

Photocrosslinking of an Ethylene–Propylene–Diene Terpolymer and the Characterization of Its Structure and Mechanical Properties

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ABSTRACT: An ethylene–propylene–diene terpolymer (EPDM) was photocrosslinked under UV irradiation with benzil dimethyl ketal (BDK) as a photoinitiator and trimethylolpropane triacrylate (TMPTA) as a crosslinker. The efficiency of the photoinitiated crosslinking system EPDM–BDK–TMPTA, various factors affecting the crosslinking process (the photoinitiator and crosslinker and their concentrations, the irradiation time, the temperature, the atmosphere and UV-light intensity, and the depth of the UV-light penetration), and the mechanical properties of photocrosslinked EPDM were examined extensively through the determination of the gel contents, infrared spectra, and mechanical measurements. EPDM samples 3 mm thick were easily crosslinked with a gel content of about 90% after 30 s of UV

irradiation under optimum conditions. The photoinitiating system of a suitable initiator combined with a multifunctional crosslinker such as BDK–TMPTA enhanced the efficiency of the photocrosslinking reaction, especially by increasing the initial rate of crosslinking. The gel content of photocrosslinked EPDM, which was determined by the content of diene in EPDM, the depth of the UV-light penetration, and the light intensity, played a key role in increasing the mechanical properties of the photocrosslinked samples in this work. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1837–1845, 2004

Key words: crosslinking; mechanical properties; structure

INTRODUCTION

In recent years, using reactive extrusion to prepare polypropylene (PP) and ethylene–propylene–diene terpolymer (EPDM) thermoplastic elastomers (TPEs) has attracted a lot of attention.^{1–7} The most important aspect of reactive extrusion is the crosslinking of the EPDM component, which imparts toughness to the PP matrix and increases the tensile strength of TPE. Moreover, crosslinked EPDM can be easily sheared into small particles and dispersed homogeneously. However, the crosslinking process of EPDM always accompanies the degradation of the PP matrix with the thermal chemical initiation method; this debases the properties of TPEs. In a previous study,⁸ we also found this problem with the dynamic photocrosslinking method. To obtain a better solution, we must focus on the crosslinking of EPDM.

The crosslinking of EPDM can be divided into three types according to the preparation process: high-energy irradiation (⁶⁰Co γ -rays or an accelerated electron beam),⁹ thermal chemical initiation (the peroxide method),¹⁰ and photocrosslinking preparation.^{11–13}

The application of high-energy irradiation is limited because of complex equipment and operation safety. Thermal chemical initiation is a traditional method, but it is not convenient for controlling the crosslinking degree. UV irradiation for the photocrosslinking of EPDM is a promising method, as suggested by Rånby and coworkers^{14,15} in recent years. However, few studies have been reported on the photocrosslinking of EPDM. Hilborn and coworkers^{10–12} examined the photocrosslinking mechanism and relative model compounds with electron spin resonance.^{10–12} The optimum photocrosslinking conditions for EPDM are absent, especially for PP/EPDM TPEs. In this work, we focused on the photocrosslinking reaction parameters and optimum conditions of EPDM and the corresponding mechanical properties of photocrosslinked EPDM. The photooxidation and thermooxidation degradation of photocrosslinked EPDM will be presented in a series of forthcoming articles.

EXPERIMENTAL

Materials

Two kinds of EPDMs were used in this work: EPDM 4045 (Mitsui Petrochemical Industries Co., Ltd., Japan) and EPDM 4770 (DuPont Dow Elastomer Co., Ltd.,

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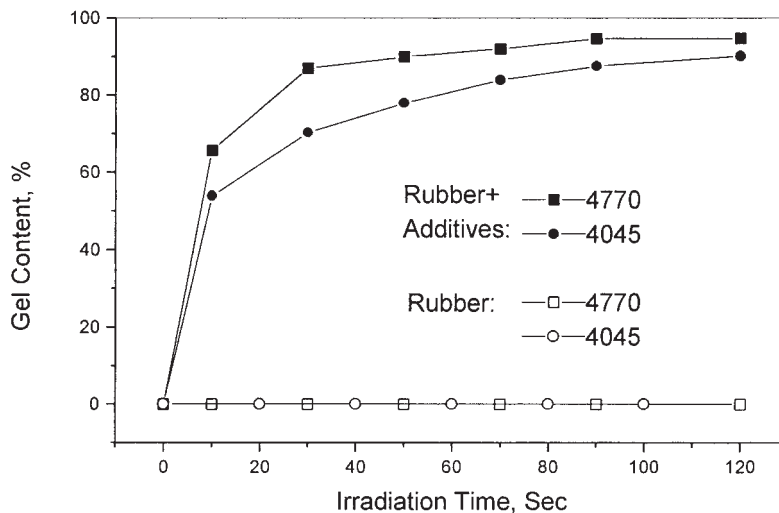


