

Gamma-Ray Irradiation Effect of Polyethylene on Dimaleimides as a Class of New Multifunctional Monomers

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ABSTRACT: Multifunctional monomers, *m*-xylylenedimaleimide, *p*-phenylenedimaleimide, *m*-phenylenedimaleimide, and *p*-phenylenedimaleimide, all of which have maleimide groups, were synthesized to increase thermal and radiation stabilities. The synthesized multifunctional monomers showed good compatibility with low-density polyethylene (LDPE). Mixtures of LDPE and these multifunctional monomers were irradiated with γ -rays from a Co-60 source at room temperature in a nitrogen atmosphere. The absorbed dose ranged from 0 to 160 KGy. Among these multifunctional monomers, *m*-xylylenedimaleimide was the best

in gel fraction enhancement. Crosslinked LDPE with *m*-xylylenedimaleimide displayed a higher modulus than that of crosslinked LDPE with triallyl cyanurate. For the elongation property, LDPE with *m*-xylylenedimaleimide as a multifunctional monomer showed better results than that with commercial multifunctional monomers such as triallyl cyanurate (TAC) and trimethylol propane triacrylate (TMPTA). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2339–2345, 2003

Key words: polyethylene; irradiation; crosslinking

INTRODUCTION

The crosslinking of polyethylene was initially studied in detail by Charlesby, and many investigations have been reported about the effects of irradiation on the chemical structures and physical properties of polymers.^{1–5} The crosslinking of polymers has been supplanted by peroxide, electron beam, and γ -rays. Radiation can extract hydrogen atoms from the polymer chain and thus generate hydrocarbon radicals. Two of these radicals combine to form an extended polymer molecule. As this process repeats, a polymer network is formed.

The crosslinking process of polyethylene is an important industrial process because a simple method for chemical change, crosslinking, results in a large change in physical properties. By crosslinking a polymer such as polyethylene, a three dimensional network of bonds is formed between polymer chains, which increases the molecular weight. Crosslinked polyethylene may improve the mechanical and chemical properties such as toughness, flexibility, impact resistance, and chemical resistance. The industrial applications of crosslinking by irradiation with γ -rays

have been used extensively for the production of heat-shrinkable polyethylene films and tubes, installation and under-floor heating tubes, foam matrices, and wire and cable in those industries.⁶

γ -Ray irradiation doses do not require catalysts, so there are no catalyst residues in the final product to interfere with physical properties. There is no heat treatment to degrade thermally sensitive components, and the dosage of irradiation can be controlled easily. The main chains may be degraded or crosslinked by the gamma-ray irradiation, with both processes usually taking place concurrently. To enhance the radiation effect of low-density polyethylene (LDPE), it is useful to add multifunctional monomers as crosslinkers. The most effective compounds until now have been shown to be multifunctional acrylates and methacrylates, such as triallyl cyanurate (TAC) and trimethylol propane triacrylate (TMPTA). Although the theoretical possibilities are almost limitless, technical feasibility is controlled by miscibility, compatibility, and melting point of the components during the irradiation phase of technology. These multifunctional monomers have a greater chance to emigrate and sweat out from the blend before the radiation crosslinking. Especially, TAC shows low melting point, which causes a large weight loss because of the high-temperature condition during the film preparation procedure.⁷

In this article we report on our study in which we synthesized four multifunctional monomers contain-

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ing maleimide groups that were thermally stable and had higher melting points than conventional monomers: *m*-xylylenedimaleimide, *p*-phenylenedimaleimide, *p*-phenylenedimaleimide, and *m*-phenylenedimaleimide. The mechanical properties, modulus, and elongation at break of crosslinked LDPE by new multifunctional monomers were investigated.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich. Bicyclo-[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (nadic anhydride) and maleic anhydride were recrystallized from toluene and dichloromethane, respectively. *N,N'*-dimethylacetamide (DMAc) and *N,N'*-dimethylformamide (DMF) were refluxed in the presence of calcium hydride and then distilled under reduced pressure. Styrene was washed with aqueous NaOH to remove inhibitors, then with water, dried for several hours with MgSO₄, and distilled at 25°C under a vacuum. LDPE (*MI* = 0.25, *M_n* = 24,172, Hanwha Co., Daejun, Korea), *m*-xylylenediamine, *m*-phenylenediamine, *p*-phenylenediamine, TAC (triallyl cyanurate), and TMPTA (trimethylol propane triacrylate) were purified by standard methods.

