to its nonpolar property and poor photodegradability and tensile strength. The concept of mo-

lecular design apply to the improvement in weak points of materials. As an example, acrylonitrile-EPDM-styrene (AES) with excellent light and weather resistances was prepared using EPDM in place of butadiene in acrylonitrile-butadiene-styrene (ABS), which has poor light and weather resistances. We have synthesized the high-performance graft polymers containing EPDM in order to overcome the deficiencies of ABS, such as poor heat and light resistances.^{5–13}

The aim of this work was to improve the wettability, photodegradability, and tensile strength of EPDM by the graft polymerizations of *N*-isopropylacrylamide (NIPAM) and *N*-phenylacrylamide (NPAM) onto EPDM. In this study, EPDM-

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g-N-isopropylacrylamide (ENIPAM) and EPDM-*g-N*-phenylacrylamide (ENPAM) were synthesized by the graft polymerizations of NIPAM and NPAM onto EPDM using benzoyl peroxide (BPO) in toluene or THF, respectively. The effects of monomer concentration, reaction time, and initiator concentration on the graft polymerizations were examined. The structures of ENIPAM and ENPAM were identified by infrared (IR) spectroscopy. Thermal stability, morphology, wettability, UV light resistance, tensile property, and ^{60}Co γ -ray resistance of ENIPAM and ENPAM were also investigated.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAM; Aldrich Chemical Co., Milwaukee, WI), acryloyl chloride (AC; Aldrich Chemical Co.) and aniline (Kokusan Co., Tokyo, Japan) were used without further purification. Triethylamine (TEA; Junsei Co., Tokyo, Japan) was refluxed with acetic anhydride and with KOH, and finally distilled. Benzoyl peroxide (BPO; Junsei Co., Japan) was dissolved in CHCl_3 and precipitated by adding an equal volume of MeOH. Ethylene-propylene-diene terpolymer, having ethylidene norbornene as a termonomer (EPDM; Aldrich Chemical Co., ethylene/propylene = 50/42 by mol %, ML50) was used as received. 1,2-Dichloroethane, toluene, tetrahydrofuran (THF), methanol, *n*-hexane, and other chemicals were purified by standard procedures.

Measurements

Infrared (IR) Spectroscopy

The IR spectra of NPAM, EPDM, ENIPAM, and ENPAM were obtained with a Jasco FT/IR-5300 spectrophotometer by using KBr or NaCl plates for analysis.

Thermogravimetry Analysis (TGA)

The thermal decomposition temperatures of EPDM, ENIPAM, and ENPAM were examined with a Shimadzu DT 30A TGA instrument at a scanning rate of $5^\circ\text{C}/\text{min}$ under nitrogen.

Scanning Electron Microscopy (SEM)

The morphologies of ENIPAM and ENPAM before and after UV light of 313 nm and ^{60}Co γ -ray

irradiation were analyzed by the SEM instrument, JEOL JSM35-CF. In the examination of graft polymer surface, the samples were metalized by gold coating prior to being installed in the SEM chamber.

Contact Angle

The wettabilities of EPDM, ENIPAM, and ENPAM were evaluated from the static contact angle, which is measured at 30 s after dropping distilled water onto the surface with a contact angle meter (ERMA).^{14–15}

Color Difference

The UV light and ^{60}Co γ -ray resistances of EPDM, ENIPAM, and ENPAM irradiated by UV light (UV lamp of 313–280 nm, fade-o-meter: Atlas; at 60°C and 65% relative humidity) and ^{60}Co γ -ray [Atomic Energy of Canada Radiochemical Company (AECR) Industrial Irradiation Division] were determined by a color difference meter (NP-101DP). The film specimens were cast from mixed solvent of THF 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 values (ΔE) of the samples after exposure to UV light and ^{60}Co γ -ray were calculated using the Hunter–Schöfield equation as a function of irradiation time.¹⁶

Tensile Property

The tensile tests of EPDM, ENIPAM, and ENPAM irradiated by UV light and ^{60}Co γ -ray 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.

