Effects of Gamma Radiation on Properties of Halogen-Free Flame Retardant EPDM-PVMQ Rubber Blends

Qiaoe Wang, Hong Ye

School of Chemical and Environmental Engineering, Beijing Technology and Business University, Beijing 100048, China

Received 12 June 2010; accepted 9 August 2010
DOI 10.1002/app.33152
Published online 30 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, the effects of gamma radiation on properties of ethylene–propylene–diene monomer (EPDM) and its blends with phenyl vinyl methyl silicon rubber (PVMQ) were studied. The samples were irradiated with the dose rate of 171.7 Gy/min, and the total dose was up to 500 kGy. Mechanical properties, electrical insulation, limiting oxygen index (LOI), crosslink density, and ATR-FTIR spectroscopy of the rubber were carried out to characterize the properties via irradiation. The results indicated that PVMQ acted as an irradiation degradation retarder for EPDM. After a postvulcanized period corresponding to 50 kGy dose, the elongation at break and electrical insulation decreased with LOI unaffected, while the crosslink density and tensile strength presented a complicated change with the increasing of radiation dose. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1566–1571, 2011

Key words: EPDM; PVMQ; gamma radiation; halogen-free flame retardant

INTRODUCTION

The effects of radiation on polymer properties are important subjects due to the possible application areas of polymers under the exposure to ionizing radiation, such as nuclear power plants, irradiators, and radioactive waste management. Ethylene–propylene–diene monomer-based (EPDM) rubbers are widely used as cable insulation and joints materials in nuclear power stations. As far as warranty of safety and reliability is concerned, degradation mechanisms and lifetime prediction of EPDM rubber exposed to high-energy radiations are relevant problems that must be solved. Besides the outstanding radiation resistance, halogen-free flame retardant with low emission of smoke and poisonous gases is another important requirement for polymer materials used in nuclear power stations. Therefore, it is necessary to study the radiation effects on properties of halogen free flame retardant polymers based on EPDM.

The properties of polymer may present a drastic deterioration due to chemical degradation under radiation. The reason is the interaction of energetic particles with polymer chains that would produce chain scission, chain branching, crosslinking, and possible oxidation in oxygen. Usually, all these phenomena coexist, so the final polymer properties are the results of a complex equilibrium among crosslinking, chain scissions, and oxidation.[1] And understanding these different degradation mechanisms and related kinetics is an essential step in predicting lifetime and selecting correct polymer formulation. Zaharescu et al.[2] studied the thermal resistance of EPDM under γ-radiation in the presence of divinyl benzene, in which the contribution of vinyl compounds to the crosslinking of the EPDM was demonstrated. Moreover, they investigated the effect of radiation on mechanical and oxidation resistance properties of EPDM-PP blends and found that EPDM brought about lower oxidizability than PP and the oxidation was slow at the first stage of exposure, and accelerated at higher irradiation doses.[3,4]

It is well known that irradiation dose and dose rate influence the interactions of gamma rays with polymers, and the behavior of polymers under irradiation was related to the environmental condition, the vulcanization and the additives.[5–7] PVMQ contains quite a few benzene rings, which are known to have a "protective" action in radiation-chemical processes.[8] In this article, the effects of gamma

Correspondence to: H. Ye (yehcn@163.com).

Contract grant sponsor: Natural Science Foundation of Jiangsu Province of China; contract grant number: BK2008577.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20906001.

Contract grant sponsors: Research Foundation for Youth Scholars of Beijing Technology and Business University.

TABLE I
Amount of EPDM, PVMQ, and MH for Different Recipes

Recipe symbols	P0M150	P10M150	P20M150	P30M150	P20M120	P20M90
EPDM	100	90	80	70	80	80
PVMQ	0	10	20	30	20	20
MH	150	150	150	150	120	90

Note: Other ingredients including silica 10 phr, zinc oxide (ZnO) 5 phr, stearic acid (HSt) 1 phr, silane coupling (A-172) 2 phr, dicumyl peroxide (DCP) 3 phr, triallyl isocyanurate (TAIC) 1 phr; *N*,*N*′-meta-phenylene-bis-maleimide (HVA-2) 0.5 phr, 2-methylbenzimidazole (MB) 1 phr, 2,2,4-trimethyl -1,2-dihydro-quinoline (RD) 2 phr, paraffin oil 15 phr.

radiation on the properties of EPDM-PVMQ blends were studied, and the influence of PVMQ and MH (halogen-free flame retardant filler) on those properties were also discussed.