Synthesis

Preparation of *m*-xylylenedimaleimide^{8,9}

A three-necked flask equipped with a dropping funnel and a nitrogen inlet was charged with a solution of maleic anhydride (7.2 g, 73.42 mmol) in DMF (15 mL), which was cooled to 0°C. A solution of *m*-xylylenediamine (5 g, 36.71 mmol) in DMF (15 mL) was added dropwise to the stirred solution at 0°C. The mixture was stirred at 0°C for 1 h and then at ambient temperature for an additional 1 h. To the remaining solution, excess acetic anhydride (15 mL) was added. The mixture was heated at 95°C for 2 h and then was poured over crushed ice. The solid obtained was filtered, washed with water, and dried in a vacuum oven at about 40°C. *m*-Xylylenedimaleimide was obtained as yellowish crystal needles [5 g (23%), mp 130.55°C]

FTIR (KBr), cm⁻¹: 1770, 1710, 1390, 699 (imide); 3106, 1607, 1487 (aromatic); 1611 (—C=C—); 2963 (—CH₂—). ¹H-NMR (DMSO-*d*₆), δ (ppm): 7.28 (m, 4H, C₆H₄), 6.9 [s, 4H, (CH=CH)₂], 4.56 [s, 4H, (CH₂)₂].

Preparation of *p*-phenylenedimaleimide¹⁰

Nadic anhydride (15.18 g, 92.47 mmol) was dissolved in glacial acetic acid (30 mL) in a three-necked flask. The solution was stirred using a magnetic stirrer and was bubbled by nitrogen. The temperature was in-

creased to 120°C. *p*-Phenylenediamine (5 g, 46.23 mmol) was added in small portions, and the solution was refluxed for 8 h. The content was cooled and poured into ice-cold water to precipitate *p*-phenylenedimaleimide. The crude product was purified by recrystallization from glacial acetic acid. *p*-Phenylenedimaleimide was obtained as white crystal needles [3.51 g (73%), mp >350°C]

FTIR (KBr), cm⁻¹: 1771, 1708, 1382, 706 (imide); 3064, 1510, 1456 (aromatic); 1623 (—C=C—); 2990, 2939, 2869 (—CH— and —CH₂—). ¹H-NMR (DMSO-*d*₆), δ (ppm): 7.2 (s, 4H, C₆H₄), 6.2 [s, 4H, (CH=CH)₂], 3.5 [s, 2H, (CH)₂], 1.8 [s, 2H, (CH)₂], 1.6 [s, 4H, (CH₂)₂].

Preparation of *m*-phenylenedimaleimide and *p*-phenylenedimaleimide^{11,12}

m-Phenylenediamine (5 g, 46.23 mmol) or *p*-phenylenediamine (5 g, 46.23 mmol) was placed in a flask containing dry DMAc (15 mL) and fitted with a nitrogen inlet and a calcium chloride drying tube. The clear solution was bubbled by dry nitrogen and was stirred. To the vigorously stirred solution an equimolar amount of maleic anhydride (9.07 g, 92.47 mmol) dissolved in DMAc (15 mL) was added dropwise at room temperature. The mixture was stirred at this temperature for 1 h and then at ambient temperature for an additional 1 h. Cyclodehydration of the amic acid was carried out by adding acetic anhydride (15 mL) and 0.5 wt % sodium acetate to the reaction solution, and the mixture was heated at 90°C for 3 h. The color of the reaction mixture gradually became dark brown. The reaction mixture was subsequently poured over crushed ice. The solid obtained was filtered, washed with water, and dried in a vacuum oven at about 40°C. *m*-Phenylenedimaleimide and *p*-phenylenedimaleimide were obtained as yellow crystal needles [7 (46%) and 6.32 g (51%), mp > 200°C and 199.2°C, respectively].