Figure 1 Kinetics of gel formation during the photocrosslinking of EPDM 4770 and EPDM 4045 with 1 wt % BDK and 1 wt % TMPTA.

United States). The ethylene and diene contents were 52 and 3 wt % and 70 and 5 wt % for EPDM 4045 and EPDM 4770, respectively. The diene used in this work was 2-ethylidene-5-norbornene. Benzophenone (BP), from Shanghai First Reagent Factory, 4-chlorobenzophenone, from Fluka AG (Switzerland), 4,4'-dichlorobenzophenone, from Novakemi AB (Belgium), and benzil dimethyl ketal (BDK; Irgacure184, Irgacure 2959, and Irgacure 907), from Ciba-Geigy (Switzerland), were used as photoinitiators. Triallyl isocyanurate (TAIC), from the Anhui Institute of Chemical Engineering (China), and pentaerythritol triacrylate (PETA), neopentylglycol diacrylate (NPGDA), and trimethylolpropane triacrylate (TMPTA), from UCB (Belgium), were used as crosslinking agents.

Sample preparation

All the samples (50-g batches of EPDM with given amounts of the photoinitiators and crosslinking agent) were mixed for 10 min at 150°C with an XSS-300 rheomixer. After being mixed, the samples were hot-pressed into sheets of suitable thicknesses for 5 min at 150°C with a Carver press. The sheet thickness was controlled with frames of different standard thicknesses.

UV irradiation

The samples were UV-irradiated in a UV-curing device constructed in our laboratory. The UV lamp, a

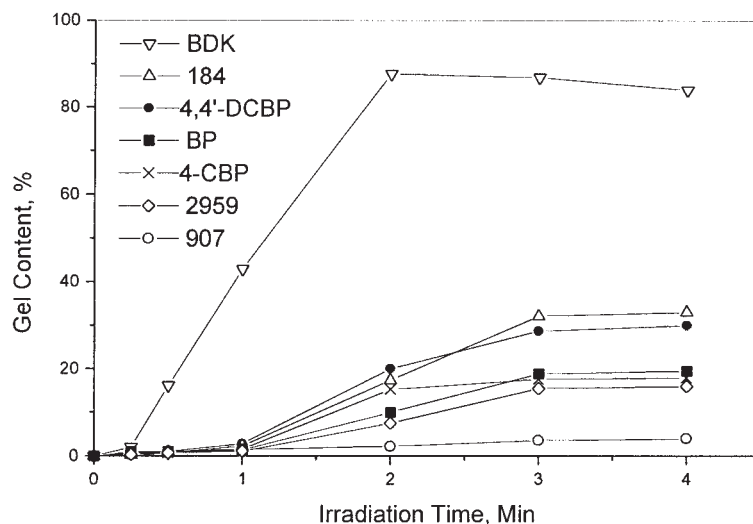


Figure 2 Comparison of the photocrosslinking of EPDM 4770 with various initiators (1 wt %).