EXPERIMENTAL

Materials and sample preparation

Phenyl vinyl methyl silicon pure rubber (PVMQ) was provided by Shanghai Zhongjun Chemical, China. It is characterized by having a phenyl content of 25 wt %, a vinyl content of 0.25–0.35 wt %, and a molecular weight of 35–40,000. Ethylene–propylene–diene terpolymer pure rubber of commercial name Nordel IP 4770P was supplied by Dow Elastomers, U.S.A. Magnesium hydroxide (MH) with the average diameter of less than 1 μm, used for halogen-free flame retardant agent, was provided by Shandong Helon Magnesium Science and Technology.

Ingredients of the materials containing different EPDM, PVMQ, and MH (Table I) were mixed carefully through a Model SK-160 open two-roll-mill (Wuxi No.1 Rubber and Plastic Machinery Company, Wuxi, China) and subsequently pressed to sample sheets of approximate 1, 2, and 3 mm in thickness by a Model QLB-25 D/Q350 × 400 mm compression molding (Wuxi No.1 Rubber and Plastic Machinery Company, Wuxi, China). Dumbbell tensile test specimens were cut from the rectangle sheets of 2 mm in thickness, which was vulcanized in hydraulic press for 20 min. Strip specimens used for LOI test were cut from the rectangle sheets of 3 mm in thickness vulcanized for 25 min. Round-shaped samples used for electrical insulation test were vulcanized in the standard round-shaped molds with thickness of (1 ± 0.2) mm and diameter of (100 ± 1) mm for 15 min. In these vulcanizations, the temperature and press are 180°C and 15 MPa, respectively.

Radiation process

The rubber blends were exposed to γ-radiation of a ^{60}Co source at a dose rate of 171.7 Gy/min for doses varying from 50 to 500 kGy. All irradiations were done open to atmosphere at the room temperature.

Properties test

Tensile strength (TS) and elongation at break (EB) were measured with a Model JPL-2500 electronic tensioner (Jiangdu Jingcheng Test Instruments Factory, Jiangdu, China) according to the Chinese National Standard GB/T1701-2001. The electrical insulation was measured using a Model ZC36 High Resistance Meter (Shanghai Precision and Scientific Instrument) at 20°C. Limiting oxygen index (LOI) was measured on the specimen of 120 mm × 6.5 mm × 3 mm according to the Chinese National Standard GB/T2406-93 by a Model HC-2 Limiting Oxygen Index Determinator (Jiangning Analytical Instruments Factory, Nanjing, China). Crosslink density was measured by solvent swelling method, using cyclohexane as swelling solvent according to the methods reported by Quanlin Z.[9]

ATR-FTIR spectroscopy

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded at 25°C on a Fourier transform infrared spectrophotometer (Perkin-/Elmer, U.S.A.) equipped with a horizontal golden gate single reflection diamond ATR cell. Spectra were obtained from the coaddition of a total of 32 scans.

RESULTS AND DISCUSSION

Mechanical properties

Table II shows the properties of the samples. As expected, the TS and EB values decreased with the increasing of PVMQ content, which was due to the low green strength and poor green elongation of PVMQ. To illuminate the effects of PVMQ and MH on the mechanical properties of irradiation samples, the percent retention rate was used in this article. It was defined as the percent ratio of property value of irradiated to that of un-irradiated sample. For example, the percent retention rate of TS of P0M150 sample exposed to 50 kGy irradiation dose, that was