FTIR (KBr), cm⁻¹: 1778, 1716, 1398, 699 (imide); 3102, 1603, 1456 (aromatic); 1611 (—C=C—). ¹H-NMR (DMSO-*d*₆), δ (ppm): 7.45 (s, 4H, C₆H₄), 7.2 [s, 4H, (CH=CH)₂].

FTIR (KBr), cm⁻¹: 1790, 1716, 1390, 691 (imide); 3095, 1584, 1421 (aromatic); 1607 (—C=C—). ¹H-NMR (DMSO-*d*₆), δ (ppm): 7.61–7.38 (d, 4H, C₆H₄), 7.2 [s, 4H, (CH=CH)₂].

Film preparation

Samples of LDPE with or without multifunctional monomers (2 mmol/100 g of LDPE) were prepared using a Haake rheometer (Haake Rheocord 9000) at 150°C for 5 min. Sheets 0.35 mm thick (ASTM D 1928)

were made by a hot press (Carver 2699 of Fred S. Carver, Inc.) at 150°C. The sheets were immediately cooled by water.

Irradiation

Irradiation was carried out on a UKAEA device (United Kingdom Atomic Authority) in nitrogen by a standard γ -ray from a Co-60 source. The irradiation intensity was 40 KGy h⁻¹ (1 Gy = 10² rad, 1 Mrad h⁻¹ = 2.78 Gy s⁻¹). The absorbed dose ranged from 40 to 160 KGy.

Measurement of gel fraction

The gel fraction was determined by weighing the 0.3-g sample from plaques prepared as above. The samples were extracted by solvent, xylene, that is, refluxing, for 24 h in 200 mL. After refluxing, the extracted samples were dried for 12 h at 40°C in a vacuum oven to constant weight and weighed.

The gel fraction was determined using the following equation:

$$\text{Gel fraction (\%)} = (W/W_0) \times 100$$

where W and W_0 are the weights of the dried sample after and before the extraction procedure, respectively.

Measurement mechanical properties

The modulus and elongation at break were measured with an Instron 4465 using a crosshead speed of 250 mm/min. All specimens were prepared according to the standard of Type IV of ASTM D 638.

Instrumentation

Melting points were determined on a Universal V2.6D TA Instruments differential scanning calorimeter at a heating rate of 10°C/min in a nitrogen atmosphere. FTIR spectra were recorded on a Nicolet Magna-IR 760 spectrometer using KBr pellets. ¹H-NMR was carried out on a Varion UNITY INOVA 300 MHz, using dimethylsulfoxide (DMSO-*d*₆) as a solvent and tetramethylsilane (TMS) as an external standard.

RESULTS AND DISCUSSION

Synthesis and characterization of multifunctional monomers

The bismaleimides were synthesized according to the method used in previous studies.⁸⁻¹² In general, a diamine is condensed with maleic anhydride to give the corresponding bismaleamic acid, which upon elimination of water yielded the bismaleimide. The

chemical structure of synthesized bismaleimides as shown in Figure 1 was confirmed by FTIR and ¹H-NMR.

From FTIR the maleimide structure was confirmed by the characteristic absorption bands appearing at 1770, 1710, 1390, and 700 cm⁻¹. In addition, all bismaleimides exhibited a weak absorption at 1610 cm⁻¹. The aromatic structure was substantiated by the absorptions appearing at about 3100, 1600, and 1450 cm⁻¹. The ¹H-NMR spectra showed a peak at 7.2–7.6 ppm, assigned to the aromatic ring. The ¹H-NMR spectrum was a multiplet in the range of 7.1–7.2 ppm, associated with the olefinic protons. The —CH₂— proton of *m*-xylylenedimaleimide and *p*-phenylenedimaleimide resonated at about 4.56 ppm and 1.6 ppm, respectively.