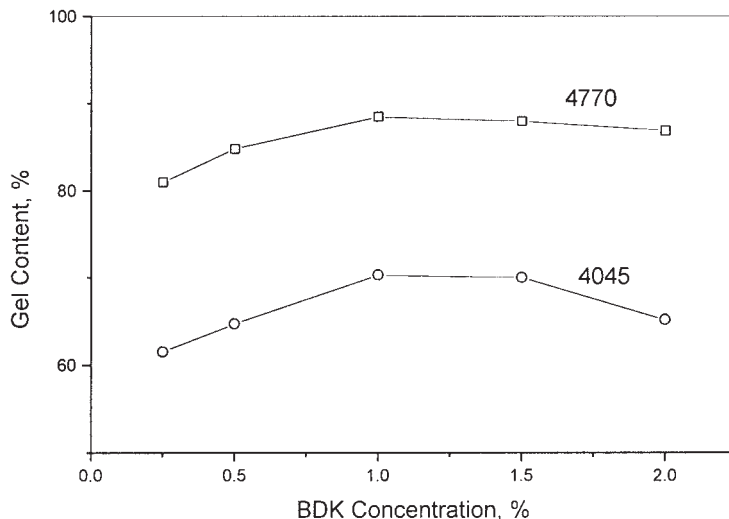


Figure 3 Effect of the initiator concentration on the photocrosslinking of EPDM 4770 and 4045 with 1 wt % TMPTA and 30 s of irradiation.

Philips HPM 15 (2 kW), was used at a distance of 10 cm from the surface of each sample. The irradiation of the samples, usually with 1 wt % BDK and 1 wt % TMPTA, was carried out at 150°C under an N₂ flow rate of 1 L/min. The sample thickness was 3 mm unless stated otherwise.

After the extraction, the basket was washed with acetone. After being dried in a vacuum desiccator at about 70°C to a constant weight, the insoluble residue (w_2) was weighed. The average gel content (wt %) in the test was calculated as $100(w_2/w_1)$. Usually, three samples were analyzed to determine the average gel content for a given set of irradiation conditions.

Gel content measurements

After being irradiated, the samples were cut into thin slices and placed in a basket made of a 200-mesh stainless steel net. The gel content of the samples was determined through the extraction of the irradiated samples (w_1) in the basket for 48 h with boiling cyclohexane stabilized by 0.2% Tinuvin 144 (an antioxidant) and with bubbling N₂ to prevent oxidation. The solvent was renewed after the first 24 h of extraction.

Mechanical property measurements

The tensile properties were measured with a universal testing machine (DCS5000, Shimadzu) at different temperatures with an oven. The crosshead speed was 100 mm/min. Dumbbell-shaped specimens were prepared according to ASTM D 412-87. Thermomechanical curves were obtained on a thermomechanical analyzer produced by Chengde (China); samples ap-

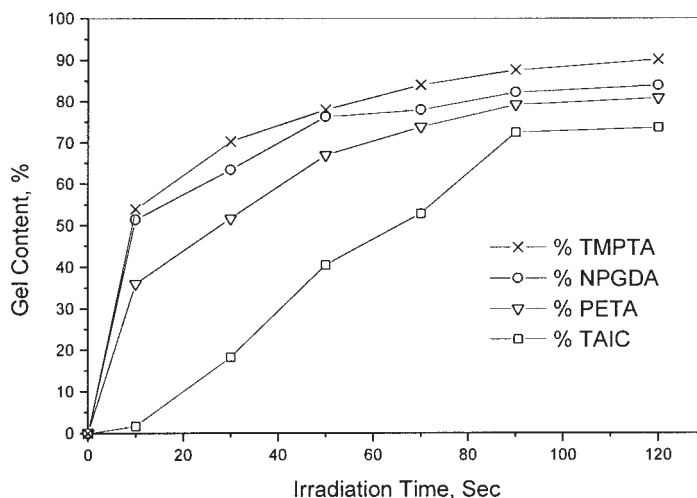


Figure 4 Effect of the crosslinker on the photocrosslinking of EPDM 4045 with 1 wt % BDK and 1 wt % crosslinker.

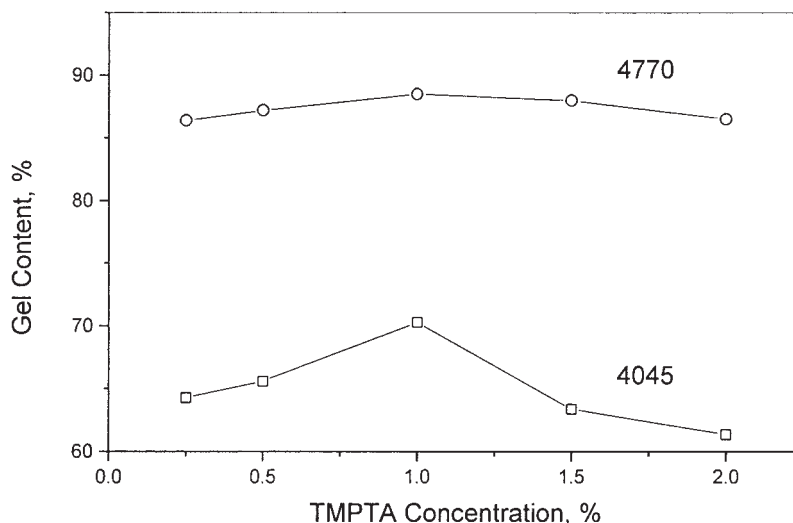


Figure 5 Effect of the crosslinker concentration on the photocrosslinking of EPDM 4770 and 4045 with 1 wt % BDK and 30 s of irradiation.