TABLE II
Properties Value of Unirradiated Samples

Recipe symbols	P0M150	P10M150	P20M150	P30M150	P20M120	P20M90
Tensile strength (N/mm^2)	9.5	7.8	5.2	4.0	6.1	7.4
Elongation at break (%)	542	512	510	446	559	608
Volume resistivity (10^{15} Ω cm)	6.1	4.2	2.1	1.2	2.2	2.6
LOI (%)	37	37	38	38	33	31
Crosslink density ($mmol/m^3$)	2.30	2.25	2.62	2.77	2.12	2.02

named as % (TS, P0M150, 50 kGy), can be calculated by formula (1) as following. As a special case, the percent retention rate of TS of unirradiated sample was 100%.

$$\%(\mathrm{TS, P0M150, 50\ kGy}) = \frac{\text{TS of P0M150 sample exposed to 50 kGY}}{\text{TS of P0M150 sample un-irradiated}} \times 100 \quad (1)$$

Figure 1 illustrates the percent retention rate of TS as a function of irradiation dose. From Figure 1(a), it can be seen that the changes of TS retention rate present a complicated tendency. First, TS retention rate increased for all samples at the first stage of exposure, and then the samples containing PVMQ below 10 phr have comparatively low TS retention rate over the dose range of 120–500 kGy, the TS retention rate of these samples rapidly decreased as the dose increasing. On the other hand, comparatively high retention rates have been obtained by samples loaded with 20 phr and 30 phr of PVMQ, and the TS retention rate for the later samples slightly decreased with the increasing of irradiation dose. The result indicates that PVMQ act effectively in raising up the retention rate of TS, which is attributed to the excellent radiation-resistant property of PVMQ. During irradiation, the energy is dispersed to the whole conjugated structure of benzene rings, which are known to have a "protective" action in many radiation-chemical processes,[8,10] and the energy acting on a single interatomic bond is reduced to less than the bond energy. Figure 1(b) shows that MH content has little effect on the TS retention of irradiated samples.

EB usually changes more greatly than TS in the course of degradation and has been used to assess the heating aging performance. Figure 2 shows the changes of percent retention rate of EB with irradiation dose. Different from TS, the retention of EB decreased with the increasing of irradiation dose. The progressive loss of elasticity is caused by the modifying rigidity as samples received higher dose. The decrease in elasticity of samples subjected to radiolysis can be attributed either to the fragmentation of elastomer molecules, or to the breakage of intermolecular connections.

Figure 2(a) indicates that the EB retention rates undergo some increase as the PVMQ content increased, it means that loading of PVMQ can enhance EB retention rate of irradiated rubber blend. That is to say, PVMQ having high phenyl content is a good modifier to decrease the EPDM sensitivity to radiation. However, as the same as TS, the content of MH has no distinct effect on EB retention rate after irradiated.

To understand the complicated changes of TS retention rate after irradiation, crosslink density is measured. The retention rates of crosslink density

