Synthesis and Photodegradable Properties of Methyl Vinyl Ketone–EPDM–Styrene Graft Terpolymer

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ABSTRACT: The graft terpolymerization of methyl vinyl ketone (MVK) and styrene (St) onto ethylene–propylene–diene terpolymer (EPDM) was carried out under various polymerization conditions. The synthesized graft terpolymer, MVK–EPDM–St (MVES), was identified by infrared (IR) spectroscopy. The effects of monomer concentration, mole ratio of MVK to St, reaction time, reaction temperature, and initiator concentration on the graft terpolymerization were examined. Upon UV irradiation in the presence of oxygen, the MVES-containing carbonyl group showed photodegradable properties caused by Norrish type II reaction. The new IR characteristic peaks, such as carbonyl, vinyl, and hydroxy groups of the photodegraded MVES, increased with increasing UV irradiation time. The tensile strength and elongation at break of MVES after UV irradiation were lower than those of before UV irradiation. The color difference of the irradiated MVES was higher than that of EPDM. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1721–1727, 1998

Key words: graft terpolymer; poly(MVK-EPDM-St); photodegradable polymer; UV irradiation; color difference; tensile strength

INTRODUCTION

The photodegradable polymers containing oxygen moiety, such as hydroperoxide, peroxide, and various carbonyl groups, have been the main subject of numerous investigations.[1–7] It is known that one of the most useful methods to obtain the photodegradable polymer is to incorporate carbonyl groups into copolymers,[8] which are able to absorb UV light and can undergo Norrish type II reaction.

The aim of this work is to synthesize a new photodegradable graft terpolymer-containing carbonyl group by using the same method as studied previously.[9–17] In this study, MVK–EPDM–St (MVES) graft terpolymer was synthesized from the reaction of methyl vinyl ketone (MVK) and styrene (St) onto ethylene–propylene–diene terpolymer (EPDM) under an argon atmosphere using benzoyl peroxide as an initiator. The structure of the synthesized MVES was identified by infrared (IR) spectroscopy. The effects of EPDM contents, mole ratio of MVK to St, reaction time, reaction temperature, and initiator concentration were studied in the graft terpolymerization. The photooxidation, photodegradation, change of molecular weight, tensile, and elongation properties and morphology of the graft terpolymer after UV irradiation were also investigated.

EXPERIMENTAL

Materials

Methyl vinyl ketone (MVK; Aldrich Chem., USA) and styrene (St; Junsei Chem., Japan) were

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Table I Graft Terpolymerization Conditions Used in the Study

Condition	Description			
Monomer concentration				
(MVK + styrene) [mol %]	0.04	0.08	0.12	0.16
BPO concentration (wt %)[a]	0.08	1.5	3.0	5.0
Mole ratio of [MVK]/				
[Styrene]	0.5	1.0	2.0	3.0
Reaction time (h)	24	36	48	72
Reaction temperature (°C)	50	60	70	80

[a] The concentration was based on the total weights containing monomers and EPDM.

purified by standard procedures. Benzoyl peroxide (BPO; Aldrich Chem.) was recrystallized from methanol. Ethylene–propylene–diene terpolymer (EPDM), having ethylidene norborene as a termonomer (ethylene-to-propylene of 50/50 by mol %, ML50; 50,500 $\bar{M}_n$; 102,000 $\bar{M}_w$) was used as received from Aldrich Chemical. Ethyl acetate, tetrahydrofuran (THF), toluene, chloroform, acetone, and n-hexane were distilled prior to use.

Synthesis of Methyl Vinyl Ketone–EPDM–Styrene Graft Terpolymer

A given amount of EPDM was dissolved in 30 mL toluene in a 1-L separable flask equipped with a modified Hopkins cooler, a thermometer, and gas inlet. A mixture of MVK and St at a given mole ratio was dissolved in 20 mL toluene, and the solution was introduced into EPDM solution with required amount of BPO based on total weights containing monomers and EPDM. The reactions were carried out under various experimental conditions, as shown in Table I.

