Effects of Peroxide and Gamma Radiation on Properties of Devulcanized Rubber/Polypropylene/Ethylene Propylene Diene Monomer Formulation

Medhat M. Hassan,[1] Nagwa A. Badway,[2] Mona Y. Elnaggar,[1] El-Sayed A. Hegazy[1]

[1]National Center for Radiation Research and Technology, Nasr City, Cairo 11731, Egypt
[2]Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt
Correspondence to: M. Y. Elnaggar (E-mail: mona_ncrrt@yahoo.com)

ABSTRACT: Mechanical and thermal properties of devulcanized rubber (DR)/polypropylene (PP)/ethylene propylene diene monomer blends (EPDM) were studied at various concentrations of dicumyl peroxide (DCP) and gamma radiation doses. The blends showed improved mechanical properties for vulcanized sample. The coupling of DR/PP/EPDM with different proportions of DCP was investigated by X-ray diffraction and scanning electron microscopy techniques. Evaluation of the developed blends, unirradiated and gamma irradiated, was carried out using elastic modulus, tensile strength, elongation at break, thermogravimetric analysis, kinetic analysis, and DSC measurements. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40611.

INTRODUCTION

The disposal of waste tires has become a great environmental concern globally due to the growing stockpiles of used tires and corresponding increase of disposal charge for discarded tires. Recycling of ground tire rubber (GRT) not only solves the waste disposal problem and maintains environmental quality but also saves the valuable and limited resource of fossil feedstock. It is reported that approximately 3 to 5 billion tires are piled up across America and the volume is increasing every year by 250 to 275 million a year. Of that 49% being recycled, 30% is burnt for energy recovery and 13% is used for retreading. Only 2% are being used for civil engineering application and 2% for crumb rubber.[1]

Thus, the reclaimed rubber produced has a degree of plasticity comparable with vulcanized rubber and thereby enable it to be blended with natural or synthetic rubber. Blend of reclaimed or ground vulcanized waste with natural rubber gives processing as well as economic advantages. Rubber powder can be mixed with virgin rubber but there is a significant drop in the tensile strength at the lower levels of addition of scrap rubber.[1–4] An improvement in property can be achieved by compounding the scrap with new rubber and sulfur and subsequent vulcanization of the compound.

A promising way of "recycling" waste ground rubber tire (WGRT) powder is to incorporate it into thermoplastics to obtain thermoplastic elastomers (TPEs) and a perfect choice for the thermoplastic is polypropylene (PP) due to its low cost and resulting protection of the environment. However, the adhesion between WGRT and a polymer matrix is usually very weak due to the crosslinked structure of WGRT. In order to solve the problem, some attempts have been made to produce thermoplastic rubbers by adding WGRT to the corresponding recipes.[5–7] It was early recognized that WGRT should be devulcanized or at least partially devulcanized to facilitate the molecular entanglement between WGRT and polymer matrix.

A considerable amount of work has been reported on the blends of polyolefin and ethylene propylene diene monomer (EPDM) due to their commercial importance. Among rubber/PP blends, the PP/EPDM blend has acquired some commercial success and finds applications in various industrial fields because the composition-dependent properties of the blends can meet the diverse requirements of industrial applications.

TPVs exhibit intermediate cost, good chemical resistance, good dynamic properties, high weatherability (measured characteristic that shows how well a product performs during exposure to outdoor weather conditions), and low compression set in comparison with simple blends of TPEs. Various research articles focus on solutions to compatibilize these two phases, the ultimate objective being to obtain a "TPE"-like behavior by combining rubber elasticity and thermoplastic matrix properties.

Table I. Chemical Compositions and Physical Properties of the Different Compositions

Ingredients	Percent		
	Composition 1	Composition 2	Composition 3
Benzoic acid	94	89	78
Zinc oxide	1	2	5
Stearic acid	1	2	5
Hydroquinone	2	4	8
Rosin	2	3	4
Physical properties			
Soluble fraction%	21.2	31.4	20.1
Gel fraction%	78.8	68.6	79.9

Many processes have been carried out to improve the mechanical behavior. The approach which gave the best results consisted in performing co-crosslinking radical reactions at the interface between rubber particles and host thermoplastic matrix. Such reactions are initiated by free radicals obtained either by the decomposition of peroxide during melt blending, or by gamma irradiation of the blend.[8–10]

Crosslinking with peroxides has been known for a long time, but gained importance with the development of the saturated synthetic elastomers. Major advantages of peroxide crosslinking is that the peroxides have the ability to crosslink saturated elastomers and even numerous other polymers, which cannot be cross-linked with other types of crosslinking agents, improved high temperature resistance, reduced compression set, and their ability to vulcanize both saturated and unsaturated rubbers and reversion resistance. Wiessner et al. compatibilized PP matrix and GTR particles using 2 wt % of dicumyl peroxide (DCP).[8]

Ionizing radiation induces chemical reactions in polymers that result in changes in both molecular structure and microscopic properties. The energy transfer from the radiation to the polymer does not take place selectively relative to the mixed components. The probability of the generation of free radicals depends on the strength of atomic bonds. The lower the bond energy the easier the bond scission will be. Radiochemical studies on crosslinking or degradation of polymer blends are important for designing new materials. When oxygen is present, radiation-induced changes are often quite different from those produced by irradiation under inert atmosphere.[11] The use of gamma radiation for composite materials offers several advantages, such as continuous operation, minimum time requirement, less atmospheric pollution, curing at ambient temperatures, increased design flexibility through process control.

Peroxide curing and γ-radiation vulcanization, both produce stable C—C bond. The most noticeable effect of the addition of the anti-oxidant DCP to polymers is the deactivation of the free radicals induced by irradiation which would otherwise react to form crosslinks.

The aim of this work is to prepare TPVs based on mechano-chemically devulcanized GTR/PP/EPDM. The impact of peroxide curing and γ-radiation vulcanization of the produced composite have been studied in terms of physical, mechanical, thermal, and structural parameters.

EXPERIMENTAL

Materials

GTR was kindly provided by Narobine Company, Cairo, Egypt, of particle size 10 mesh from the tread and sidewalls of passenger and truck tires. It contained: ∼59.8% hydrocarbon (30% Nature rubber, 40% (Styrene butadiene rubber), 20%-Nitrile butadiene rubber, and 10% butyl and halogenated butyl rubber), 24% carbon black, 15% acetone extract, ∼0.92% sulfur, and ∼0.98% ZnO. High crystalline PP (575P) supplied by SABIC/ Europe Company with MFI = 2.16 g/10 min, density 905 kg/m,[3] and crystallinity of 93.1% was implemented. Chemical materials used in the devulcanization process are Benzoic acid (extra pure grade, $C_7H_5O_2$, minimum: 99%, F.W.: 122.12), zinc oxide (B.P. 2004°C), stearic acid (octadecanoic acid, extra pure grade, $C_8H_{36}O_2$, minimum: 99%, F.W.: 284.48), and hydroquinone (M.W. 110.11, melting point 170–174°C) are products of El-Nasr Pharmaceutical Chemicals Company. Rosin is a solid form of resin obtained from pines and some other plants mostly, conifers. It chiefly consists of different resin acids especially abietic acid (EPDM-Roylene375 was supplied by Uniroyal Chemical Company, USA). The ethylene to propylene ratio is ∼75:25 wt % about 2% dicyclopentadiene as diene monomer. DCP was obtained from China National Medicine (Group) Shanghai Chemical Reagent Corporation, whose half-life time is about 0.25 min at 200°C.