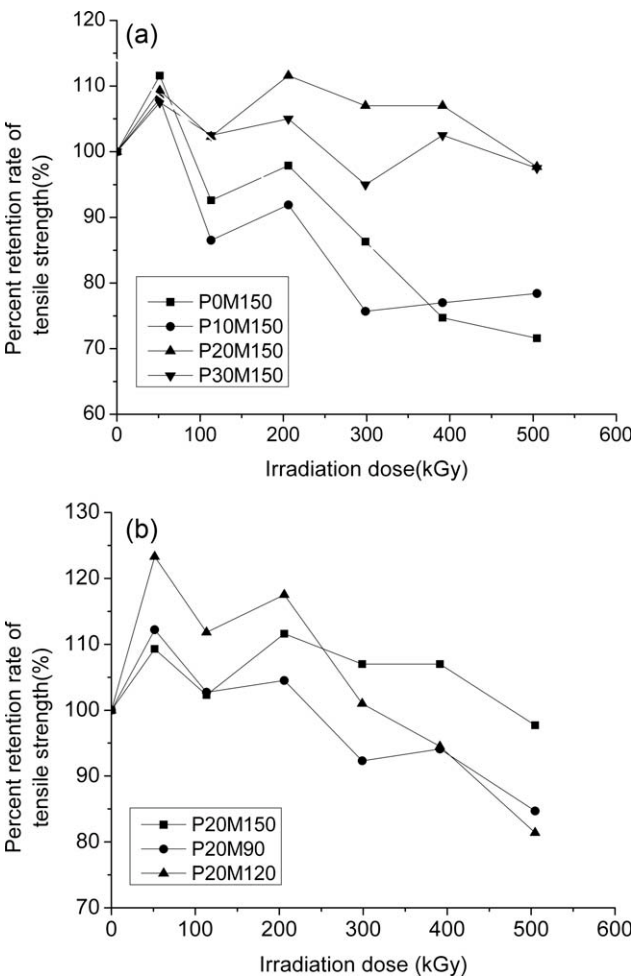

Figure 1 Changes of percent retention rate of tensile strength with irradiation dose for EPDM-PVMQ blends loaded with different amount of PVMQ (a) and MH (b).

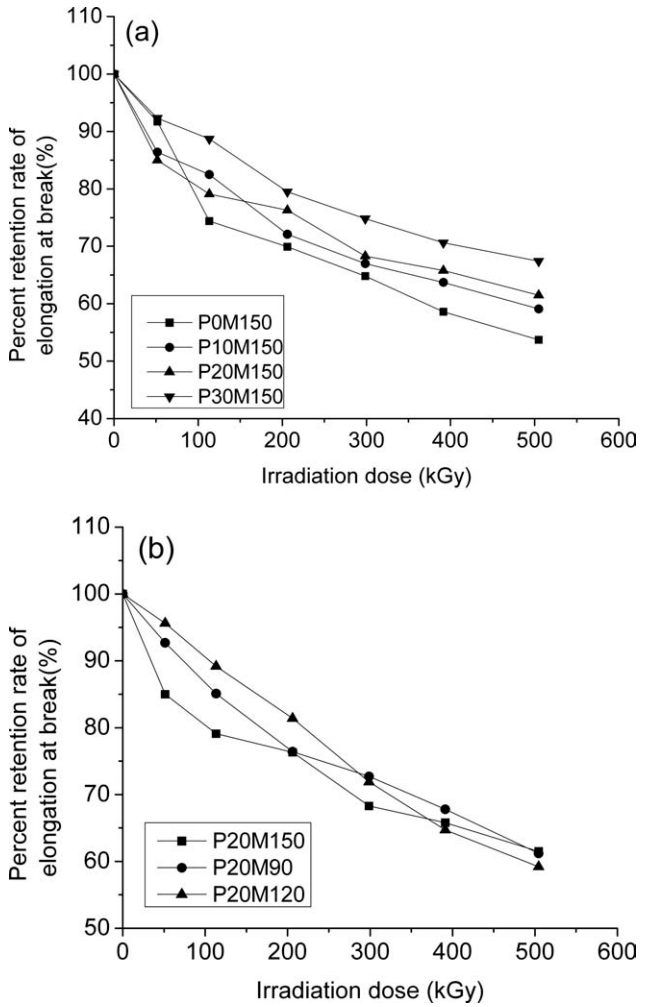

Figure 2 Changes of percent retention of elongation at break with irradiation dose for EPDM-PVMQ blends loaded with different amount of PVMQ (a) and MH (b).

for all recipes at different irradiation dose are shown in Figure 3. It is shown that the retention rates of crosslink density for all samples also exhibit the similar changes as that of TS retention rate. Moreover, it can be seen from Figure 3(a) that samples containing PVMQ, especially its concentration more than 20 phr, present a comparatively low slope from 200 to 500 kGy. The result further makes it clear that PVMQ plays an important role in improving irradiation-resistance of EPDM-PVMQ rubber blend. Figure 3(b) shows that MH content has no distinct effect on the irradiation-resistance of EPDM-PVMQ rubber blend. This is in line with that inferred from mechanical properties.