Synthesis of N-Phenylacrylamide (NPAM)

A solution of aniline (22.78 mL, 0.25 mol) and TEA (41.81 mL, 0.30 mol) in 1,2-dichloroethane of 100 mL was refluxed for 2 h, with precaution being taken to exclude moisture from the atmosphere, and then the clear solution was cooled to 0°C in ice bath. The AC solution (24.37 mL, 0.30 mol) was slowly added dropwise to 50 mL 1,2-dichloroethane with vigorous stirring for 2 h at 0°C . The produced triethylamine hydrochloride salt was filtered out and the filtrate was concen-

Table I Graft Polymerization Conditions Used in the Study

Condition	Description			
Monomer concentration (NIPAM or NPAM) [mol/L]	0.25	0.50	0.75	1.00
Initiator concentration (BPO) [wt %] ^a	1	2	3	4
Reaction time (h)	24	48	72	96
Reaction temperature (°C)	70			

^a The concentration was based on the total weights containing monomer onto EPDM.

trated on a rotary evaporator. The concentrated solution was slowly added to 500 mL distilled water. After removing the soluble part, the obtained yellow powder was washed with *n*-hexane and dried under reduced pressure to obtain pure NPAM in 77% yield, mp 103.6°C. The FTIR spectrum of NPAM exhibited characteristic absorption bands at about 3400 to 3300 cm⁻¹ (N—H stretching), 1680 cm⁻¹ (C=O stretching), 1610 cm⁻¹ (N—H bending), and 760 cm⁻¹ (aromatic C—H out-of-plane). In ¹H-NMR spectra, the peaks of NPAM indicated amide proton at 8.1 ppm, aromatic protons at approximately 7.2 to 7.8 ppm, and vinyl protons at about 5.7 to 6.6 ppm.

Syntheses of ENIPAM and ENPAM

The ENIPAM was prepared by the graft polymerization of NIPAM (CH₂=CHCONHCH(CH₃)₂) onto EPDM as the following procedure: EPDM of 4 g and 2 wt % of BPO were dissolved in 80 mL toluene, and the solution was poured into a round-bottomed flask under a nitrogen atmosphere. The flask was then placed in a regulated thermostat at 70 ± 0.05°C with vigorous stirring. After 5 min, the solution of a given amount of NIPAM dissolved in 40 mL toluene was slowly dropped into the flask with vigorous stirring for 1 h and then the mixed solution was left for 48 h without stirring. The polymerizations were carried out under various experimental conditions as shown in Table I.

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. ENIPAM was isolated from the reaction mixture by extraction in Soxhlet apparatus using *n*-hexane to remove unreacted EPDM according to Figure 1.

ENPAM was prepared from NPAM(CH₂=CHCONHC₆H₅) and EPDM in THF by the same procedure as that for NIPAM. The isolation procedures of ENIPAM or ENPAM were schematically shown in Figure 1.

Grafting efficiency was estimated from the following equation:

Grafting efficiency (%)

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

RESULTS AND DISCUSSION

Characterization

Figure 2 shows the FTIR spectra of EPDM, ENIPAM, and ENPAM. The FTIR spectrum of ENIPAM exhibited characteristic adsorption bands at 3400–3300 cm⁻¹ (N—H stretching), 2930 cm⁻¹ (aliphatic C—H stretching), 1641 cm⁻¹ (C=O stretching), and 1550 cm⁻¹ (N—H bending). For ENPAM, the FTIR spectrum showed characteristic adsorption bands at 3400–3300 cm⁻¹ (N—H stretching), 3025 cm⁻¹ (aromatic C—H stretching), 2920 cm⁻¹ (aliphatic C—H stretching), 1660 cm⁻¹ (C=O stretching), 1550 cm⁻¹ (N—H bending), and 760 cm⁻¹ (aromatic C—H out-of-plane bending).