Compatibility test

To consider the compatibility effect through blending multifunctional monomers with LDPE, multifunctional monomers were dissolved with toluene as an apolar solvent.

As a result, the multifunctional monomers showed good solubility in toluene at 110°C except for *p*-phenylenedimaleimide. *p*-Phenylenedimaleimide and *m*-phenylenedimaleimide formed a yellowish color solution, and *m*-xylylenedimaleimide formed a colorless solution in toluene. For *p*-phenylenedimaleimide, polymer particles were observed in solution. We confirmed the compatibility of multifunctional monomers using the indirect method, a solubility test. Samples of LDPE without and with multifunctional monomers (2 mmol/100 g of LDPE) were prepared in a Haake rheometer at 150°C for 5 min. The mixture of LDPE with *m*-xylylenedimaleimide, *p*-phenylenedimaleimide, or *m*-phenylenedimaleimide was blended clearly, but the mixture of LDPE with *p*-phenylenedimaleimide was blended opaquely, as expected, in a solubility test in toluene.

Gel fraction determination

Generally, the extent of the irradiation-induced crosslinking of polymers can be estimated from gel fraction determination. Figure 2 shows the percentage of the gel formed in LDPE with synthesized multifunctional monomers as a function of the radiation dose. The gel fraction is approximately the same value, about 40% at 120 KGy. In any case, however, it increased more rapidly for LDPE with *m*-xylylenedimaleimide at a low doses. For *p*-phenylenedimaleimide there should be poor compatibility with LDPE; however, it has been reported that the nadimide group was degraded by thermal energy and that the degraded group could then make a high-molecular-weight polymer.¹³ So it showed a good gel fraction despite the poor miscibility.

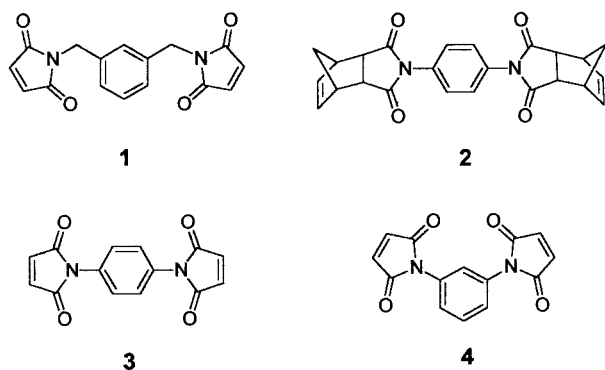


Figure 1 Structure of multifunctional monomers.

It is also known that a vinyl group of a maleimide group has excellent reactivity to the vinyl group of styrene because of the charge transfer effect.¹⁴ Styrene and 1,3-diisopropenylbenzene were also used as the monomer of copolymerization by a charge transfer agent, and the results using these compounds are shown in Figure 3. LDPE mixed with both *m*-xylylenedimaleimide and styrene showed the best gel fraction enhancement among other systems, that is, a multifunctional monomer with a charge transfer agent showed a higher gel fraction than that without a charge transfer agent.

Mechanism of changes in polymer structure

Chemical changes are central to an understanding of the effects of radiation on polymers. Chemical changes on the basis of the explanation of physical changes and the establishment of the exact nature of a chemical change is a prerequisite to an understanding of the reaction mechanism. The most important effects are crosslinking analogous to dimerization and degradation analogous to main-chain scission, respectively. In most polymers one of these processes predominates.⁶ For polyethylene, because crosslinking predominates, the ultimate effect of irradiation will produce a network polymer in which molecules are joined to each other. It is also well known that a multifunctional unsaturated monomer is capable of promoting the crosslinking efficiency of polyethylene by irradiation.¹⁵ It has been reported by Peter and Richard that bismaleimides could crosslink a wide variety of polymers including polyethylene in the presence of peroxide under thermal conditions.¹² The illustrated reaction sequences were proposed as the principal mode of crosslinking by bismaleimides. The initiating free radical is made from polyethylene by γ -ray irradiation. Then polyethylene radical attacks a bismaleimide molecule to give the new free radical. After a chain-transfer reaction to give the maleimide unit, the other maleimide unit proceeds through an analogous sequence, which results in crosslinking.