Preparation of Devulcanized Rubber

The devulcanization process was carried out as follows: One hundred grams of the GTR particles were subject to three various compositions of the devulcanizing chemical materials (Table I). The latter were being poured whilst GTR particles were being introduced between mill rolls at a temperature of nearly 70°C for 20 min. Each material contributes in devulcanization of GTR as follows: Benzoic acid is proton donor that breaks the sulfur bonds between atoms/molecules in vulcanized rubber and renders the sulfur passive. Zinc oxide builds new bonds between macromolecules for latter revulcanization. Stearic acid reacts with the metal oxide and builds new bonds between macromolecules. Hydroquinone acts as inhibitor that prevents reattachment of sulfur radicals with each other before the proton donor attaches itself to the sulfur. Rosin used to prevent sliding of the waste rubber between the rollers. Mechano-chemical devulcanization maintains the macromolecules of waste rubber, renders the sulfur passive. Vulcanized rubber networks contain three bonds[C—C, C—S, and S—S] differ in strength [S—S < C—S < C—C], hence, can be affected by mechanical devulcanization. When benzoic acid is added, the COOH group of the benzoic attacks the S—S bond and easily donates hydrogen. The extent of devulcanization was monitored by measurement of sol content, gel content; FTIR, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) of GTR.[12–14] Accordingly, composition 2 was adopted to apply to this study.

Preparation of Blend

The preparation of devulcanized rubber (DR)/PP blend melted in Brabender Plasti-corder PL2100 Mixer with a volume capacity of

Table II. Physical Parameter of Unirradiated and Irradiated Composition of DR/PP/EPDM at Different Concentrations of DCP Exposed to Different Gamma Radiation Doses

Sample composition DR/PP/EPDM/ DCP wt %	Dose (kGy)	Gel fration %	Crystallinity %	Interplanar distance d (°A)	Activation Energy E_a (kJ/mol)
(45/25/30/0)	0	72.5	18.9	2.68	208.2
(45/25/30/0.5)	0	92.4	14.4	2.45	435.6
(45/25/30/1)	0	93.1	16.9	2.39	402.8
	25	94.7	16.5	2.35	409.38
	50	93.1	16.2	2.69	393.6
	100	92.5	16.2	2.35	374.7
(45/25/30/1.5)	0	94.1	16.3	2.41	361.49

about 200 cm³ at 190–195°C, 60 rpm for10 min, where PP was first inserted into the mixer for about 2 min. Thereafter, DR was introduced to mix with the molten PP for about 3 min then EPDM added and mixed omitted for 7 min then added DCP until uniform dispersion, the weight ratios of the composite reported as DR/EPDM/PP/DCP (45/30/25) with varying % of DCP (0, 0.5, 1, 1.5).

Molding. Sheets of 1 mm thickness were obtained by compressing molding between Holland cloth in clear and polished molds, adjusted beforehand to the melting point temperature of PP at 195°C for about 10 min. Pressure of 10 MPa was experienced by the press on the mold surfaces for 5 min. Moldings were then cooled under compression.

Gamma Radiation Treatment. Irradiation was carried out at the National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt. The samples were subjected to gamma radiation (gamma cell type 4000 A, India), in air, at ambient humidity and temperature. The absorbed doses were 25, 50, 75, and 100 kGy at a radiation dose rate of 3 kGy/h.

Measurements
Sol–Gel Analysis. The degree of reclamation of DR was evaluated by determining soluble (sol) and gel fractions using soxhlet extraction through toluene. In general, the lower is the gel content, the more efficient is the devulcanization process. The sol fraction is calculated as follows:

Scheme 1. Decomposition mechanism of DCP.

Sol. fraction (%) = $(W_o - W_1)/W_o \times 100$

where W_o is the dry weight of sample sheet before extraction and W_1 is the dry weight after extraction. The gel fraction can be calculated using the following equation: Gel fraction % = 100 − sol fraction.

Mechanical Properties. The tensile strength was measured using dumbbell shaped test pieces at a crosshead speed of 500 mm/min at 25 ± 2°C using tensile testing machine Zwick computer aided testing machine, United Kingdom. The ISO 527-2 standards and ASTM D 412a-98 were followed to measure tensile strength and elongation at break, respectively. The average value of the mechanical properties was calculated using at least three samples. A cross head speed of 50 mm/min was used and the tests were performed at 25°C.

Hardness Measurements. Samples of at least 0.12 mm in thickness with flat surface were cut for hardness test. The measurement was carried out according to ASTM D 2240 using 306L type A Durometer. The unit of hardness is expressed in (Shore A).

Differential Scanning Calorimetry (DSC). The thermal properties of all composites were investigated by using a DSC Shimadzu Type DSC-50 calorimeter system under constant operating conditions 20 mL/min within the temperature range from ambient to 200°C at a heating rate of 10°C/min.

Thermogravimetric Analysis. TGA was performed with a Shimadzu TGA-50 system, Japan, and heated within the temperature range 20–600°C at a rate of 20°C/min, under a controlled dry nitrogen flow of 20 mL/min.

X-ray Diffraction (XRD). Samples were measured with a Bruker XRD D8-advance Germany. All the diffraction patterns were examined at room temperature and under constant operating conditions.