Effects of Reaction Conditions

Effect of Monomer Concentration

Figure 3 shows the effect of the monomer concentration on the graft polymerization. The graft

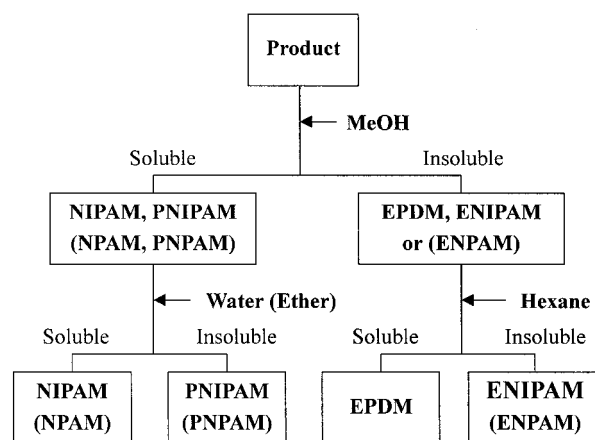


Figure 1 Block diagram of isolation procedure for the graft polymers.

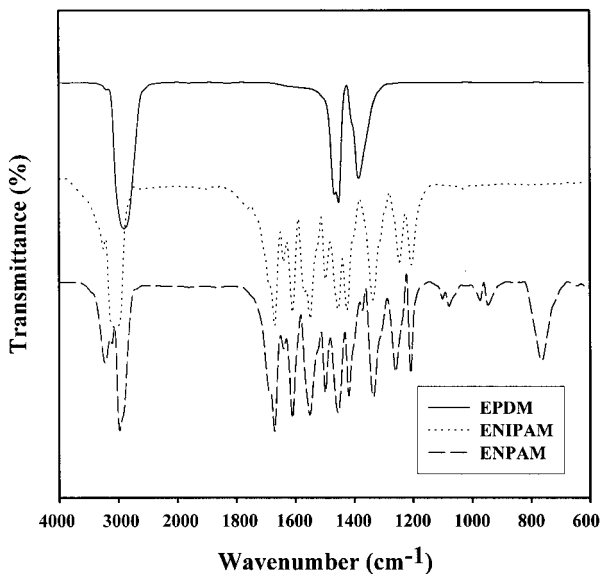


Figure 2 FTIR spectra of EPDM, ENIPAM, and ENPAM (NaCl, Film Phase).

polymerizations were carried out with 4 g of EPDM; several concentrations of NIPAM such as 0.25, 0.50, 0.75, and 1.00 mol/L; and 2 wt % BPO in toluene at 70°C for 48 h. The grafting efficiency for NIPAM rapidly increased with increasing NIPAM up to 0.75 mol/L; thereafter, it slowly decreased. In the case of NPAM, the graft polymerizations were carried out in the same condi-

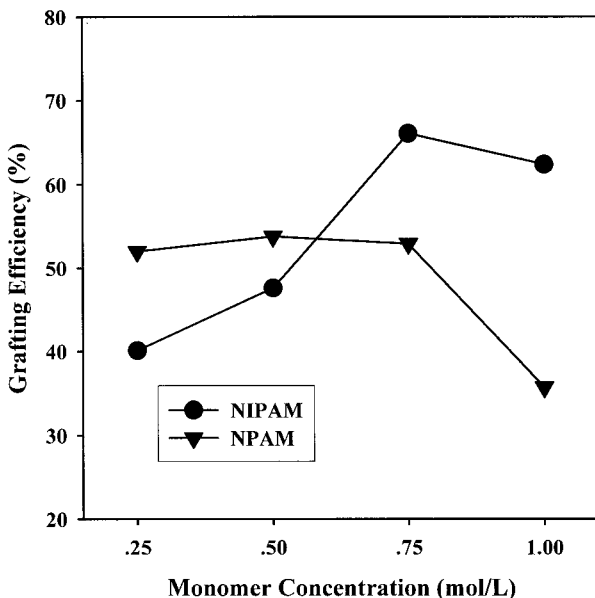


Figure 3 Plot of grafting efficiency versus monomer concentration.