proximately 3 mm thick were pressed by a cylindrical weight of 500 g. The deformation was recorded as the temperature increased at 10°C/min.

Infrared (IR) spectroscopy

IR spectra were recorded on a Nicolet Magna IR 750 spectrometer.

RESULTS AND DISCUSSION

Characteristics of photocrosslinking

The gel contents of photocrosslinked EPDM 4045 and EPDM 4770 are shown in Figure 1. In the presence of BDK and TMPTA (1 wt % each), the gel contents of the

samples rapidly increased after a short irradiation time and then increased gradually. The gel contents were greater than 80 and 90%, respectively, after irradiation for 70 s. This shows that the BDK-TMPTA photoinitiating system was very efficient.

The kinetic characteristics of the crosslinking of the two EPDM samples had the same features: (1) the initial rate of crosslinking during the first 30 s was very fast; (2) after 30 s, the rate decreased to a certain level; and (3) the final gel content was almost constant. However, a difference in the crosslinking rate existed between 4045 and 4770, and the difference in the gel contents of the samples was attributed mainly to the different contents of diene in the molecular structure of EPDM. A large amount of diene provided more

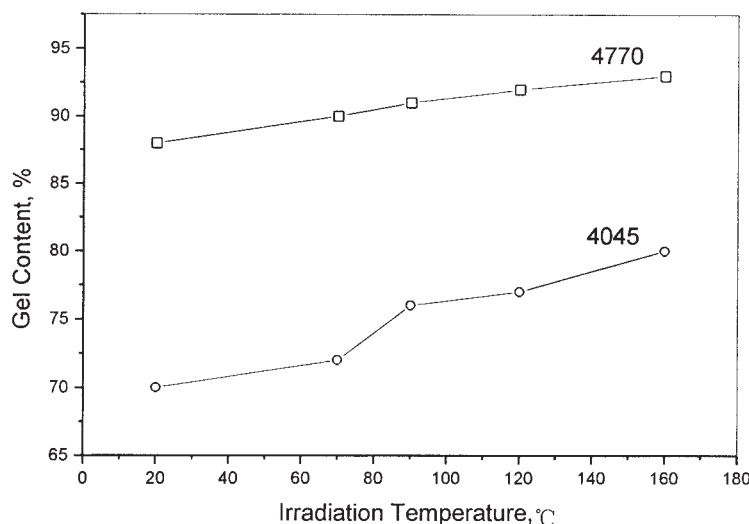


Figure 6 Influence of the irradiation temperature on the crosslinking rate for EPDM 4045 and 4770.

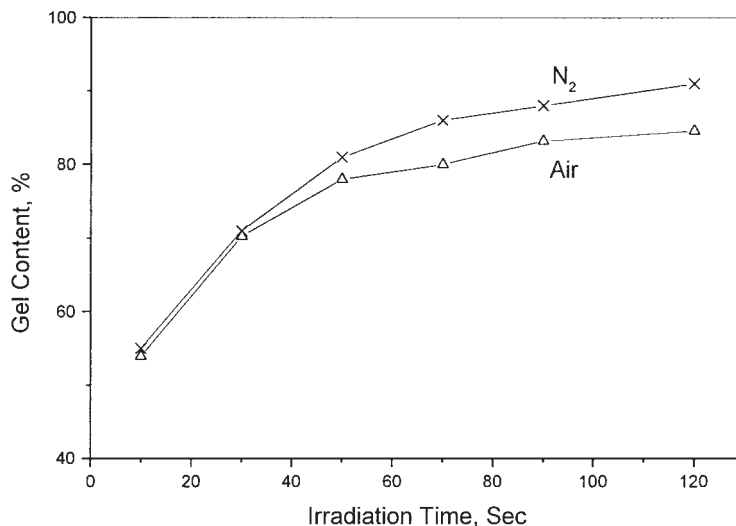


Figure 7 Influence of the irradiation atmosphere on the crosslinking rate of EPDM 4045.

unsaturated sites for the crosslinking reaction. This explained why EPDM 4470 had a higher rate and a higher gel content than EPDM 4045.