Both EPDM and PVMQ rubbers are categorized as predominantly radiation crosslinkable type of polymers,[5] i.e., that their crosslink density would increase as irradiated. But, in fact, chain-scission, accompanied with the decrease of crosslink density, occurs simultaneously,[11] which is confirmed by the tacky surface of irradiated samples. The complicated change tendency of TS and crosslink density is a consequence of the competition between irradiation initiated crosslinking and chain-scission reactions. Usually, complete curing of silicon rubber can be realized only after two stages vulcanization. In the first stage, curing is done at low temperature of around 170°C for a short time and in the second stage, curing is done at high temperature of around 200°C for several hours in air.[5] So, it is reasonable to think that the significant increase of crosslink density within the dose range from 0 to 50 kGy is caused by the postcuring of PVMQ induced by irradiation. This can be further confirmed by the much lower increase of the crosslink density for pure EPDM. With increased doses of radiation, the second period curing of PVMQ gradually completed, causing the gradual reduction of crosslinking speed. When irradiation dose increased to 50 kGy, crosslinking speed reduced to less than oxidation degradation speed with the result of the decrease of crosslinking density until irradiation dose of 120 kGy, after which crosslinking speed is faster than that of

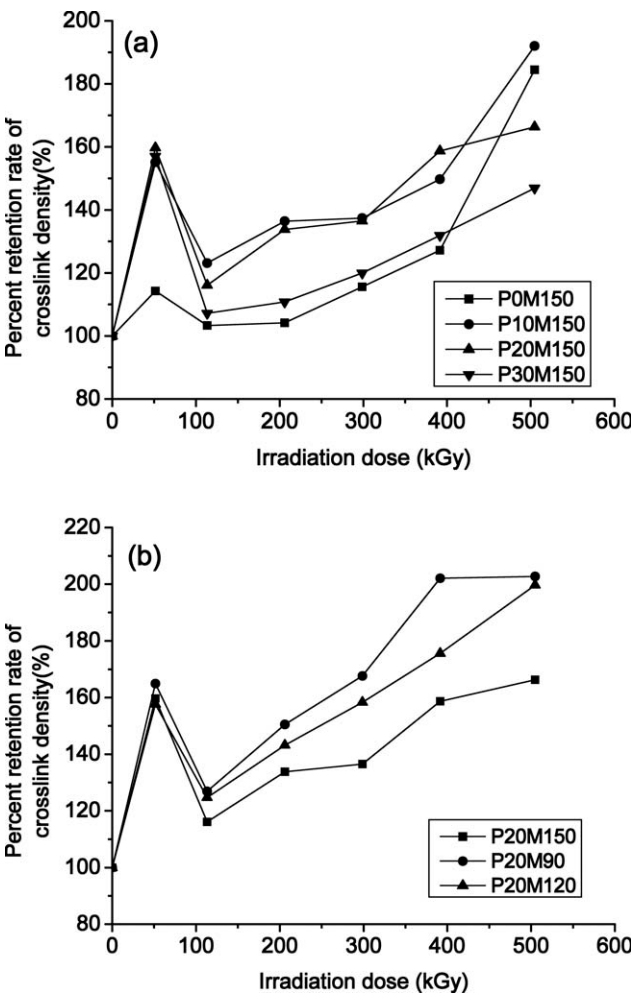

Figure 3 The percent retention rate of crosslink density at different irradiation dose for EPDM-PVMQ blends loaded with different amount of PVMQ (a) and MH (b).

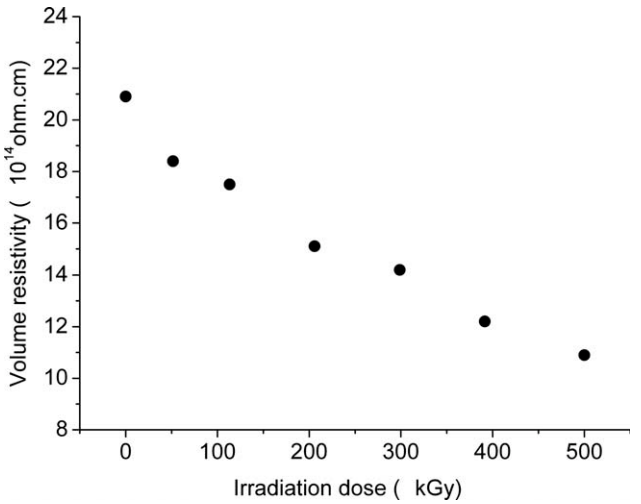

Figure 4 Volume resistivity of EPDM-PVMQ blends (P20M150) at different irradiation dose.