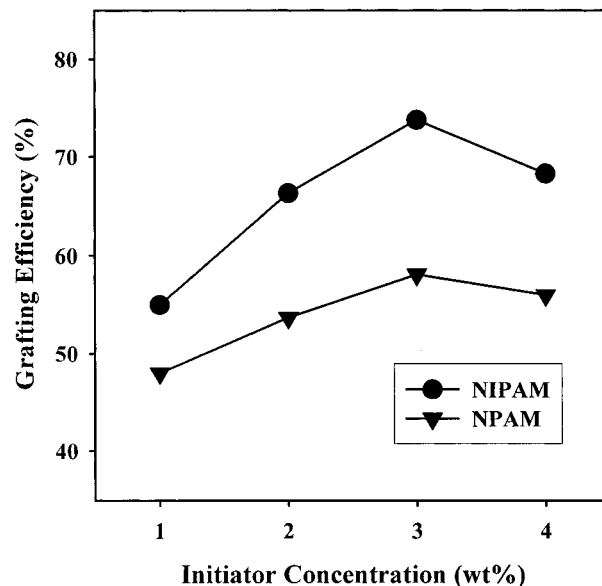


Figure 4 Plot of grafting efficiency versus polymerization time.

tions described for NIPAM. The grafting efficiency did not show large differences up to 0.75 mol/L and thereafter it rapidly decreased. The decrease in the grafting efficiency at higher monomer concentration is explained by the fact that the formation of the homopolymer is easier than that of the graft polymer. As shown in Figure 3, the decreasing tendency of NPAM was found to be larger than NIPAM at high monomer concentration. This result means that the reactivity of NPAM to the homopolymerization is higher as compared with that of NIPAM.

Effect of Initiator Concentration

The effect of initiator concentration on the graft polymerization is shown in Figure 4. The graft polymerizations of NIPAM or NPAM were carried out with 2 g of EPDM and 0.75 mol/L of NIPAM in toluene or NPAM in THF, using several initiator concentrations at 70°C for 48 h, respectively. The grafting efficiencies were increased up to 3 wt % of initiator but decreased at 4 wt %. The decreasing phenomena are generated such that the homopolymer is formed more favorably than the graft polymer at a high concentration of initiator. As shown in Figure 4, the graft efficiency for NIPAM was greater than NPAM.

Effect of Polymerization Time

The effect of polymerization time on the grafting process is shown in Figure 5. The graft polymer-

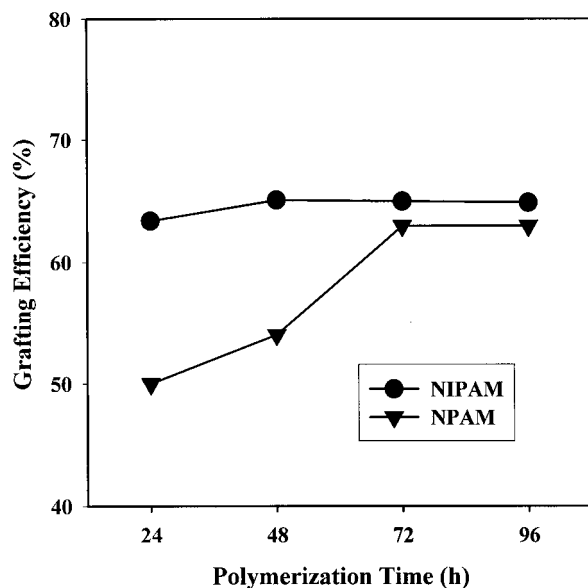


Figure 5 Plot of grafting efficiency as a function of initiator concentration.

izations were conducted with 2 g of EPDM, 0.75 mol/L of NIPAM, and 2 wt % of BPO under various reaction times at 70°C. The grafting efficiency for NIPAM did not much change up to 96 h. This phenomenon may be attributed to the similar rate of formation of homopolymer and graft polymer. In the case of NPAM, the graft polymerizations were carried out under the same conditions as those of NIPAM. The grafting efficiency is increased with increasing polymerization time up to 72 h and thereafter it leveled off.

Thermal Stability

The TGA curves of synthesized ENIPAM and ENPAM together with EPDM are shown in Figures 6 and 7, respectively. In these figures, the thermal decomposition temperatures of ENIPAM and ENPAM decreased with an increasing concentration of NIPAM or NPAM moiety in corresponding graft polymers. The thermal stability of ENPAM was found to be better than that of ENIPAM due to the phenyl group of NPAM moiety in ENPAM.