All multifunctional monomers have two maleimide units, but why does *m*-xylylenedimaleimide provide the highest crosslinking efficiency? We suggest that some other multifunctional monomers have four functional groups for the radical reaction such as in a previous study,¹² whereas *m*-xylylenedimaleimide has eight functional groups for radical reaction, as shown

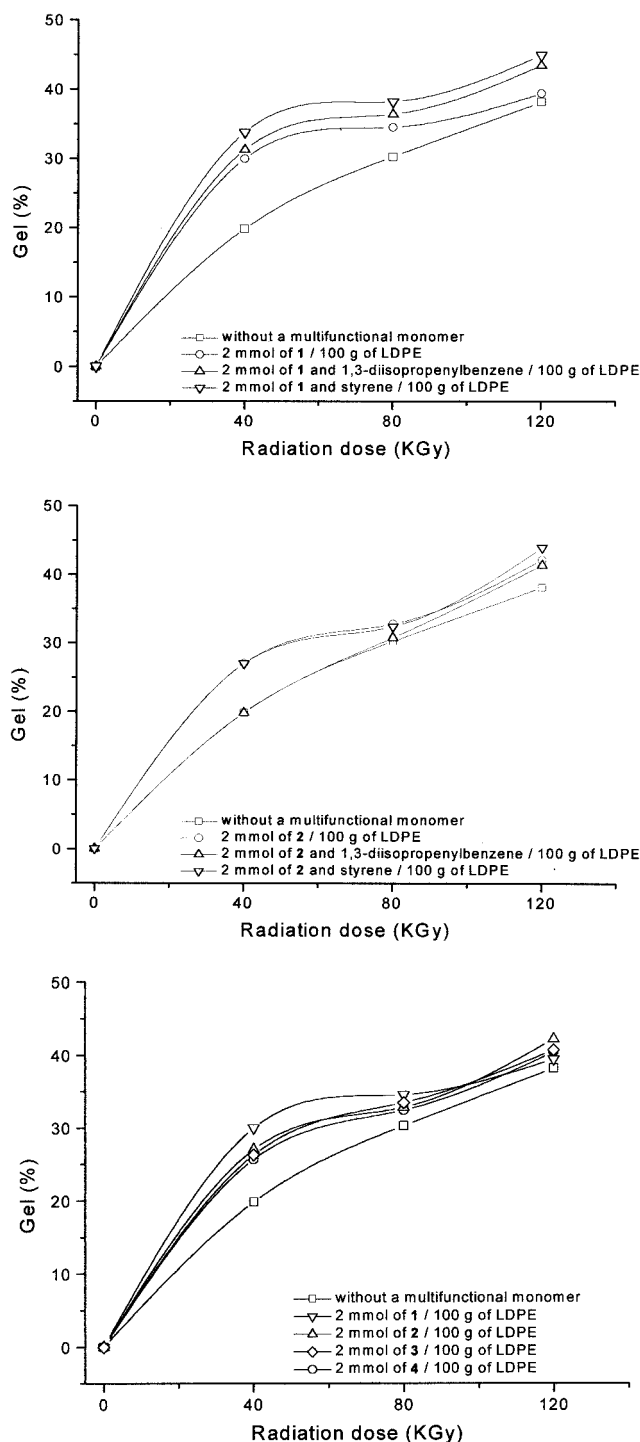


Figure 2 Effect of various multifunctional monomers on gel fraction.