The obtained product was precipitated in excess methanol. The precipitate was collected by filtration and then dried in a vacuum oven until a constant weight. The nongrafted EPDM was removed by extraction using n-hexane in Soxhlet apparatus. The synthesized MVES was isolated from mixtures of several homopolymers and copolymers, such as polystyrene (PS), poly(methyl vinyl ketone) (PMVK), poly(MVK-co-St), poly-(EPDM-g-MVK)(EMVK), and poly(EPDM-g-St) by using ethyl acetate and THF-to-n-hexane (50/50% by volume) mixed solvent, as shown schematically in Figure 1. The total conversion, grafting ratio, and grafting efficiency were estimated using the following equations.[18]

Total conversion (%)

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

Grafting ratio (%)

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

Grafting efficiency (%)

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

Measurements

Infrared Spectroscopy

The structure of graft terpolymer was confirmed by IR spectrophotometer (Perkin–Elmer 1330). The photooxidation trends of the MVES were determined by the changes in the characteristic IR peaks due to carbonyl, vinyl, methyl, and hydroxy groups after UV irradiation by using a Fade-o-Meter at 25°C.

Gel Permeation Chromatography

The average molecular weights of EPDM, PMVK, and MVES were determined by gel permeation chromatography (GPC) (Waters–Water 244) calibrated with polystyrene standards. THF was used as the eluent.
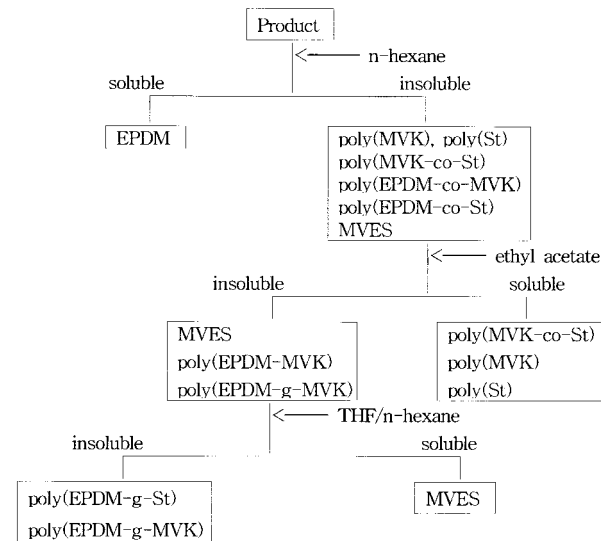

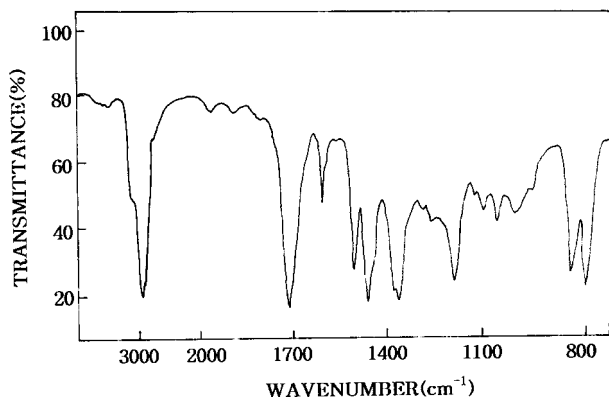**Figure 1** Block diagram of isolation procedure for MVES.

Figure 2 IR spectrum of methyl vinyl ketone–EPDM–styrene (MVES) graft terpolymer.

Photodegradation Properties

The photodegradation was determined by a Fade-o-Meter (Atlas) at 60°C and 65% relative humidity and a color difference meter (ND-101 DP). The prepared film specimens were cast from toluene solutions (approximately 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 a constant weight. The cross-sectional area of the films was 5×10 cm^2, with a thickness of 35 μm. The color difference value (ΔE) of the films after exposing to UV was calculated using the Hunter–Schofield equation.[19]

Tensile Properties

The tensile properties 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

The IR spectrum of the synthesized graft terpolymer, MVES, is shown in Figure 2. The spectrum shows characteristic peaks at 3050 cm^{-1} (aromatic C—H bond; stretching vibration), 2950 cm^{-1} (aliphatic C—H; stretching vibration), 1700 cm^{-1} (C=O bond; stretching vibration), 1465 cm^{-1} (CH$_2$; scissoring), 1375 cm^{-1} (CH$_3$; bending) and 900–790 cm^{-1} (aromatic =C—H bond; out-of-plane vibration), respectively.