Reaction conditions

Photoinitiators

Seven different photoinitiators are used to study the effect on the crosslinking reaction of EPDM, as shown in Figure 2. Those photoinitiators were divided into two groups: (1) those that underwent photofragmentation (e.g., BDK, Irgacure184, Irgacure 2959, and Irgacure 907) and (2) those that abstracted hydrogen in the excited state (e.g., BP and its derivatives). Figure 2 compares their photoinitiating efficiencies for EPDM 4045 with 1 wt % initiator and without a crosslinker.

Apparently, the system with BDK had the highest photoinitiating efficiency and gel content.

The data in Figure 3 show the dependence of the gel content on the concentration of BDK for two EPDM samples. The optimum concentration of BDK was about 1 wt % with respect to EPDM for both systems. A further increase in the amount of the initiator did not increase the gel content. The gel content of EPDM 4045 even decreased with 2 wt % BDK. This was due to the fact that some ketyl radicals, formed by photoinitiators, combined with polymer radicals and prevented crosslinking at higher concentrations.

Crosslinkers

The addition of a multifunctional crosslinker greatly accelerated the crosslinking process. Figure 4 shows

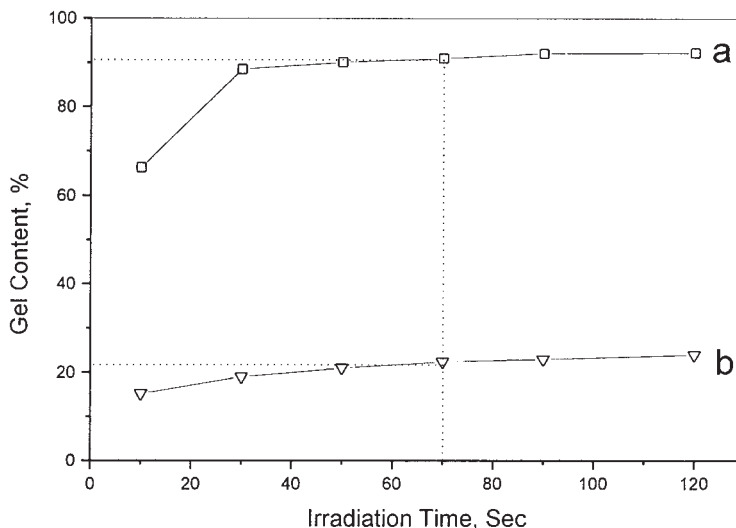


Figure 8 Crosslinking processes of EPDM 4770 irradiated with different light intensities: (a) 40 and (b) 20 mW/cm².

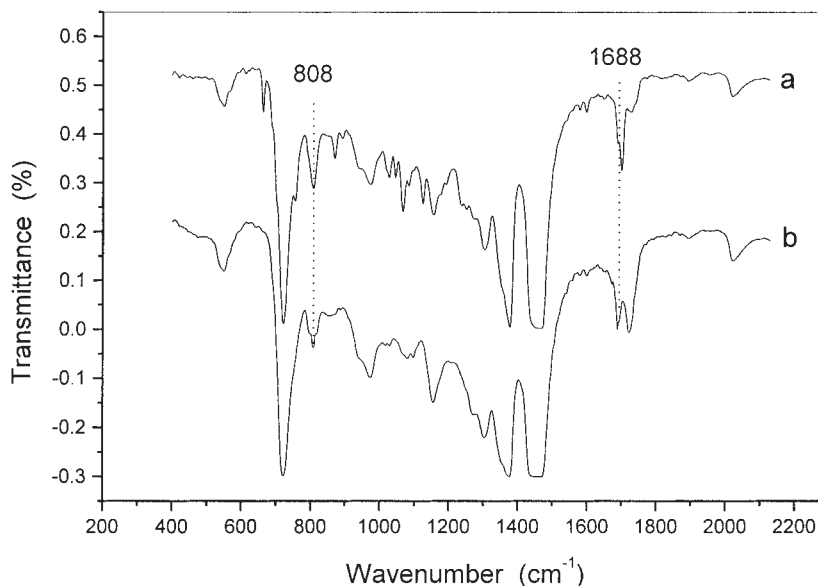


Figure 9 FTIR spectra of EPDM 4045 (a) before and (b) after photocrosslinking.