The area under the X-ray diffractograms was determined in arbitrary units. The degree of crystallinity, $X\%$, was calculated using the following relationship[15]:

$$X\% = \frac{I_a}{I_a + I_c}$$

where I_c and I_a are the integrated intensities of the crystalline and the amorphous phase, respectively, and d interplanar distance (A°) were calculated as follow:
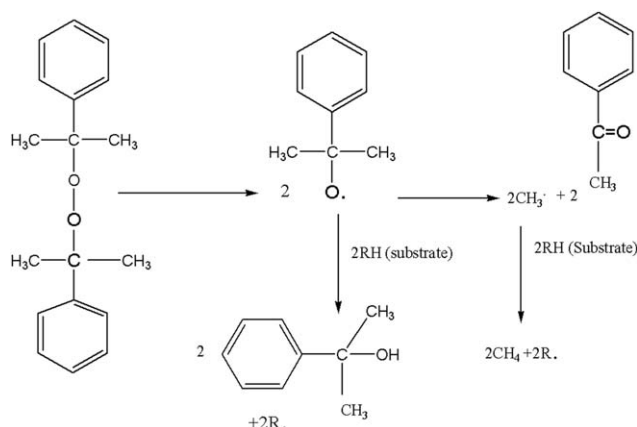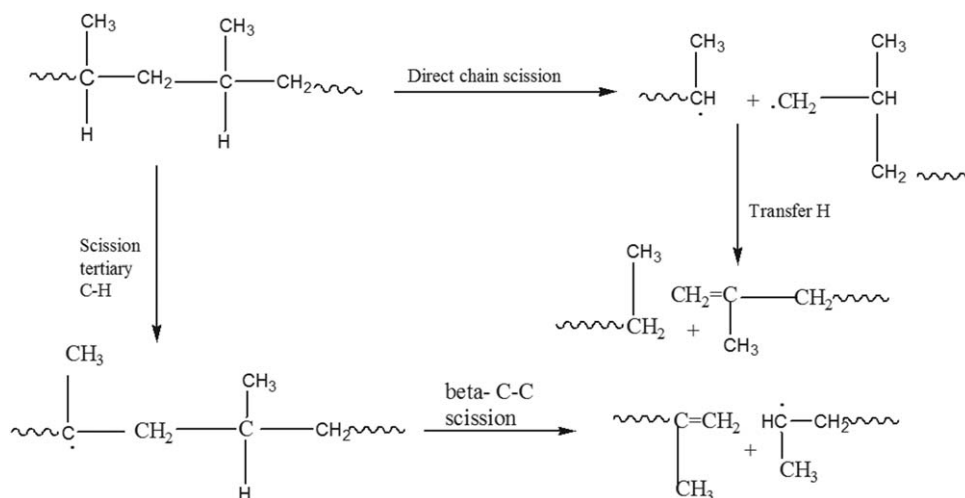
Scheme 2. Possible types of chain scission of PP under high shearing action and high temperature in the presence of DCP.

$$d = \lambda/2 \ \sin\theta$$

where λ is the wavelength of the X-ray radiation referenced to Cu, 1.548.

Kinetic Analysis

The kinetic parameters at a heating rate of 20°C/min were used for calculating the activation energy of DR/PP/EPDM composite. Decomposition conversion x can be calculated by:

$$x = W_o - W_t/W_o - W_f \qquad (1)$$

where W_o is the original mass of the test sample; W_t is the mass at time t and W_f is the final mass at the end of decomposition and so the composite decomposition reaction equation may simply be expressed by the following formula:

$$dx/dt = A \ \exp(-E_a/RT)(1-x) \qquad (2)$$

where A is the pre-exponential factor, E is activation energy, T is temperature, and t is time. Rearranging eq. (2) followed by integration gives:

$$\ln[-\ln(1-x)/T^2] = \ln[AR/HE_a(1-2RT/E_a)] - E/RT \qquad (3)$$

The expression $\ln[AR/HE \ (1-2RT/E_a]$ is essentially constant, where R is gas constant = 4.813 JK^{-1} mol^{-1}. If the left side of

eq. (3) is plotted versus $1/T$, a straight line may be obtained if the process is a first-order reaction. From the slope, $-E_a/R$, the activation energy E_a can be determined.

Morphological Characterization (SEM)

The ISM-5400 scanning electron microscope, JEOL, Japan, was used for the morphological observation of coated with gold fracture samples in liquid nitrogen.

RESULTS AND DISCUSSION

Gel Fraction Analysis

Thermal decomposition mechanism of DCP in composite is presumed to start from the homolytic cleavage of the DCP at low temperature. It is a very rapid process and the resulting cumyloxy radicals easily interact with the PP chains via intermolecular hydrogen abstraction at the tertiary carbon centers of the polymer backbone.

Table II summarizes the influence of the peroxide feed ratio, namely 0.5, 1, and 1.5%, on the gel content of the prepared DR/EPDM/PP (45/30/25) composite. Incorporation of 0.5% DCP raised the pristine gel percent with ≈20%. Further load was associated with increase in gel percent, indicating establishment of peroxide-induced crosslinking in the rubber moiety.[16]
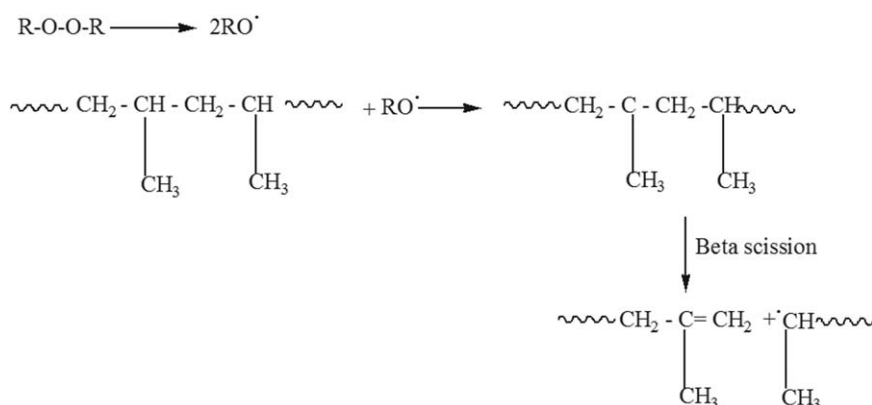
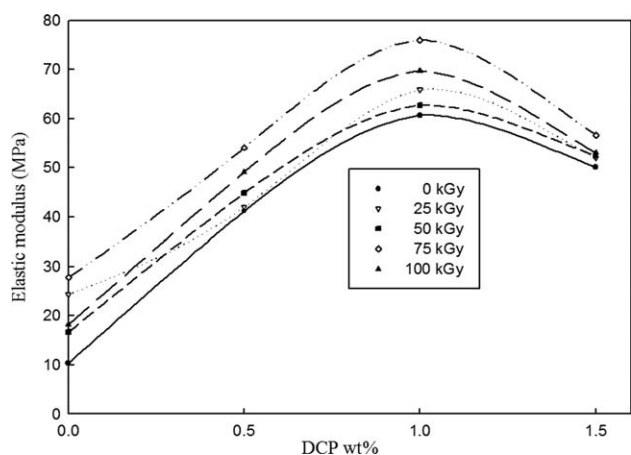**Scheme 3.** Simplified reaction for peroxide degradation of PP by β-scission.

Figure 1. Elastic modulus (MPa) of DR/PP/EPDM (45/25/30) composites at various peroxide concentration and gamma radiation dose.

Figure 3. Elongation at break % of DR/PP/EPDM (45/25/30) composites at various concentration of DCP and gamma radiation dose.

The utmost gel fraction value, 94.1, was recorded under conditions of 1.5% DCP.