Effect of Reaction Conditions on the Graft Terpolymerization

Effect of Mole Ratio

Figure 3 shows the mole ratio effects of MVK to St on the graft terpolymerization onto EPDM. The reaction was carried out in toluene with BPO (3 wt %) as an initiator at 70°C for 48 h. The grafting efficiency had the highest value of 23% at the mole ratio of 1.0, and, thereafter, it leveled off. This effect may be explained by the reactivity ratio of St ($r_1 = 0.29$) and MVK ($r_2 = 0.35$) in the radical copolymerization.[20] This means that the growing radicals consisting of St and MVK attack EPDM more favorably when the mole ratio of St and MVK is unity. When the mole ratio of MVK and St is higher than unity, the formation of homopolymer, PMVK, and graft copolymer, EPDM-*g*-MVK, occurs more easily than that of terpolymer consisting of St, MVK, and EPDM.

Effect of Initiator Concentration

The effect of initiator concentration on the graft terpolymerization is shown in Figure 4. The grafting efficiency increased with increasing initiator concentration up to 3.0 wt %, but, thereafter, it decreased. This result shows that the homopolymers are formed more readily than the graft terpolymer at higher initiator concentration. This is in agreement with Voek's work.[21]

Effect of Reaction Time

The effect of grafting time on the graft terpolymerization is shown in Figure 5. In this case, the reaction was carried out in toluene at 70°C with constant concentrations of EPDM (1.0 g) and BPO
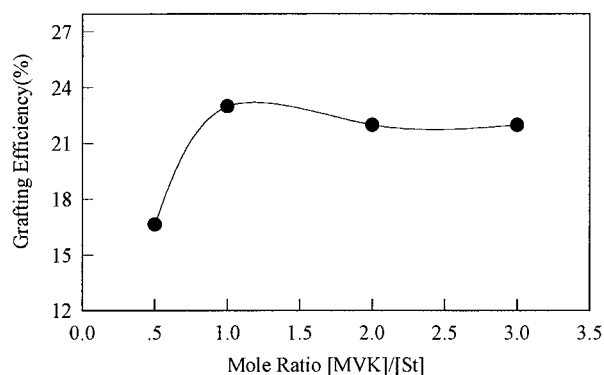

Figure 3 Effect of mole ratio of MVK to St on the graft terpolymerization of MVK and St onto EPDM: reaction temperature, 70°C; reaction time, 48 h; solvent, toluene; BPO, 3 wt %; EPDM, 1.0 g.
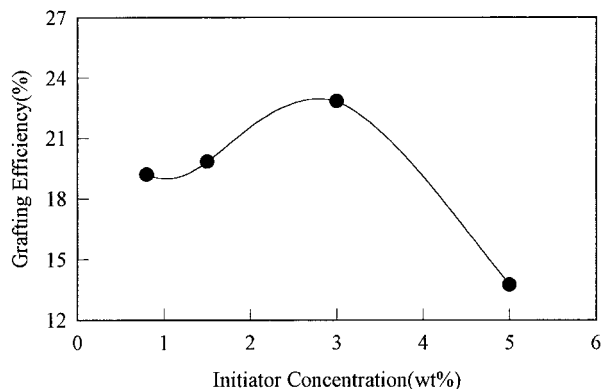
Figure 4 Plot of grafting efficiency versus initiator concentration: [MVK]/[St] = 1.0; reaction temperature, 70°C; solvent, toluene; reaction time, 48 h; amount of initiator is based on the monomers + EPDM (wt %).