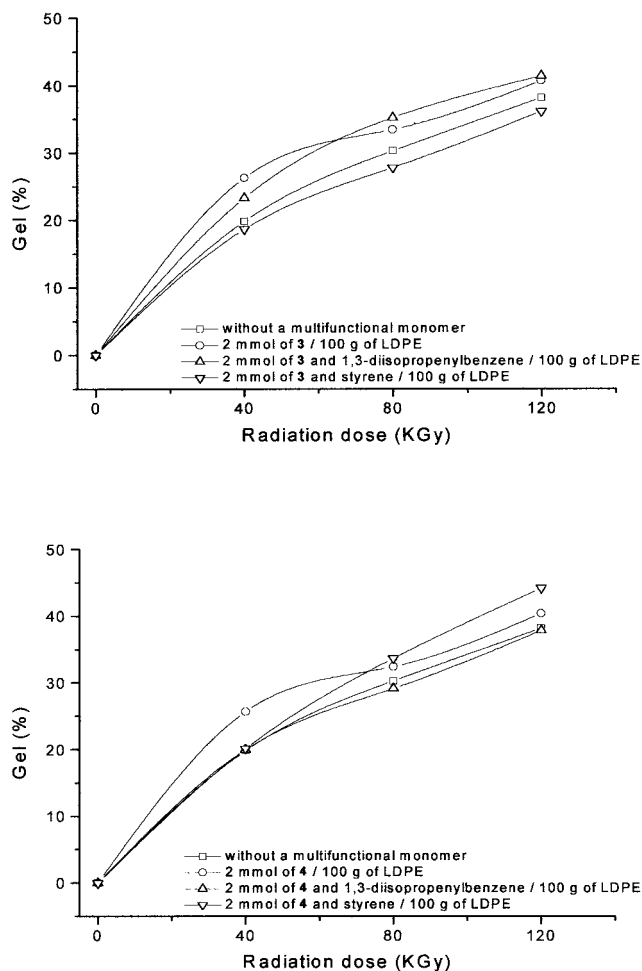
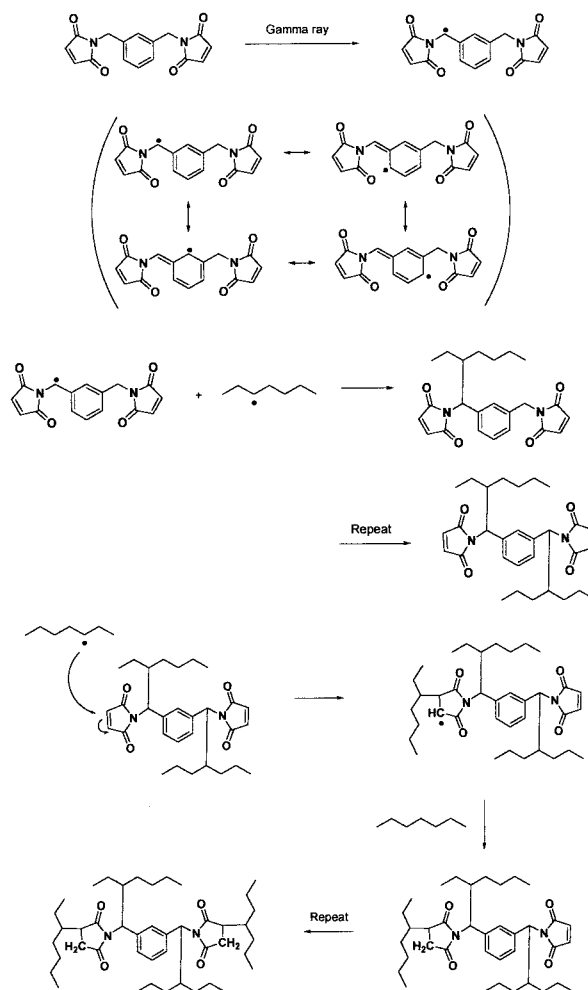


Figure 3 Effect of various multifunctional monomers with charge transfer agent on gel fraction.