Morphology

Figure 8 shows the surface micrographs of ENIPAM and ENPAM before and after irradiation of UV light of 313 nm or 15 Mrad ^{60}Co γ -ray. The micrographs of ENIPAM(c) and ENPAM(d) after UV irradiation and ENIPAM(e) and

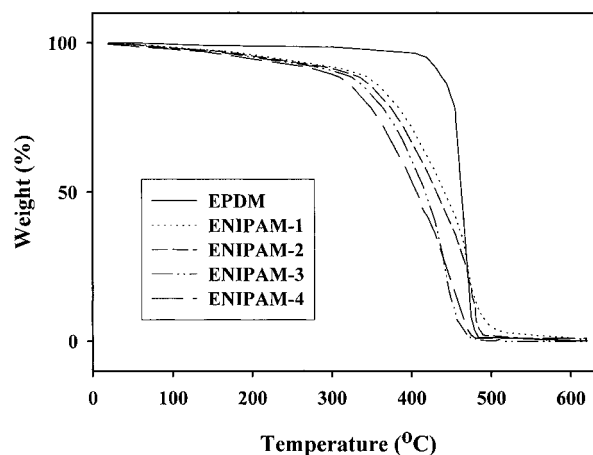


Figure 6 TGA curves of EPDM and ENIPAM.

ENPAM(f) after ^{60}Co γ -ray irradiation showed many gel particles as compared with those of ENIPAM(a) and ENPAM(b) before irradiation. This result was consistent with photodegradable property.¹⁷ As shown in Figure 8 (e) and (f), the micrograph of ENPAM irradiated by ^{60}Co γ -ray showed less broken surface than that of ENIPAM. This result is caused by the phenyl ring in ENPAM, because the phenyl ring can stabilize by resonance.

Wettability

Figure 9 shows the effects of concentration of NIPAM and NPAM moiety on the contact angle of corresponding ENIPAM and ENPAM. The wettability of EPDM in this figure for comparison was included. The contact angle values of ENIPAM

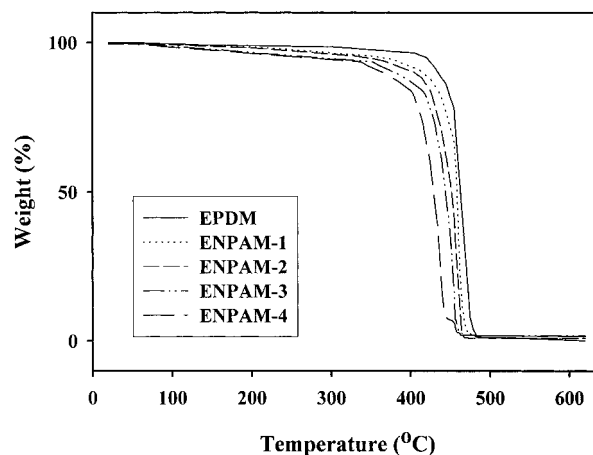


Figure 7 TGA curves of EPDM and ENPAM.