Figure 6 Effect of reaction temperature on the graft terpolymerization of MVK and St onto EPDM: [MVK]/[St] = 1.0; reaction time, 48 h; solvent, toluene; BPO, 3 wt %.

(3 wt %). The mole ratio of MVK to St was fixed at 1.0. The grafting efficiency gradually increased with increasing reaction time. This result implies that the growing radicals consisting of MVK and St have more time for graft terpolymer.

Effect of Reaction Temperature

Figure 6 shows the effect of reaction temperature on the graft terpolymerization. The reaction was performed in toluene with 3 wt % of BPO and 1.0 mole ratio of MVK to St for 48 h. The grafting was carried out at 50, 60, 70, and 80°C, respectively. On increasing the temperature, the grafting efficiency passes through a maximum at 70°C. It may be related to the decomposition rate of BPO as the function of temperature.[22,23]

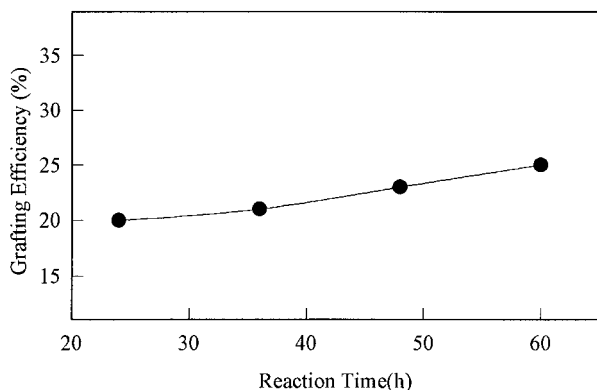### Effect of Monomer Concentration

As shown in Figure 7, the reaction condition was fixed with 1.0 for the ratio of MVK to St and 1.0 g of EPDM, respectively. The grafting efficiency decreased rapidly with increasing monomer concentration up to 0.1, and, thereafter, it maintained at the nearly constant value. The initial decreasing phenomenon means that the formation rates of homopolymers of MVK and St, as well as graft copolymers of MVK or St, onto EPDM are greater than that of the graft terpolymer of MVK and St onto EPDM.

Figure 5 Effect of reaction time on the graft terpolymerization of MVK and St onto EPDM: [MVK]/[St] = 1.0; reaction temperature, 70°C; solvent, toluene; BPO, 3 wt %.

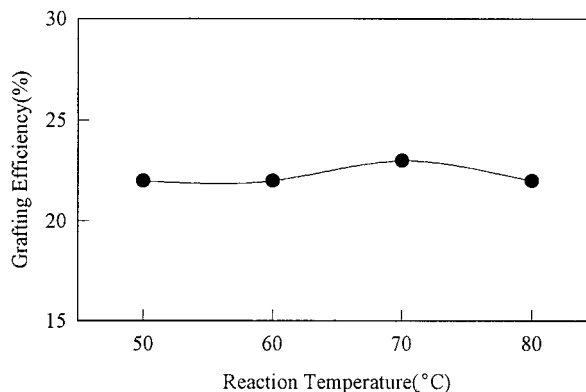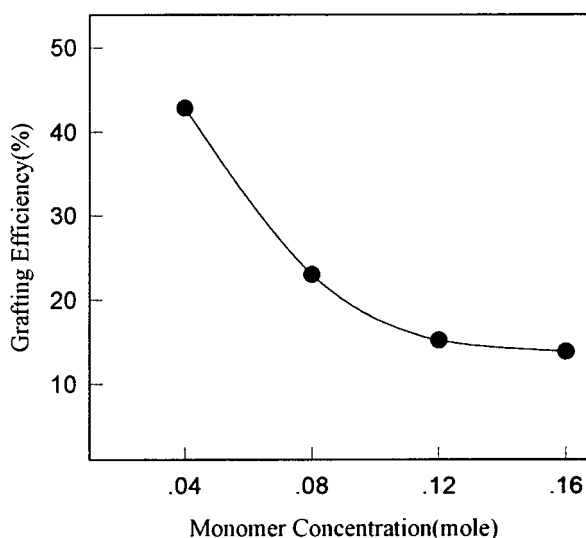**Figure 7** Effect of monomer concentration on the graft terpolymerization of MVK and St onto EPDM: [MVK]/[St] = 1.0; reaction time, 48 h; solvent, toluene; reaction temperature, 70°C; BPO, 3 wt %.