in Scheme 1. For *m*-xylylenedimaleimide, a benzylic C—H radical is easily formed by γ -rays, and the formed radical can be stabilized by resonance.¹⁶ Then the formed radical could combine with other formed radicals or the unsaturated site in polyethylene. We think that the network could be formed by repeating this procedure. Moreover, the vinyl groups of maleimides remain as a radical reaction site for the other network. It is well known that the homolytic dissociation bond energy of C—H in polyethylene is 94.5 kcal/mol and that of C—H in benzylic is 85 kcal/mol.¹⁷ Although the maleimide group can affect the homolytic bond dissociation energy of benzylic proton adjacent to the maleimide group, these values indicate that the latter may easily be formed to the radical by γ -rays.

In our work an analysis was done of decreases in the degree of unsaturation, that is, a vinyl group was monitored by FTIR, as shown in Figure 4. Vinyl groups have transmittance at both 1610 and 890 cm^{-1} , but only the transmittance at 890 cm^{-1} was used in this study as it is not possible to measure 1610 cm^{-1} because of an overlap



Scheme 1 Proposed mechanism of crosslinking with *m*-xylylenedimaleimide and polyethylene.

from the aromatic transmittance. It was noticed that the vinyl group of maleimide participated in the crosslinking reaction in the polymer.

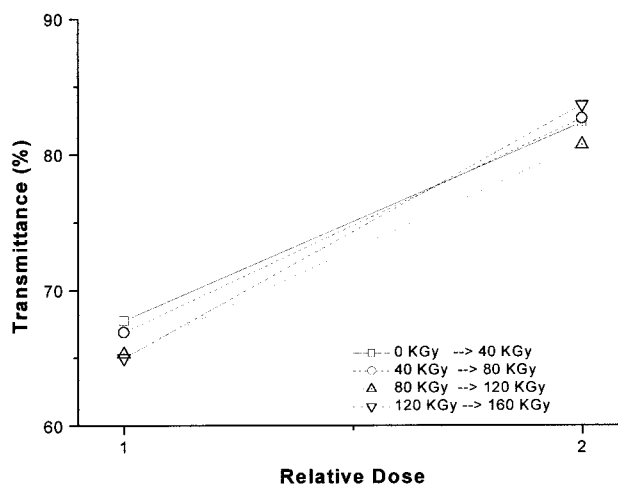


Figure 4 Effect of relative dose of residual monomer unsaturation for *m*-xylylenedimaleimide.

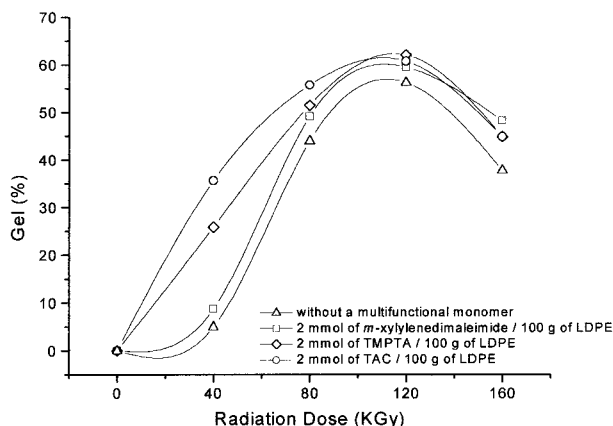


Figure 5 Effect of LDPE with *m*-xylylenedimaleimide and conventional multifunctional monomers on gel fraction.

Comparison of *m*-xylylenedimaleimide with conventional multifunctional monomers on LDPE

Figure 5 is a plot of the gel fraction of the LDPE with various multifunctional monomers irradiated with γ -rays under a nitrogen atmosphere at room temperature with respect to the irradiation dose. The gel fraction was approximately the same in every case, and the maximum value of the gel fraction obtained was the same up to 120 KGy. However, it increased more rapidly for TMPTA at a dose lower than 40 KGy.