Table II illustrates the impact of irradiation on the peroxide-treated samples. The synergistic maximum gel content value, 94.7%, was reported for the 1% DCP treated-sample irradiated with 25 kGy. The insignificant increment in gel fraction via radiation-induced crosslinking revealed a paramount effect of the peroxide-radical mechanism.[16] Furthermore, higher doses showed radiation-induced degradation as indicated by the respective recorded gel percents.

Mechanical Properties

The ordering of macromolecules and their entanglement and connections with neighbors affect the mechanical behavior of polymers. In DCP, the actual crosslinking occurs by 2-phenylpropanoxy radicals, mainly by methyl radicals (Scheme 1). DCP radicals degraded the PP molecules particularly by the β-scission mechanism, as shown in Schemes 2 and 3. The reaction results in a decrease in the viscosity of the PP moiety. The synergistic effect of peroxide and radiation dynamic vulcanization on the mechanical properties, namely elastic modulus,
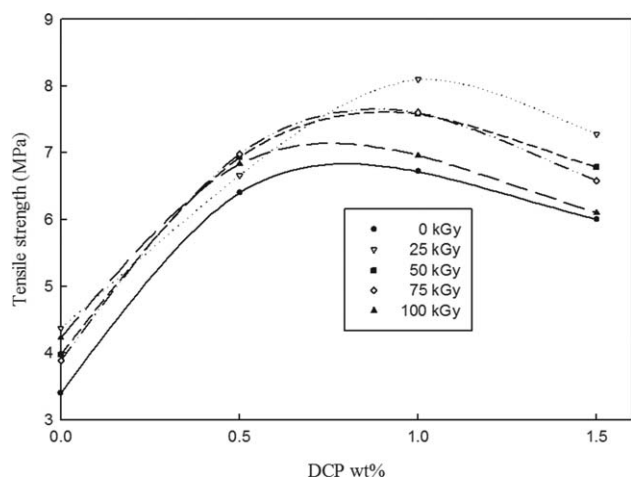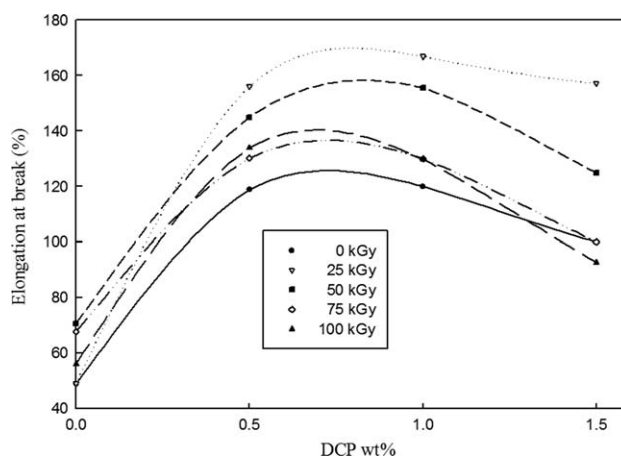
tensile strength, and elongation at break, is, respectively, given in Figures 1–4. Notably, the recorded values revealed increase with the increase in peroxide content up to 1% feed ratio. Gamma irradiation may additionally affect the polymeric structure of the composite. It was found that utmost elasticity was determined at DCP feed ratio of 1% as dose increased up to 75 kGy. Similarly, tensile strength and elongation at break values increased by increasing dose but only up to 25 kGy. Accordingly, it can be presumed that a radiation dose as minimum as 25 kGy can sufficiently induce radiation crosslinking.[15]

Thus, the examined parameters emphasized the establishment of crosslinking, and hence compatibilization, by moderate levels of radiation dose and peroxide. Exceeding peroxide 1% feed ratio barrier may lead to hard clusters of radicals that adversely affect matrix microstructure and hence lower mechanical properties.[17] Also, excessive irradiation may give rise to a predominant degradation process, mainly in the thermoplastic component. Figure 4 shows the variation of the hardness values of DR/PP/EPDM (45/25/30) blend as a function of DCP % and dose. Significant increase in hardness was observed with increasing DCP load up to 1 wt % and radiation dose up to 25%.
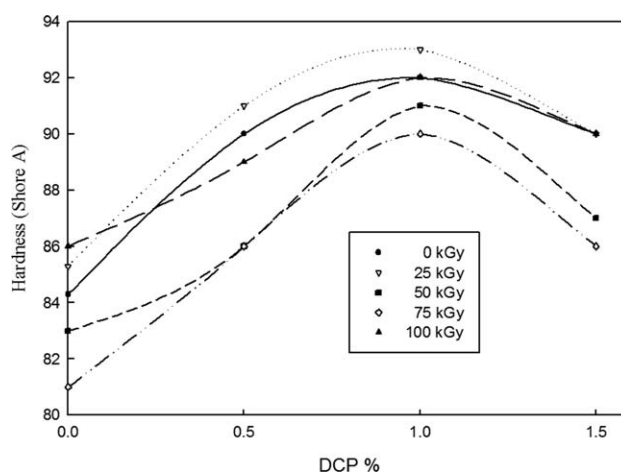

Figure 2. Tensile strength (MPa) of DR/PP/EPDM (45/25/30) composites at various peroxide and gamma radiation dose.

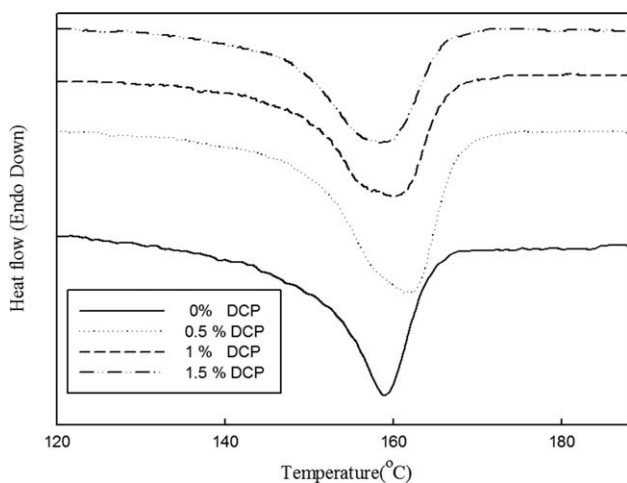**Figure 4.** Hardness of DR/PP/EPDM (45/25/30) composites at various concentration of DCP and gamma radiation dose.

Figure 5. DSC thermographs of ternary DR/PP/EPDM (45/25/30) wt % at various DCP concentration.

Figure 7. X-ray patterns of DR/PP/EPDM (45/25/30) composite at various concentration of DCP.