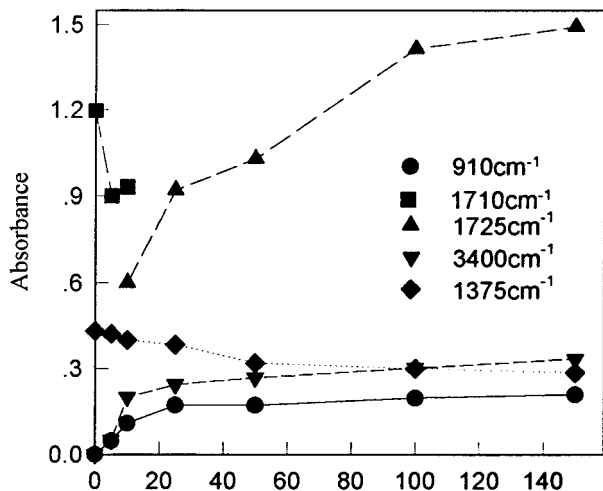**Figure 8** The changes in IR characteristic peaks of MVES on the photooxidation under oxygen atmosphere.

Photodegradation Properties

Photooxidation

The polymers containing carbonyl group have been shown to undergo mainly Norrish type I or II reaction.[24,25] Norrish type II occurs mainly in the molecules having carbonyl group at the side chain bound directly to main chain. Thus, the graft terpolymer after UV irradiation shows new several IR characteristic peaks due to the vinyl, methyl, carbonyl, and hydroxy groups at 910, 1375, 1725, and 3400 cm^{-1}, respectively.

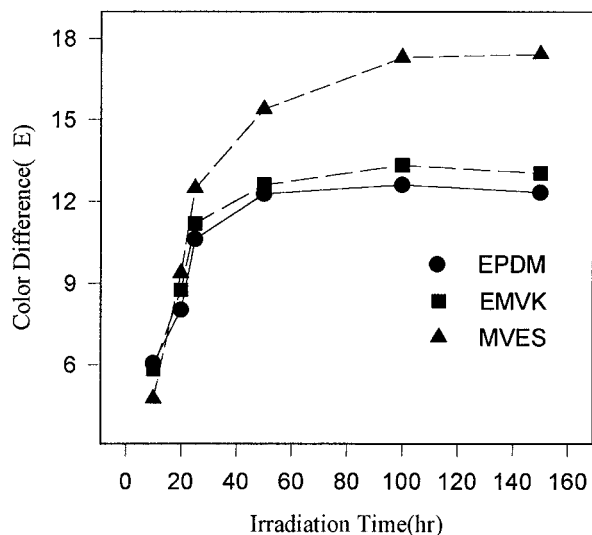The changes of the characteristic peaks in the IR spectrum of photooxidized MVES under oxy-

Figure 9 Plot of color difference versus irradiation time for EPDM, EMVK, and MVES.

Table II The Changes in Average Molecular Weight of MVES

Samples	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
EPDM	50,500	102,000	2.02
PMVK	2,500	14,000	5.60
MVES-0[a]	174,100	492,600	2.83
MVES-300[b]	800	1,500	1.88

[a] MVES-0: before UV irradiation.
[b] MVES-300: after 300 h UV irradiation.

gen atmosphere are shown in Figure 8. Initially, the carbonyl absorption bands decrease at 1710 cm^{-1}, but the new peak begins to increase at 1725 cm^{-1} due to the photooxidation for 20 h. This may be ascribed to a new carbonyl peak, which results from Norrish type II reaction. The hydroxy absorption peak that may have been obtained from reduction of the carbonyl group increases steadily in the region of 3400 cm^{-1} with increasing irradiation time. The IR characteristic peak of the terminal vinyl out-of-plane vibration appears at 910 cm^{-1}, which may be caused by the breakage of polymer due to the Norrish type II reaction.