oxidation degradation. Therefore, crosslinking density began to increase gradually. The change of crosslink density within the dose range from 50 to 500 kGy is perfectly consistent to what Tonguç Özdemir reported.[12]

In generally, a increase of crosslink density results in a peak-like change of TS (TS first increasing to the maximum value at a certain degree of crosslinkage and then decreasing with the further increase of crosslinking) and a steady decrease of EB, while chain-scission play a contrary role on the same parameters. The complicated change trend of the retention rates of TS and the decreasing of the retention rates of EB could be well explained by this.

Electrical properties

Figure 4 shows the volume resistivity of P20M150 sample exposed to different irradiation dose. It is can be seen that the volume resistivity gradually decreases with the increasing of irradiation dose, but all of the values of resistivity are larger than 10^{15} Ω cm. It indicates that EPDM-PVMQ rubber blend with PVMQ content of 20% exhibit an excellent insulation behavior. The decrease of the volume resistivity can be explained by the oxidation degradation. According to the report by Zaharescu et al.,[3,4] if polymer is exposed to irradiation in air, the irradiation oxidation would happen resulting in the accumulation of the main oxygenated products containing carbonyl and hydroxyl functions, such as ketones, carboxylic acids, alcohols, peroxides, esters, and lactones. In electric field, these polar molecules and groups will occur, when polarization, orientation, and transfer process with the result of the decrease of the volume resistivity.

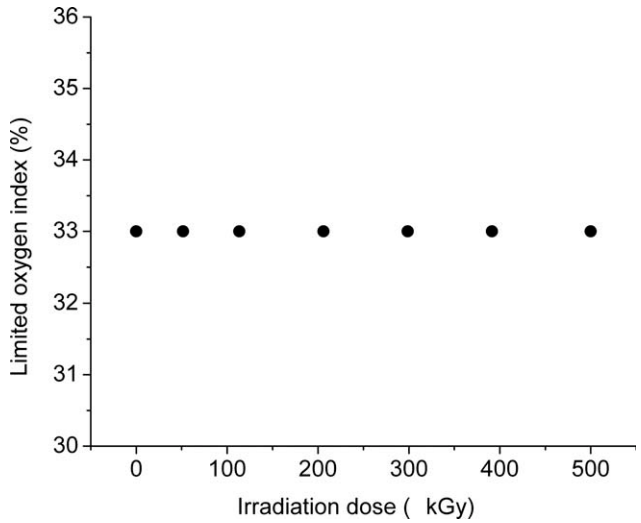

Figure 5 Limited oxygen index of EPDM-PVMQ blends (P20M120) at different irradiation dose.

Flammability of the EPDM-PVMQ blend

Figure 5 shows the LOI of P20M120 sample as a function of radiation dose. It can be seen that the LOI values for the irradiated samples remain 33% within the whole range from 0 to 500 kGy.

ATR-FTIR

According to the references,[3,4] irradiation can induce the chain-scission of polymer and generate free radical, which would react with molecular oxygen to generate oxidation initiators (peroxyl radicals) and irradiation oxidation. The oxygenated products are mainly compounds containing carbonyl and hydroxyl functions, such as hydroperoxides, ketones, carboxylic acids, alcohols, peroxides, and ester. So, the absorbance in the carbonyl and hydroxyl absorption region (1900–1650 cm^{-1} and 3800–3000 cm^{-1},

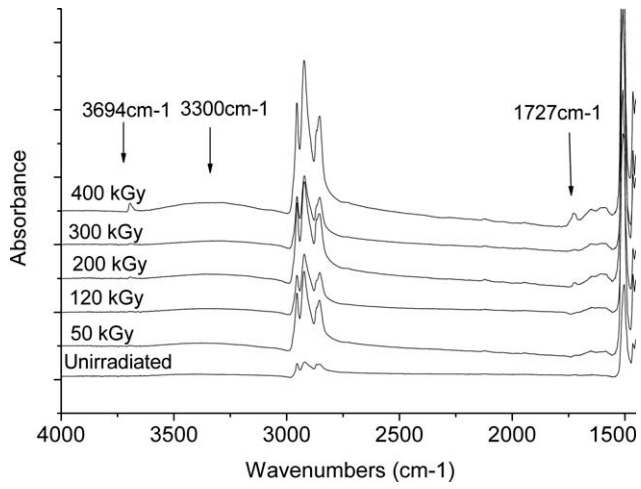

Figure 6 FTIR spectra of EPDM-PVMQ blend (P20M150) at different radiation dose.

respectively) in the IR spectrum is a measure of the degree of the oxidation degradation.