Evidently, the mechanical testing results reflect the establishment of a network within the matrix induced by DCP and radiation developed radicals. This can be occurred via two mechanisms in the unsaturated polymers: DCP radicals transfer to the double bonds in the rubber moiety and the hydrogen atom abstraction where the two unpaired electrons will couple and form a covalent bond or crosslink between the polymer chains.[18] Alternatively, the formation of macroradicals via β-scission in PP backbone, created by the attack of DCP radicals, results in radical recombination, competing the degradation process of PP tertiary alkyl radicals.

Differential Scanning Calorimetry (DSC)

The shape of the calorimetric melting curve provides valuable information on the thermal history and structural characteristics of the sample. The DSC outputs showed the characteristics of the PP phase, mostly governed by crystalline PP alone, as rubber is known as amorphous polymer.[19]

Figure 5 represents the heating endotherms of the composite at various DCP feed ratios. Addition of peroxide up to 1% led to
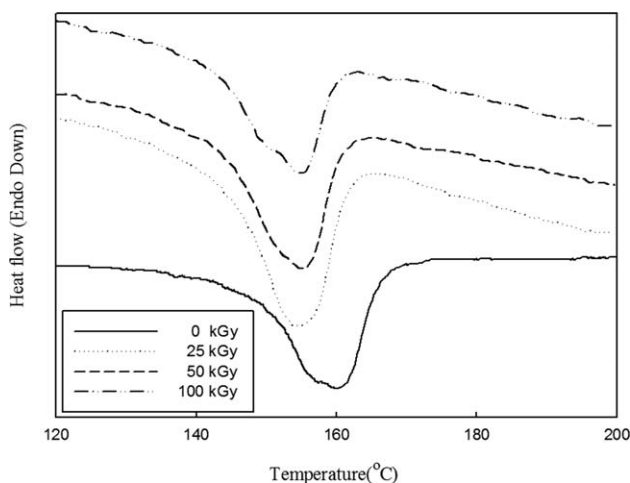

Figure 8. X-ray patterns of DR/PP/EPDM/DCP (45/25/30/1) composite at various gamma radiation dose.
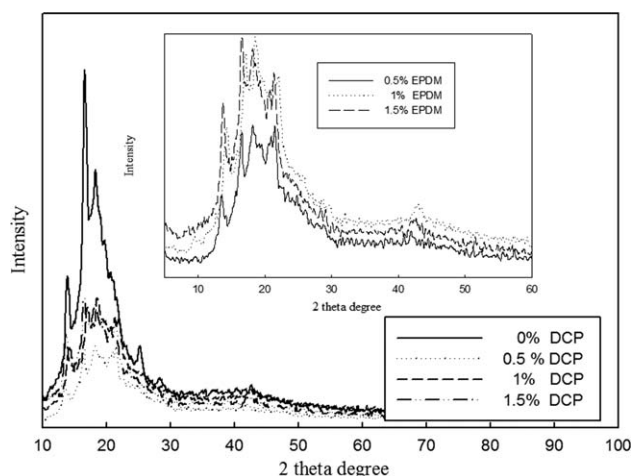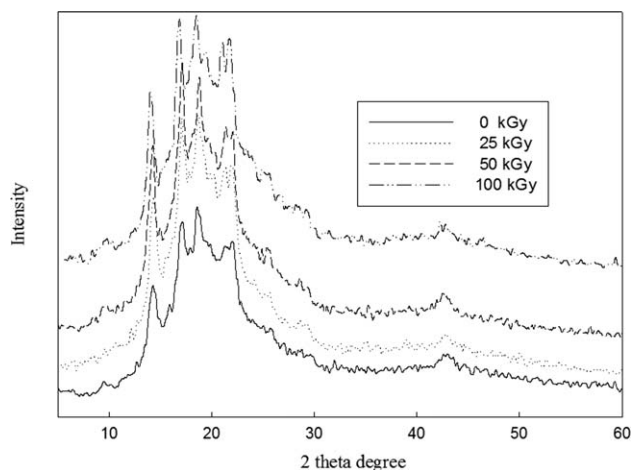

Figure 6. DSC thermographs of DR/PP/EPDM/DCP (45/25/30/1) wt % at various gamma radiation doses.
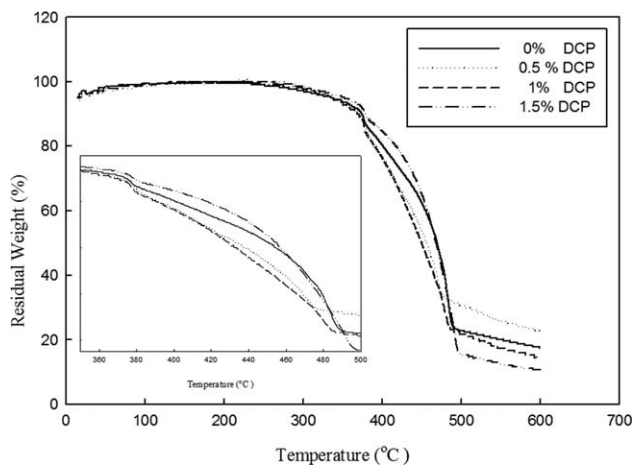

Figure 9. TGA thermograms of ternary PP/DR/EPDM (25/45/30) wt % at different DCP concentration.
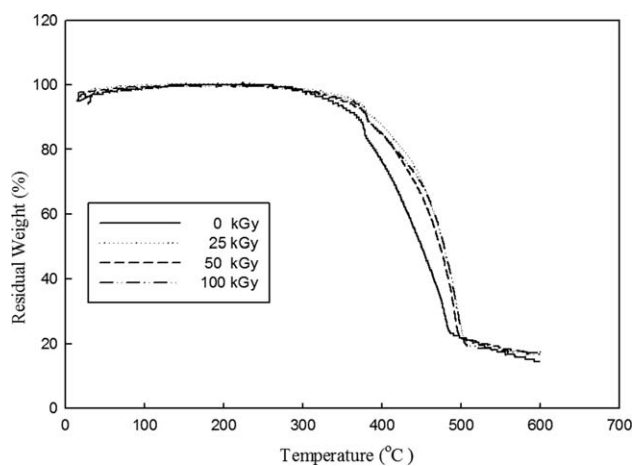
Figure 10. TGA thermograms of DR/PP/EPDM/DCP (45/25/30/1) wt % at various gamma radiation doses.