the gel content of EPDM 4045 with different amounts of crosslinkers. TMPTA was the most efficient. This was due to its three double bonds per molecule, which resulted in a higher crosslinking density in a short irradiation time. The effect of the TMPTA concentration on the gel content is shown in Figure 5. The results demonstrate that 1 wt % TMPTA was an optimal amount for gel formation. The further addition of TMPTA had only a minor effect. Even at 2 wt % TMPTA, the gel contents of 4770 and 4045 decreased. This situation suggests that excessive TMPTA formed a low-molecular-weight homopolymer and was extracted by toluene. Therefore, the TMPTA homopolymer reduced crosslinking between EPDM and

TMPTA, and this caused a reduction of the gel content.

Irradiation temperature

The irradiation was performed from 20 to 160°C, and the results are shown in Figure 6. The gel content increased with the temperature because there was more free volume in EPDM as the temperature rose. The free volume provided sufficient space for the motion of relatively long segments of the polymer chains. The molecular mobility, therefore, made the separation of the initiator radicals and the generation of macroradicals easy, and this enhanced the crosslink-

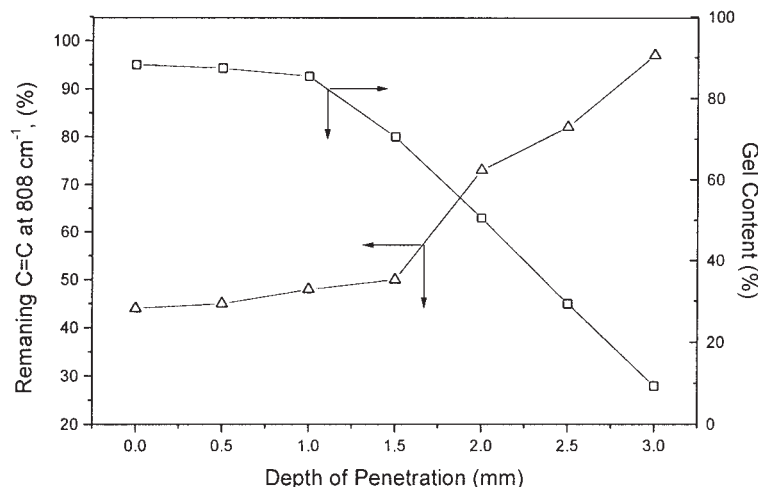


Figure 10 Double-bond conversion and gel content with the depth of light penetration (microtome sectioning of photocrosslinked EPDM 4770).

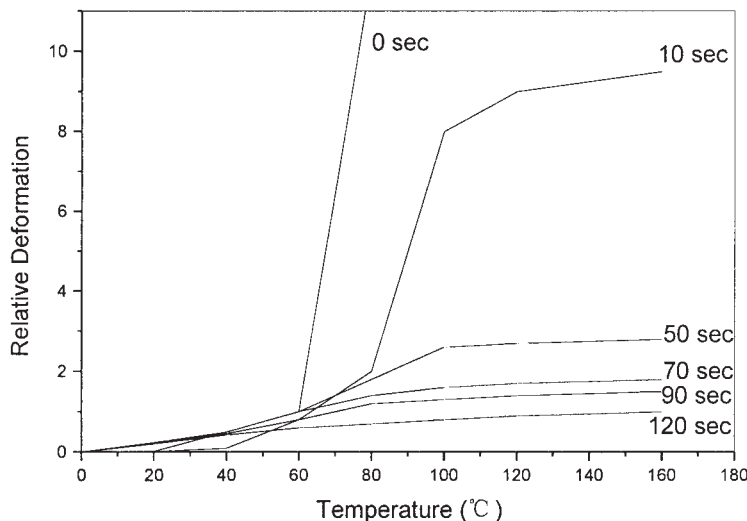


Figure 11 Thermal deformation curves of photocrosslinked EPDM 4770 after increasing irradiation times.