Modulus is plotted as a function of the irradiation dose for LDPE with *m*-xylylenedimaleimide and conventional multifunctional monomers, as shown in Figure 6. For LDPE with TMPTA, a maximum value of modulus occurred at 120 KGy. However, the others showed a maximum value at 90 KGy and had a lower modulus value than the system using TMPTA. In general, the modulus for LDPE increased with an increase in irradiation dose up to 80 KGy.

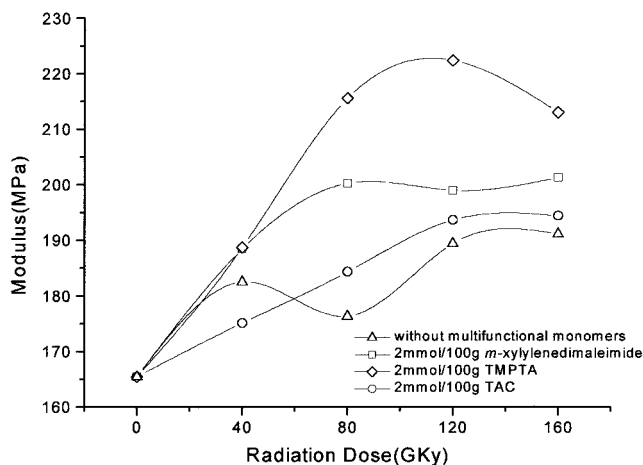


Figure 6 Effect of LDPE with *m*-xylylenedimaleimide and conventional multifunctional monomers on modulus.

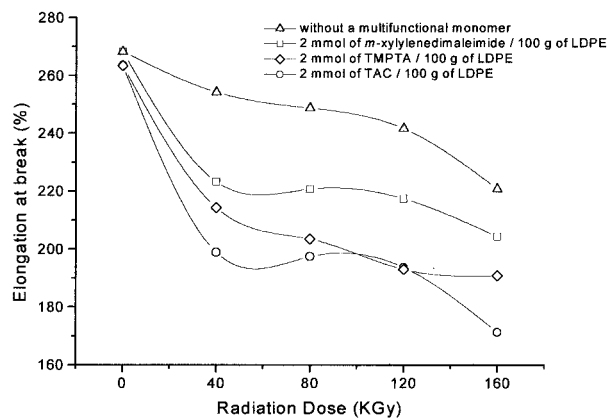


Figure 7 Effect of LDPE with *m*-xylylenedimaleimide and conventional multifunctional monomers on elongation.

The plots of the elongations at break versus the irradiation dose for the blends with various multifunctional monomers are shown in Figure 7. As the polymer chains were formed into a network, their freedom of movement was decreased. As the number of crosslinks between polymer chains increased, the chains could not move relative to each other as easily, and the elongation at yield decreased.^{15,18} Because the elongation was dependent on the crosslink density, the monomer efficiency followed the same trend as gel fraction increased. It was found that increasing the radiation dose caused an increase in the gel fraction and decrease in the elongation of the crosslinked LDPE. It is known that crosslinked LDPE, which is used in the cable materials of nuclear power plants, decreases elongation property by exposure to irradiation or aging. Because of this disadvantage, applicable crosslinked LDPE is required for the higher value of elongation at break. In this work crosslinked LDPE with *m*-xylylenedimaleimide showed more improved property in elongation at break than that did commercial multifunctional monomers such as TAC and TMPTA.

CONCLUSION

In this work a few multifunctional monomers with an maleimide group were synthesized, and they showed good compatibility with LDPE. Among them, crosslinked LDPE with *m*-xylylenedimaleimide provided the highest enhancement gel fraction by irradiation of γ -rays. It also had the same gel fraction (about 60% at 120 KGy) in comparison with crosslinked LDPE containing conventional multifunctional monomers. But the results of mechanical properties, modulus, and elongation at break exhibited the same trend as in previous studies. Moreover, the crosslinked LDPE with *m*-xylylenedimaleimide showed better modulus than TAC and better elongation at break than that of TAC and TMPTA.

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