T_m shifts toward higher temperature, as a result of crosslinking which makes PP chain unfolding plausible.[20] Nevertheless, it was observed that, T_m decreased as DCP load increased up to 1.5%, suggesting occurrence of slight PP chain scission by the creation of excessive DCP radicals. Another likelihood is the application of a coagent, here EPDM, may assist the crosslinking process in the PP phase. The coagent stabilizes PP macroradicals by addition reaction through the coagent double bonds. Those stable radicals then preferably decay by recombination with other PP macroradicals, giving rise to crosslinking.[21]

Figure 6 reveals shifts in the T_m peak toward lower temperature with the increase in radiation dose. This can be accounted for the decrease in the tie-molecules within the PP amorphous regions which consequently weakens the interlamellar connections resulted from chain scissions. These changes could lead to structural rearrangements and to more defected crystallites of smaller surface tension.[22]

X-ray Diffraction
The X-ray diffraction of the unirradiated blends incorporated with different concentrations of DCP was discussed to clarify the change in the crystalline structure of PP due to the blending process, Figure 7 and Table II. It can be seen that the blend XRD maximum intensities decreased with increasing DCP feed ratio and the position of (2θ) at maxima was shifted to higher

values. Reduction in intensity may indicate that PP crystallinity ratio decreased and the orientation of molecules changed. On the other hand, the half-widths showed insignificant variation, indicating that the crystallite size remained unchanged.[23] PP crystallinity ratio remarkably decreased by prolonging the curing process, i.e., reduction in size, amount of crystallites, and averting molecule orientation.

Gamma irradiation is a statistical process in which any volume of a sample is equally likely to be irradiated.[24] Gamma irradiation up to 100 kGy of the sample containing 1% DCP did not induce important qualitative changes in the PP diffraction spectra. Further, the increase in radiation dose did not give rise to peak diffraction nor caused disappearance of the present ones, Figure 8 and Table II. This means that irradiation-induced scission or crosslinking in the macromolecules did not produce macromolecular reorganizations able to create new crystalline symmetries.

It was noticed that, crystallinity % of the 1% DCP sample slightly decreased with dose, this effect is mainly associated with considerable changes in the molecular characteristics of the individual polymers and correspondingly affects the microstructural arrangements of the chains. It is thought that, the main effects of dose on the molecular structure of PP are the reduction of molecular size and the incorporation of chemical groups, like carbonyl and hydroperoxides.[25] These processes destroy the ordered structure of PP crystals and correspondingly hinder the crystallization process. The synergistic eventual XRD results may suggest the prominent impact of the introduction of DCP with respect to the role of irradiation, as was aforementioned.

Thermogravimetric Analysis
The DCP molecules have no boiling point because they are easy to cleave and the half-life temperature is low.[26] Figure 9 and Table III show the mass loss curves of unirradiated DR/PP/EPDM composite vulcanized with DCP as a function of temperature. It was noticed that the decomposition temperature decreased as DCP wt % increased. This can be attributed to a degradation process taking place in the backbone of the macromolecules, as crosslinking creates tertiary carbon atoms in the polymer more susceptible to thermal degradation.[27] The utmost char yield was observed for the DCP 0.5 wt % treated sample which thereafter decreased by excessive load. The reported least

Table III. TGA Data of Unirradiated and Irradiated Blends of DR/PP/EPDM at Different Concentration of DCP Exposed to Different Gamma Radiation Doses

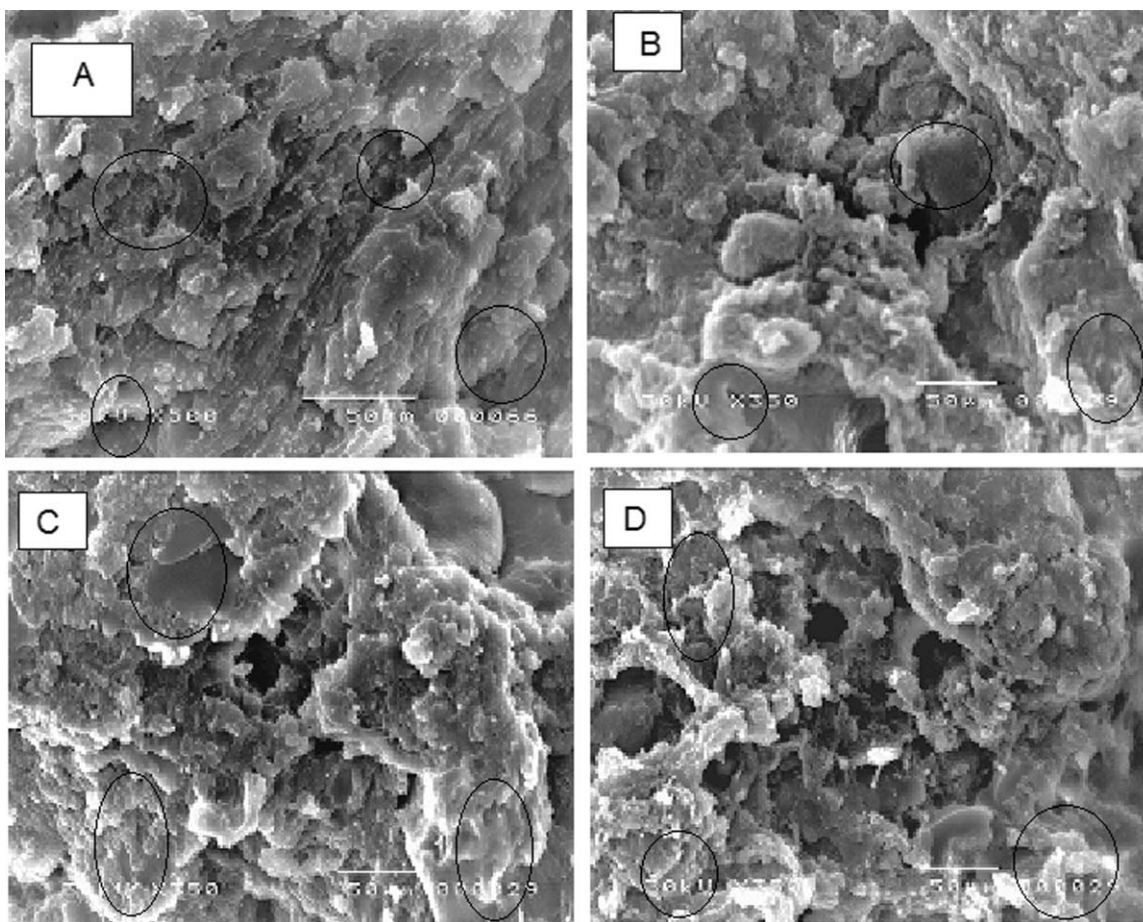| Sample composition	Dose (kGy)	$T_{(0.25)}$	$T_{(0.50)}$	$T_{(0.75)}$	Residual weight % at 600°C
DR/EPDM/PP/DCP (45/30/25/0) wt %	0	416.1	469.5	488.1	17.4
DR/EPDM/PP/DCP (45/30/25/0.5) wt %	0	404.8	456.5	468.7	22.8
DR/EPDM/PP/DCP (45/30/25/1) wt %	0	402.5	450.5	483.2	14.49
	25	440.6	478.4	499.5	17.5
	50	428.7	473.6	494.5	16.8
	100	433.4	478.4	499.4	16.7
DR/EPDM/PP/DCP (45/30/25/1.5) wt %	0	431.6	468.1	489.5	10.7

Figure 11. Scanning electron micrographs of unirradiated DR/ PP/EPDM (45/25/30) blends with different concentration DCP: (a) 0%, (b) 0.5%, (c) 1%, and (d) 1.5%.

char value was found associated with the DCP feed ratio 1.5 wt % which may be attributed to carbon black residue.