ing of the polymer. However, below the glass-transition temperature of EPDM, the efficiency of the reaction was extensively reduced, and no gel content could be determined because the molecular motion was largely restricted according to experimental data reported by Bousquet et al.¹⁶

Irradiation atmosphere

The effect of the irradiation atmosphere (N₂ or air) on gel formation at a flow rate of 1 L/min through a reactor is shown in Figure 7. Although oxygen did suppress the crosslinking process, the effect was rather small (a few percent in the gel concentration) during a short irradiation time. This was understand-

able because the samples were rather thick (3 mm) and the solubility of oxygen in EPDM was very low. However, when the irradiation time was prolonged beyond 1 min, the gel content for EPDM 4045 irradiated in air was lower than the gel content for EPDM 4045 irradiated in N₂.

Surface oxidation took place in crosslinked EPDM 4045 during irradiation lasting more than 30 s. The surface of an extracted sample appeared ropy.

UV intensity

An alteration in the UV-light intensity was achieved through a change in the distance between the lamp and the sample. The light intensity at different dis-

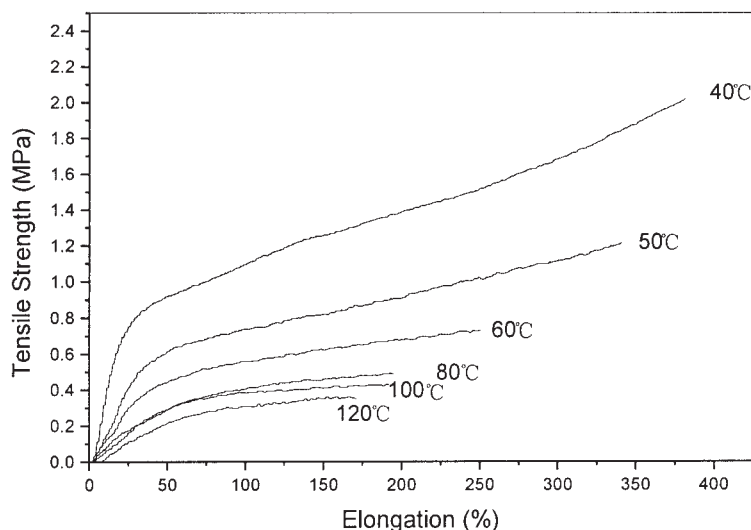


Figure 12 Tensile strength and elongation at break for crosslinked 4770 samples with 90 s of irradiation at different temperatures.

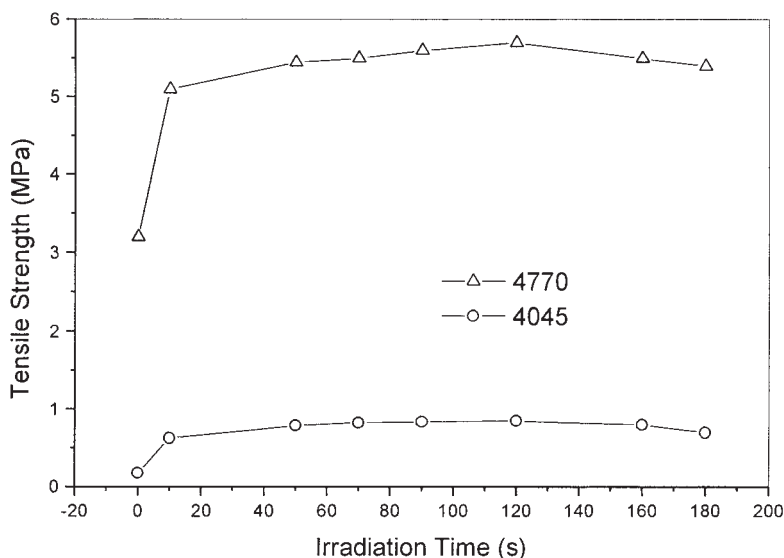


Figure 13 Tensile strength of photocrosslinked EPDM versus the irradiation time.

tances was measured with an actinometer (UV Irradiance Meter A, Photoelectric Instrument Factory of Beijing Normal University). EPDM 4045, containing 1 wt % BDK and 1 wt % TMPTA, were crosslinked under different light intensities.