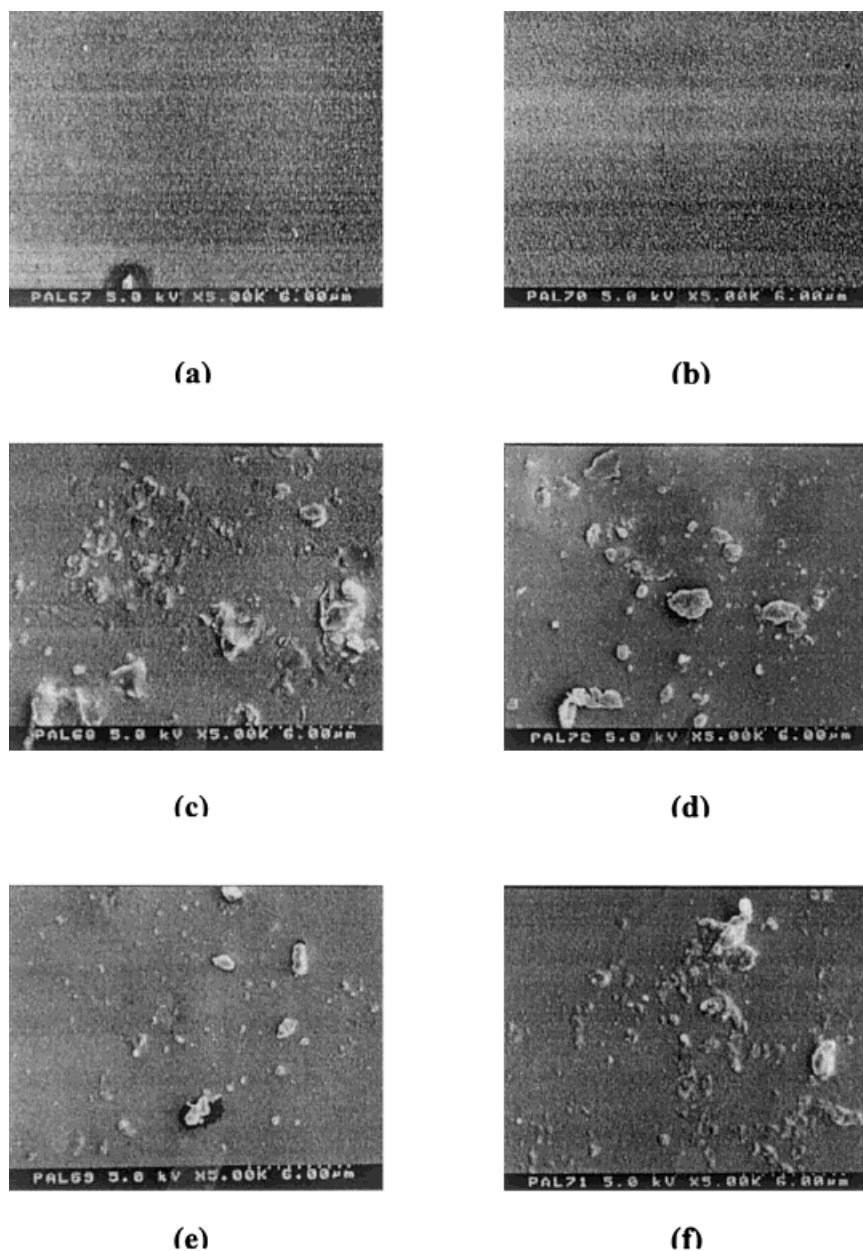


Figure 8 Scanning electron micrographs of ENIPAM(a) and ENIPAM(b) before irradiation, ENIPAM(c) and ENIPAM(d) irradiated with UV light of 313 nm, and ENIPAM(e) and ENIPAM(f) irradiated with 15 Mrad ^{60}Co γ -ray.

and ENPAM increased slowly with increasing concentration of NIPAM or NPAM. As can be seen in this figure, the contact angle values of ENIPAM and ENPAM were much higher than that of EPDM. From these results, the wettabilities of the synthesized graft polymers were much improved as compared with that of EPDM. This result can be explained by increasing of the polarity of the synthesized graft polymers.

Light Resistance

Figures 10 and 11 show the light resistances of EPDM, ENIPAM, and ENPAM. The light resistance was semiquantitatively expressed in terms of ΔE with a National Bureau of Standards Unit.¹⁸ The smaller ΔE means better light resistance. The light resistance of ENIPAM and ENPAM synthesized in this work was worse than