Within the temperature range 100–300°C, the mass loss is due to evaporation or decomposition of extender oil and other organic nonpolymeric additives present in the rubber compound.[28] For the tire rubber, the extender oil is typically a mixture of hydrocarbons such as aromatic oil which serves to soften the rubber and improve process ability. Another two stages of mass loss between 300 and 500°C correspond to the decomposition of rubber components. The low-temperature (~375°C) and high-temperature (~420°C) decompositions occurred due to the decomposition of natural rubber and styrene–butadiene rubber and/or polybutadiene rubber, respectively.[29] The degradation products of PP involves the monomers, 2-methyl-1-pentene, 2,4-dimethyl-1-heptene, 2-pentene, and isobutene.[30]

Figure 10 demonstrates positive correlation between thermal stability and dose. This may be explained by the thermal loss amongst the existing low molecular weight components which are either radiation-induced crosslinked or embedded in radiation-induced crosslinked structure.[31] Thus, the thermograms suggest the effective structural impact of irradiation with respect to the initial DCP induced-crosslinked structure.

Kinetic Analysis

Table II illustrates that the activation energy values (E_a) decreased by the elevation of DCP %, suggesting lesser thermally stable composites with respect to the pristine. This may be ascribed to the peroxide decomposition and its radical half-life time. A paramount increase in E_a reaching 242.3 kJ/mol was reported for the 1% DCP treated sample irradiated with 25 kGy. This outcome may shade light on the promoted crosslinked structure at such synergistic levels, which was thereafter relatively degraded by further irradiation via radiation-induced chain scission.

Scanning Electron Microscopy

In principle, TPVs show dispersed phase morphology in which crosslinked rubber particles are dispersed in continuous thermoplastic matrix as microgels. The DR particles have a rather broad distribution in size and the morphology of TPVs is often rather heterogeneous in space.[32] Figure 11 represents TPVs of irregularly shaped rubber particles.

Reduction in the domain size was determined, which can be attributed to the immobilization of rubber particles resulted from the induced crosslinking.[33] The dark areas are voids decreased as DCP wt % increased, revealing improvement in the network structure.
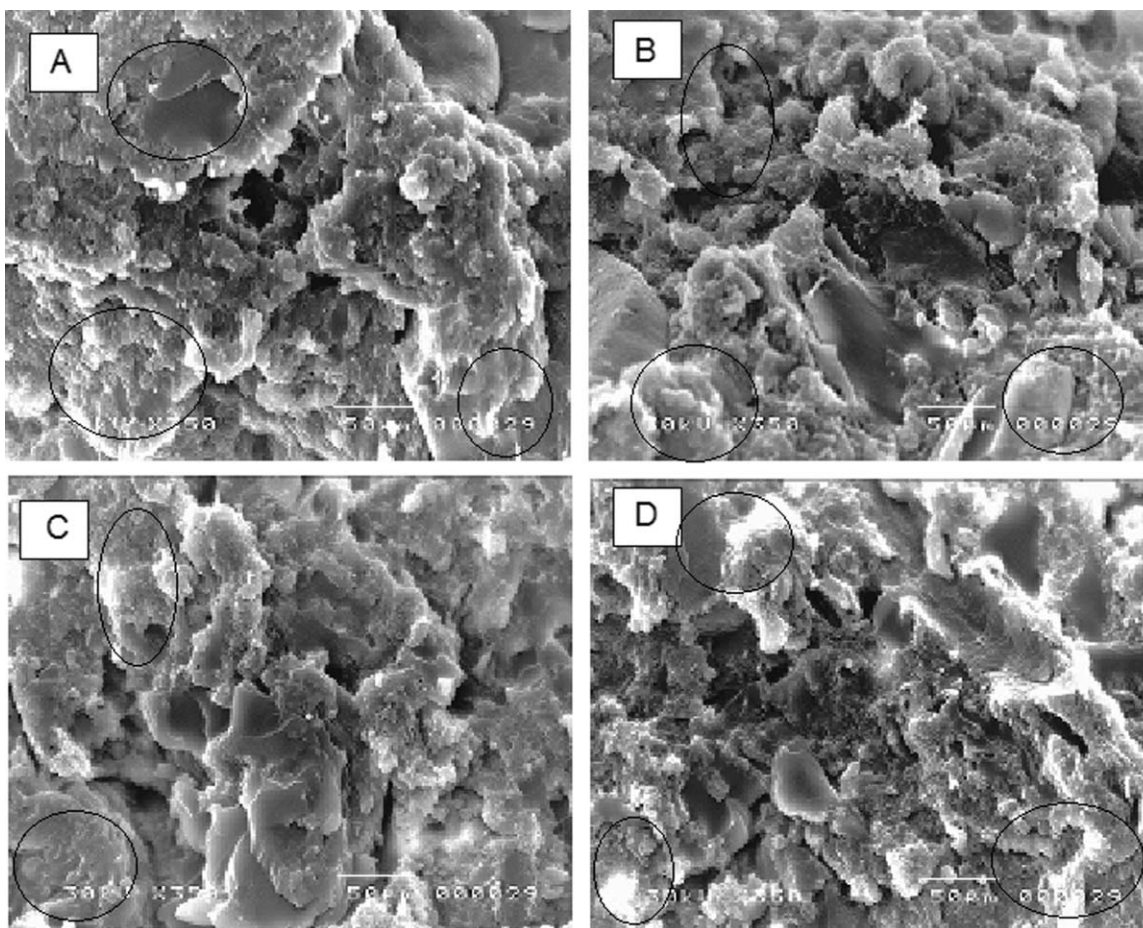
Figure 12. Scanning electron micrographs of DR/PP/EPDM/DCP (45/25/30/1) composite at various gamma radiation doses : (a) 0 kGy, (b) 25 kGy, (c) 50 kGy, and (d) 100 kGy.

The morphological investigation may support the mechanical testing yields of the DCP 1% treated samples irradiated up to 25 kGy, Figure 12, as the roughness in microstructures decreased with dose. Phase separation at the boundary surfaces was no longer observable as a result of radiation-induced cross-linking. However, at higher doses, oxidative degradation in the plastic phase was distinctive.