Figure 8 shows that the gel content of the sample was 90% with the irradiation of an HPM 15 lamp at a distance of 10 cm for 70 s. However, the light intensity decreased to half its initial value when the lamp distance from the sample increase; this resulted in a gel concentration of 23%. This means that the crosslinking rate was proportional to the second order of the light intensity and suggests that a high-power output lamp is important for attempts at increasing the crosslinking rate in industrial applications.

Crosslinked EPDM analyzed by IR spectroscopy

IR spectra of the original EPDM 4045 elastomer and a crosslinked sample without TMPTA for 30 s are shown in Figure 9. The 1688-cm^{-1} peak can be clearly seen before and after crosslinking, but it was obscured by photoinitiator residues or byproducts from the photoinitiator after crosslinking. The 808-cm^{-1} peak was reduced by more than half of its original value.

The gel content and double-bond conversion in different layers of EPDM 4770 are shown in Figure 10. A continuous decrease in the gel content was found in layers from the top down to 3 mm, especially within the range of 1–3 mm; this was due to the UV light being shielded by the elastomer as the depth of pen-

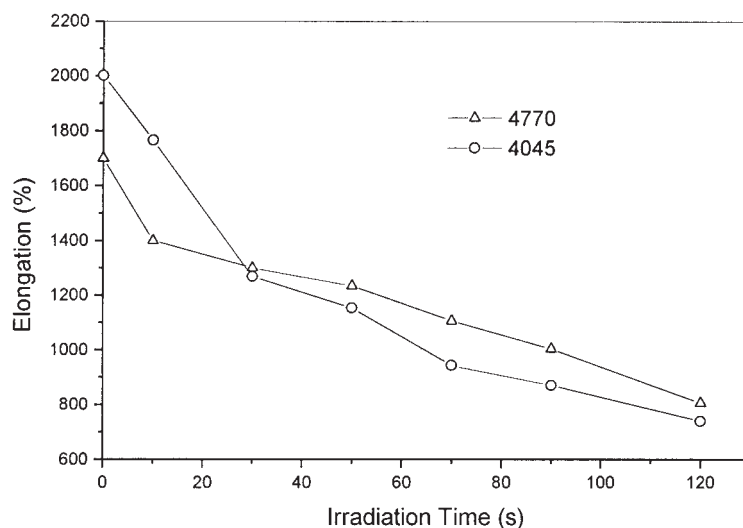


Figure 14 Elongation at break of photocrosslinked EPDM versus the irradiation time.

etration increased. This situation was also proved by the double-bond conversion of EPDM in different layers. The remaining C=C at 808 cm^{-1} increased as the depth of penetration increased because a higher double-bond conversion yielded a higher value of the gel content for the formation of networks between molecules of EPDM.

Physical properties

Figure 11 demonstrates that the process of photocrosslinking was so efficient that only 10 s of irradiation made the EPDM rubber resistant to thermal deformation to some degree. As the irradiation time increased, the change in the mechanical deformation gradually became smaller. As a result, the mechanically stable temperature could easily be increased from 60 to at least 140°C by photocrosslinking.

Figure 12 shows the tensile-strength/elongation data of irradiated EPDM 4770 samples for 90 s at different temperatures; the temperature had a significant effect on the mechanical properties of the samples. When the temperature increased from 40 to 120°C , the tensile strength and elongation at break dropped sharply. It may be that the relaxation of the chains was effective at high temperatures and easily broken at the same time.

Figure 13 shows the relationship between the tensile strength (at break) of the samples and the irradiation time at room temperature. During the first stage of photocrosslinking, the strength increased with the irradiation time. However, if the sample was overirradiated (e.g., $>120\text{ s}$), the tensile strength decreased as a result of degradation in both EPDM samples.

The elongation at break decreased with increasing irradiation time (Fig. 14) because crosslinking made the structure of the macromolecular network more rigid.

CONCLUSIONS

EPDM sheets 3 mm thick were photocrosslinked at a high crosslinking rate. A sample with BDK and TMPTA was most effective in enhancing the crosslinking rate. The irradiation temperature and UV-light intensity were crucially important for increasing the photocrosslinking of the thick EPDM sheets. The chemical composition of EPDM determined the photocrosslinking process of the crosslinked samples and their properties, including the gel content, elongation, and tensile strength. The experimental results showed that the EPDM irradiation was dependent on the thickness of the samples. Crosslinking EPDM increased the capacity for thermodeformation and the tensile strength but reduced the elongation at break.

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