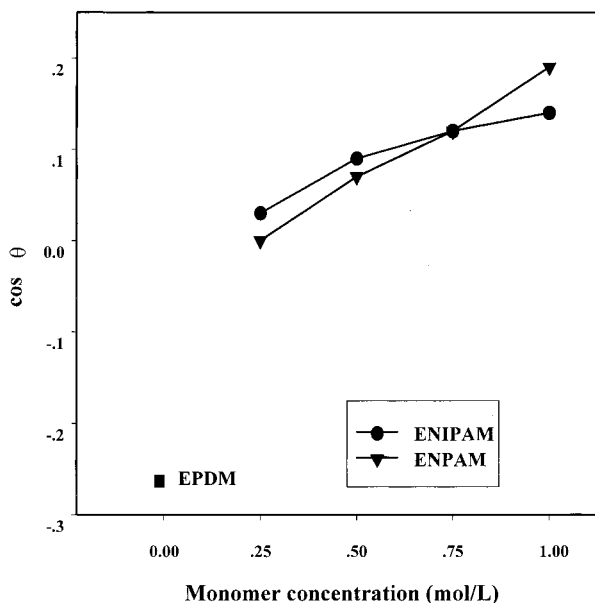


Figure 9 Cos θ values of graft polymers versus monomer concentration in feed.

EPDM due to the carbonyl group in NIPAM and NPAM. The color difference of ENPAM was larger than that of ENIPAM due to the double bond of the aromatic ring of NPAM moiety in ENPAM.

Tensile Property

The tensile properties of EPDM, ENIPAM, and ENPAM are shown in Table II. The tensile

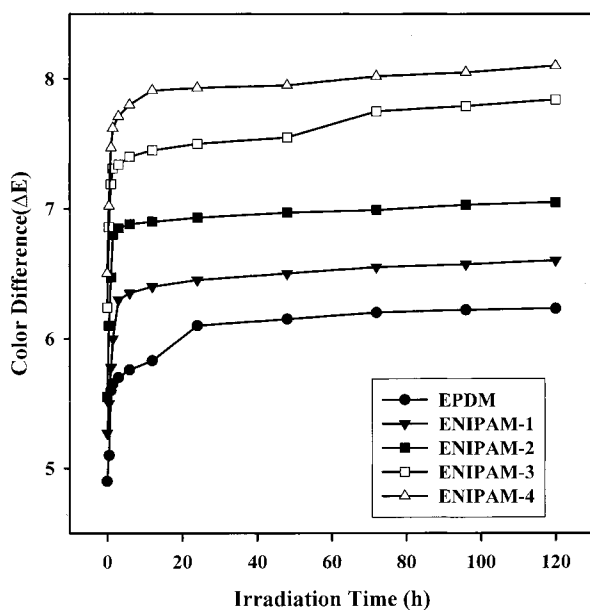


Figure 10 UV light resistances of EPDM and ENIPAM.

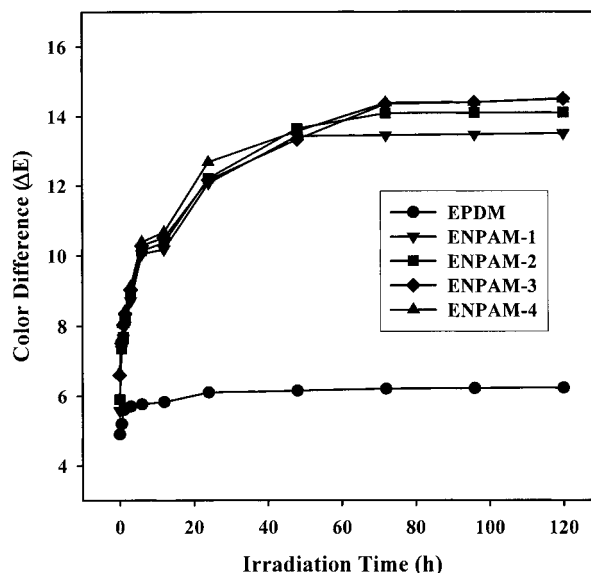


Figure 11 UV light resistances of EPDM and ENPAM.

strengths of ENIPAM and ENPAM were higher than that of EPDM and the elongations at break of ENIPAM and ENPAM were smaller. It was attributed to hard property of poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N*-phenylacrylamide) (PNPAM).

⁶⁰Co γ -Rays Resistance

Tables II and III show the tensile properties and color difference of EPDM, ENIPAM, and PENPAM before and after ⁶⁰Co γ -ray irradiation. After irradiation, tensile strength and elongation at break of ENIPAM and ENPAM decreased and their color differences increased. The color difference of ENPAM, especially, was smaller than that of ENIPAM due to the aromatic ring of NPAM moiety in ENPAM, which can stabilize by resonance.