CONCLUSIONS

The DR/EPDM/PP (45/30/25) wt % composite was successfully prepared and subjected to varying ratio of DCP and γ-irradiation at various levels of dose. Incorporation of DCP raised gel percent of the pristine by $\approx$20%. Meanwhile, radiation dose hardly added to the developed gel fraction within the cited dose range. Thus, it can be concluded that, the development of the crosslinking network structure can be mainly accounted for the DCP radical yield. Maximum sample gel fraction could be attained at moderate synergistic levels, 1% DCP and 25 kGy dose, whereby mechanical, thermal, and physical investigations indicated thorough crosslinking and compatibilization. Tensile strength, elongation at break, and hardness increased by increasing dose up to 25 kGy. Higher doses gave rise to prevailing degradation process, mainly in the thermoplastic component.

Addition of peroxide up to 1% led to T_m shifts toward higher temperature, as a result of crosslink formation which makes PP chain unfolding plausible. However, as DCP load increased up to 1.5% T_m decreased, suggesting insignificant PP chain scission by the excessively produced DCP radicals. T_m slight shifts to lower temperature by irradiation reflects the subsequent insignificant contribution of the radiation-induced chain scission mechanism. XRD results of the synergistic impact suggest respective prominent influence of DCP incorporation. TGA thermograms emphasized higher thermal stability, provided by irradiation, than that by the initial DCP induced-crosslinked structure. A paramount increase in E_a, reaching 242.3 kJ/mol, was reported for the DCP 1% treated sample irradiated with 25 kGy. These outcomes may shade light on efficient crosslinked structure fabricated at such levels. TPVs have been developed for various applications in seals, wire and cable, bumpers, and automotive interiors.

REFERENCES

1. Debapriya, D.; Sukumar, M.; Basudam, A. *J. Appl. Polym. Sci.* **1999**, *73*, 2951.

2. Jacob, C.; De, P. P.; Bhowmick, A. K.; De, S. K. *J. Appl. Polym. Sci.* **2001**, *82*, 3293.

3. Jacob, C.; Bhattacharya, A. K.; Bhowmick, A. K.; De, P. P.; De, S. K. *J. Appl. Polym. Sci.* **2003**, *87*, 2204.

4. Ismail, H.; Nordin, R.; Noor, A. M. *Polym. Test.* **2002**, *21*, 565.

5. Naskar, A. K.; Bhowmick, A. K.; De, S. K. *J. Appl. Polym. Sci.* **2002**, *84*, 622.

6. Radeshkumar, A.; Karger-Kocsis, J. *Plast. Rubber Compos.* **2002**, *31*, 99.

7. Zhang, S. L.; Zhang, Z. X.; Kang, D. J.; Bang, D. S.; Kim, J. K. *e-Polymers* **2008**, *160*, 1.

8. Wiessner, S.; Wagenknecht, U.; Zichner, M.; Michael, H.; Heinrich, G. In 21st Polymer Processing Society, Leipzig (Westin Hotel), Germany, June 19–23, **2005**.

9. Tantayanon, S.; Juikham, S. *J. Appl. Polym. Sci.* **2004**, *91*, 510.

10. Sonnier, R.; Leroy, E.; Clerc, L.; Bergeret, A.; Lopez-Cuesta, J. M. *Polym. Degrad. Stab.* **2006**, *91*, 2375.

11. Abou-Zeid, M. M.; Rabie, S. T.; Nada, A. A.; Khali, A. M.; Hilal, R. H. *Nucl. Instrum. Methods Phys. Res. Sect. B* **2008**, *266*, 111.

12. Hassan, M. M.; Badway, N. A.; Elnaggar, M. Y.; Hegazy, E. A. *J. Ind. Eng. Chem.* **2013**, *19*, 1241.

13. Goldshtein, V.; Kopylov, M. U.S. Pat. 6,541,526 B1 (**2003**).

14. Hassan, M. M.; Aly, R. O.; Abdel Aal, S. E.; El-Masry, A. M.; Fathy, E. S. *J. Ind. Eng. Chem.* **2013**, *19*, 1722.

15. Rath, T.; Kumar, S.; Mahaling, R. N.; Khatua, B. B.; Das, C. K.; Yadaw, S. B. *Mater. Sci. Eng. A* **2008**, *490*, 198.

16. Ratnam, C. T.; Nasir, M.; Baharin, A.; Zaman, K. *Eur. Polym. J.* **2001**, *37*, 1667.

17. Sartomer Company. Liquid 1,2-Polybutadiene Resin as Coagent for EPDM. Technical Report. Appl. Bull. 5710. Sartomer Company: USA, **2005**.

18. Ismail, H.; Akil, H. M. *Polym.-Plast. Technol. Eng.* **2005**, *44*, 1217.

19. Kim, B. C.; Hwang, S. S.; Lim, K. Y.; Yoon, K. J. *J. Appl. Polym. Sci.* **2000**, *78*, 1267.

20. Halimatuddahliana, H. I. *Polym.-Plast. Technol. Eng.* **2009**, *48*, 34.

21. Babu, R. R.; Singha, N. K.; Naskar, K. *Mater. Des.* **2010**, *31*, 3374.

22. Stojanovic, Z.; Kacarevic-Popovic, Z.; Galovic, S.; Milicevic, D.; Suljovrujic, E. *Polym. Degrad. Stab.* **2005**, *87*, 279.

23. Senna, M.; Abdel-Fattah, A.; Abdel-Monem, Y. *Nucl. Instrum. Methods Phys. Res. Sect. B* **2008**, *266*, 2599.

24. Stojanovic, Z.; Popovic, Z.; Galovic, S.; Milicevic, D.; Suljovrujic, E. *Polym. Degrad. Stab.* **2005**, *87*, 279.

25. Otaguro, H.; deLima, L. F.; Parra, F.; Lugão, A. B.; Chinelatto, M. A.; Canevarolo, S. V. *Radiat. Phys. Chem.* **2010**, *79*, 318.

26. Xue, F.; Takeda, D.; Kimura, T.; Minabe, M. *Polym. Degrad. Stab.* **2004**, *83*, 461.

27. Marcovich, N. E.; Villar, M. A. *J. Appl. Polym. Sci.* **2003**, *90*, 2775.

28. Scuracchio, C. H.; Waki, D. A.; Silva, M. L. C. P. *J. Therm. Anal. Calorim.* **2007**, *87*, 895.

29. Sulkowski, W. W.; Danch, A.; Moczynski, M.; Radon, A.; Sulkowska, A.; Borek, J. *J. Therm. Anal. Calorim.* **2004**, *78*, 917.

30. George, S.; Varughese, K.; Thomas, S. *Polymer* **2000**, *41*, 5485.

31. Yasin, T.; Khan, S.; Chang, Y.; Ahmad, R. *Radiat. Phys. Chem.* **2012**, *81*, 421.

32. Machado, A. V.; Duin, M. *Polymer* **2005**, *46*, 657.

33. Perera, R.; Albano, C.; González, J.; Silva, P.; Ichazo, M. *Polym. Degrad. Stab.* **2004**, *85*, 741.