Photodegradation

The photodegradation was semiquantitatively expressed in terms of color difference (ΔE) with National Beaureau of Standards Unit,[9] as shown in Figure 9. The EPDM, EMVK, and MVES were tested in a Fade-o-Meter in the range from 0 to 150 h. It is shown that MVES synthesized in this study exhibits higher photodegradable property than EPDM and EMVK after 20 h irradiation. The higher photodegradation of MVES may be related to the inherent photodegradable property of carbonyl group in MVK unit and aromatic ring in styrene unit in the graft terpolymer. The photodegradation of all samples showed the same trends after 30 h irradiation as shown in Figure 9.

The Change of Molecular Weight

Polymers containing carbonyl groups can be expected to undergo the dissociation at the main chain by UV irradiation as explained in photooxidation. The average molecular weight and polydispersity indices of MVES before and after UV irradiation, determined by GPC, are shown in Table II together with EPDM and PMVK, in order to compare the average molecular weight of related polymers. The number-average molecular weight
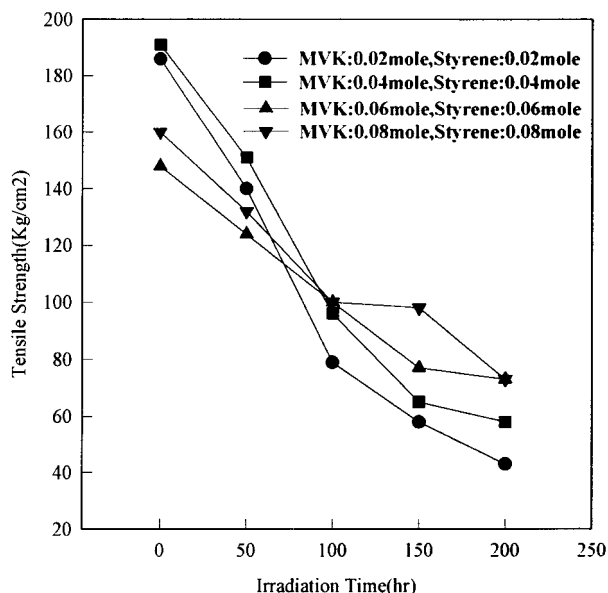
Figure 10 Plot of tensile strength versus irradiation time on the different monomer concentrations.

$(\bar{M}_n)$ of MVES after 300 h irradiation was 800, and it was pale yellow solid. As shown in Table II, the $\bar{M}_n$ of UV irradiated MVES was lower than about 200-fold compared with that of MVES before irradiation.