CONCLUSIONS

ENIPAM and ENPAM were synthesized by the graft polymerizations of NIPAM and NPAM onto EPDM using benzoyl peroxide (BPO) as an initiator in toluene or THF. The properties of EPDM, ENIPAM, and ENPAM were investigated. The important results are summarized as follows:

1. The characteristic peaks of ENIPAM and ENPAM exhibited at 1660–1641 cm^{-1}

Table II Tensile Strengths and Elongations at Break of Graft Polymers Before and After ^{60}Co γ -Ray Irradiation

Materials	Tensile Strength (MPa)			Elongation at Break (%)		
	Before Irradiation (TS ₁)	After Irradiation (TS ₂) ^a	TS ₁ - TS ₂	Before Irradiation (EB ₁)	After Irradiation (EB ₂)	EB ₁ - EB ₂
EPDM	1.2	1.0	0.2	1710	1005	705
ENIPAM-1	2.3	1.7	0.6	1170	108	1062
ENIPAM-2	3.6	2.7	0.9	1040	115	925
ENIPAM-3	3.9	2.9	1.0	710	138	527
ENIPAM-4	4.1	3.0	1.1	560	165	395
ENPAM-1	2.5	1.8	0.7	1178	125	1053
ENPAM-2	3.0	2.1	0.9	1020	165	855
ENPAM-3	3.1	2.1	1.0	780	201	579
ENPAM-4	3.9	2.4	1.5	610	233	377

^a Value after 15 Mrad ^{60}Co γ -ray irradiation.

(C=O) and 3400–3300 cm^{-1} (—NH) caused NIPAM and NPAM moieties and ENPAM showed the peak caused out-of-plane of aromatic C—H at 760 cm^{-1} .

- The highest grafting efficiency of NIPAM was obtained at 0.75 mol/L of NIPAM, 3 wt % of BPO, 48 h, and 70°C; and that of NPAM was obtained at 0.50 mol/L of NPAM, 3 wt % of BPO, 72 h, and 70°C.
- The thermal decomposition temperatures of ENIPAM or ENPAM decreased with an increasing concentration of NIPAM or NPAM moiety in the corresponding graft polymers.
- The morphology of ENIPAM or ENPAM after UV light or ^{60}Co γ -ray irradiation

Table III Color Difference Values of Graft Polymers Irradiated by ^{60}Co γ -Ray

Polymer	Color Difference (ΔE)			
	Before	5 Mrad	10 Mrad	15 Mrad
EPDM	1.7	3.1	10.3	15.1
ENIPAM-1	1.6	3.9	13.2	15.4
ENIPAM-2	1.1	4.1	15.0	17.7
ENIPAM-3	1.1	4.8	15.2	17.9
ENIPAM-4	1.4	5.5	16.5	20.0
ENPAM-1	0.9	1.3	1.4	1.5
ENPAM-2	1.4	1.4	1.5	1.6
ENPAM-3	1.5	1.5	1.6	1.6
ENPAM-4	1.5	1.6	1.7	1.8

showed many gel particles as compared with those of ENIPAM and ENPAM before irradiation.

- The contact angles of ENIPAM and ENPAM decreased with an increasing concentration of NIPAM and NPAM, due to polarity of NIPAM and NPAM; that is, the wettabilities of ENIPAM and ENPAM increased with an increasing concentration of NIPAM and NPAM moiety in the corresponding polymers, respectively.
- The light resistance of ENIPAM or ENPAM was worse than that of EPDM, due to the carbonyl group in NIPAM and NPAM moiety. The color difference of ENPAM was larger than that of ENIPAM because of the double bond of the aromatic ring of NPAM moiety.
- The tensile strengths of ENIPAM and ENPAM were higher as compared with that of EPDM and the elongation at break for ENIPAM and ENPAM was small due to the hard property of NIPAM and NPAM homopolymers.
- After ^{60}Co γ -ray irradiation, the tensile strength and elongation at break of ENIPAM and ENPAM decreased and the color differences increased. The color difference of ENPAM, especially, was smaller than that of ENIPAM due to the aromatic ring of NPAM moiety.

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