To observe the radiation effect on the oxidation degradation of EPDM-PVMQ blend, the FTIR spectra of EPDM-PVMQ blend (P20M150) irradiated at different radiation dose were displayed in Figure 6. In Figure 6, an absorption band is noticeable near 1727 cm^{-1}, which is attributed to the carbonyl group. Moreover, an obtuse and broad band in the 3500–3200 cm^{-1} interval and another sharp and narrow band near 3694 cm^{-1}, corresponding to the coalescent and free hydroxy groups, respectively, are also visible in Figure 6. In addition, it can be seen that the intensity of bands, corresponding to both hydroxyls and carbonyls, increases with the radiation dose. It means that more hydroxyls and carbonyls accumulate when irradiation dose increases, and the higher the radiation dose is, the faster the oxidative degradation induced by irradiation runs.

CONCLUSIONS

From the results obtained in this article, the following conclusions were obtained. The mechanical properties of EPDM-PVMQ blend with the PVMQ content over 20 phr deteriorated to a comparatively lower degree than that of pure EPDM and its blend with 10 phr PVMQ when exposed to irradiation. PVMQ acted as an irradiation degradation retarder for EPDM, while MH had no obvious effect on the radiation stability of EPDM-PVMQ blend. At the first stage of exposure i.e., within 50 kGy dose, EPDM-PVMQ blend possibly underwent the post-vulcanization with the result of an improvement of mechanical properties and flame-resistance. With the increase of radiation dose, elongation at break, and electrical insulation property decreased, limited oxygen index remained constant and whereas crosslink density and tensile strength presented a wave-like change. Oxidation degradation induced by radiation occurred more easily when samples were exposed to higher radiation dose.

We acknowledge Prof. Guoxing Gu for irradiation of the samples and Dong Chun for her assistance in sample preparations.

References

1. Davenas, J.; Stevenson, I.; Celette, N.; Vigier, G.; David, L. Nucl Instrum Methods Phys Res Sect B: Beam Interact Mater Atoms 2003, 208, 461.
2. Zaharescu, T.; Feraru, E.; Podina, C. Polym Degrad Stab 2005, 87, 11.
3. Zaharescu, T.; Chipara, M.; Portolache, M. Polym Degrad Stab 1999, 66, 5.
4. Zaharescu, T.; Jipa, S.; Setnescu, R.; Setnescu, T. Nucl Instrum Methods Phys Res, Sect B: Beam Interact Mater Atoms 2007, 265, 260.
5. Davenas, J.; Stevenson, I.; Celette, N.; Cambon, S.; Gardette, J. L.; Rivaton, A.; Vignoud, L. Nucl Instrum Methods Phys Res, Sect B: Beam Interact Mater Atoms 2002, 191, 653.
6. Zaharescu, T.; Giurginca, M.; Jipa, S. Polym Degrad Stab 1999, 63, 245.
7. Magda, M.; Abou, Z. Eur Polym Mater 2007, 43, 4415.
8. Perera, R.; Albano, C.; González, J.; Silva, P.; Ichazo, M. Polym Degrad Stab 2004, 85, 741.
9. Quanlin, Z.; Xiaogang, L.; Jin, G. Polym Degrad Stab 2007, 92, 1841.
10. Fu, Z. Rubber property and Design M. Chem Industry Press: Beijing, 2003.
11. Spadaro, G.; Valenza, A. Polym Degrad Stab 2000, 67, 449.
12. Tonguç, Ö. Radiat Phys Chem 2008, 77, 787.