Physical Properties and Morphology

The tensile strength and elongation at break of MVES containing different monomer concentrations are shown, respectively, in Figures 10 and 11 on varying the UV irradiation time. The physi-
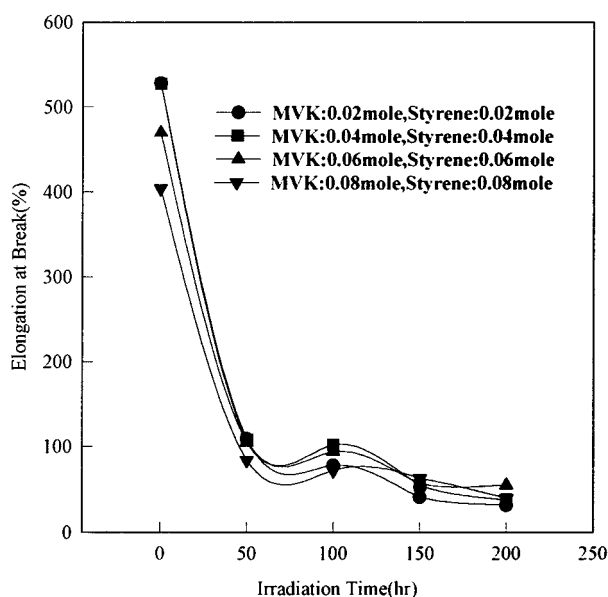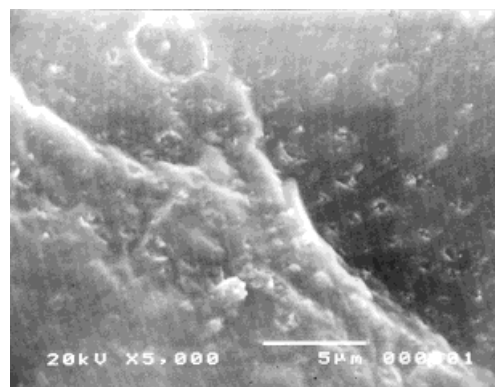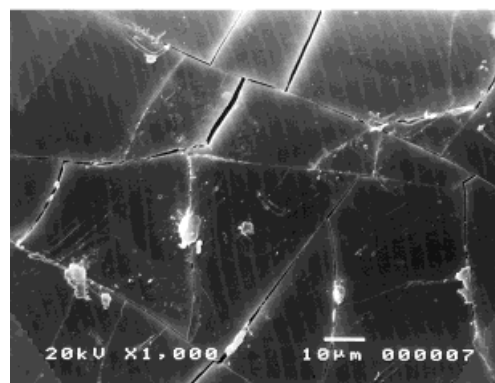

Figure 11 Plot of elongation at break versus irradiation time on the different monomer concentrations.

(A) before UV irradiation (×5,000)

(B) after UV irradiation (×1,000)

Figure 12 Scanning electron micrographs of MVES before and after UV irradiation: (A) before UV irradiation (×5000); (B) after 300 h UV irradiation (×1000).

cal properties of MVES may depend on the contents on monomer units in graft terpolymer. Therefore, the tensile strength of MVES after 100 h irradiation exhibited lower value at the each monomer concentration of 0.02. The elongation properties of all samples decreased rapidly up to 50 h irradiation, thereafter, they slowly decreased. In the morphology of MVES analyzed by scanning electron microscopy (SEM), Figure 12 shows the surface differences of MVES before irradiation (A) and after 300 h irradiation (B). The magnifying power for micrograph [Fig. 12(B)] was adjusted to 1000 times since cracks in the micrograph were too large to observe and phase morphology was not clearly defined when the magnification was 5000. The micrograph of MVES after 300 h irradiation shows the surface crack due to photodegradation as compared with the micrograph of MVES before irradiation. This result was consistent with photooxidation and photodegradation properties.

CONCLUSIONS

MVK–EPDM–St (MVES) graft terpolymer was synthesized from the reaction of methyl vinyl ketone (MVK) and styrene (St) onto EPDM using benzoyl peroxide as an initiator by the solution polymerization technique. The effects of monomer concentration, mole ratio of MVK to St, reaction time, reaction temperature, and initiator concentration were studied in the graft terpolymerization. The various photodegradable properties after UV irradiation were also investigated. The important results are summarized as follows.

1. The grafting efficiency for the graft terpolymerization of MVK and St onto EPDM showed the highest value when the mole ratio of MVK to St, initiator concentration, and reaction temperature were 1, 3.0%, and 70°C, respectively.

2. The grafting efficiency decreased rapidly with increasing monomer concentration up to 0.1, and, thereafter it was maintained at the nearly constant value.

3. The MVES-containing carbonyl group showed new several IR characteristic peaks of the carbonyl, hydroxy, methyl, and vinyl groups by photooxidation via Norrish type II reaction.

4. The photodegradation of MVES tested by Fade-o-Meter showed better property than EPDM and EMVK.

5. The number-average molecular weight of MVES estimated by GPC after UV irradiation was 800 as compared with 174,100 of MVES before irradiation.

6. The tensile strength and elongation at break of MVES after UV irradiation decreased rapidly with increasing irradiation time up to 100 and 50, respectively.

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