

EPDM recycling assisted by γ -processing

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Abstract The integration of waste ethylene–propylene–diene terpolymer (EPDM), containing carbon black into pristine EPDM can be achieved by γ -irradiation as a versatile procedure to process ethylene–propylene elastomers. The presence of acrylic acid in the material formulation allows the formation of intermolecular bridges by threefold increase in gel content. The possibility of achieving greater stability by the addition of acrylic acid in EPDM systems was analyzed. The start materials were EPDM containing 30 and 50 phr of EPDM powder loaded with 40 phr of carbon black aged by pre-exposure to electron beam irradiation. The advanced γ -irradiation exceeding 100 kGy represented the optimal radiation processing condition. Two procedures of chemiluminescence under isothermal and non-isothermal regimes for the evaluation of radiation stability were applied on γ -irradiated samples. The thermal strength of irradiated samples was characterized based on the radiolysis mechanism of EPDM. The variation in the activation energy required for the thermal oxidation of these samples and the modification in gel contents due to the gelation action of acrylic acid were presented for the validation of proposed recycling radiochemical technique. Charlesby–Pinner representation provided different values for the ratios between radiochemical yields of cross-linking and scission, proving that the presence of acrylic acid

promoted the conversion of EPDM wastes into valuable materials.

Keywords EPDM · Radiation compatibilization · Recycling

Introduction

The recycling process through which the waste materials are reclaimed to achieve an economically feasible route allows the recycling of polymer materials under various formulations [1]. The classical compatibilization of two polymers becomes effective under the thermodynamic conditions of miscibility and follows Flory–Huggins relationship [2]. Several examples of polymer mixtures verify the possibility of blend homogenization for further applications [3–5]. The high energy irradiation (exposure to electron beams or gamma rays) is a proper procedure by which the materials are turned onto desired products to be available for other technologies [6, 7]. In essence, the polymer recycling by radiation processing is based on the possibility to break chemical bonds followed by the addition of desired structures existing in different appropriate formulations or on the transformation into useful and stable materials.

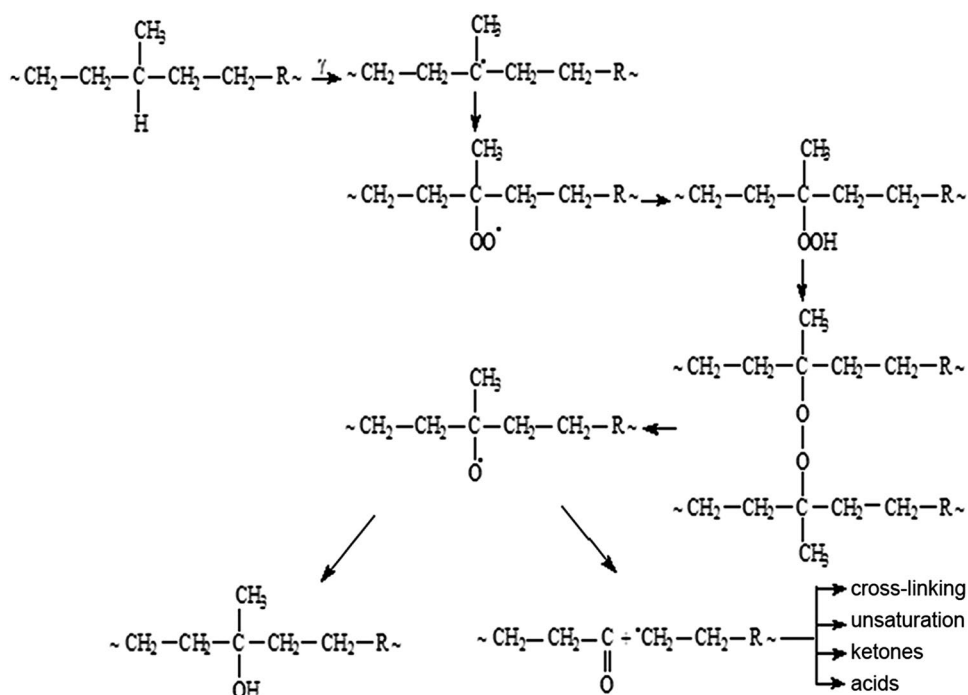
The radiation effects on ethylene–propylene–diene rubber (EPDM) have been reported earlier. Rivaton et al. [8] demonstrated that the radical mechanism generally adopted for polyolefins would lead to random chain breaking, but the larger proportion of radical generation was provided by tertiary carbon atoms. According to Ito [9] and Zaharescu et al. [10], the chain degradation preferentially starts on propylene and so far the dominant feature that influences oxidation of irradiated EPDM is the constitutive ethylene/propylene ratio [11]. Davenas et al. [12] analyzed

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Fig. 1 Proposed γ -radiolysis mechanism of EPDM



the progress in the oxidative degradation induced by ionizing radiation and discussed the importance of structural features on the manner and rate of Radio oxidation in the context of irradiation processing of EPDM as a crosslinkable polymer. Fuzail et al. reported the linearly increased concentration of radicals found by ESR spectroscopy [13], while the mass distribution turned to inferior intervals at higher doses in direct proportionality between relative variation of weight-average molecular weight and factor $[G(S)-4G(X)]$, where $G(S)$ is scission radiochemical yield and $G(X)$ is cross-linking radiochemical yield [14]. For ethylene-propylene-diene rubber, $G(X)$ is lower than that of $G(S)$, such that the degradation prevails compared to cross-linking.

The oxidative degradation is influenced by the degree of ordering in the polymer materials processed by radiochemical techniques [15, 16]. Over low and medium dose range the crystalline and semi-crystalline macromolecular materials exposed to γ -irradiation are not subjected to any significant changes in their structural configurations even the irradiation would be carried out at medium temperatures. As it would be expected, the diffusion rate of oxygen would not be meaningfully influenced by light morphological modifications in the context of the preservation of oxidation barrier like crystalline phase. The analogy between thermal degradation and radiation degradation concerning their mechanisms allows γ -exposed EPDM to present different values of activation energies required for oxidation determined by different proportions of propylene segments. This property can be foreseen, because the proportion

of higher substituted carbon atoms defines the polymer strength against oxidation. A detailed analysis of the distribution of oxygenated stable products in the γ -radiolysis of polymers [10] reveals that the scission of long unsubstituted chain generates carboxylic acids as primary structures, while the break of a bond belonging to a substituted carbon atom creates ethers and alcohols as dominant oxidation products [17, 18]. In addition, significant amounts of water appear from the degradation on secondary or tertiary carbon atoms. The general mechanism for the oxidation of EPDM based on the preferential scissions at tertiary carbon atoms followed by the γ -scission of tertiary hydroperoxides present in large amount is shown in Fig. 1, as suggested earlier for polypropylene [19, 20].

The addition of compatibilizer such as a monomer with vinyl structure may create three-dimensional network after the cleavage of double bonds [21, 22]. For example, the acrylic structure is suitable for scavenging free radicals into a cured fraction with high stability material. The stability of acrylic-based structures restrains the material aging and prolongs the life time of polymers [23].

Experimental

Ethylene-propylene-diene rubber (EPDM) was provided by Lanxess, Brazil. Rubber powder of EPDM was obtained from RPolymers LTDA (Brazil). Blending was accomplished on an open mill from Cope according ASTM D-3182 at 50–60 °C to prepare a preformulation

(masterbatch) containing 50 % of EPDM and 50 % of EPDM powder. The pre-irradiation of EPDM powder was accomplished in an electron beam accelerator, whose dosimetry was monitored by electrometry. The irradiation of compounded specimens was done in air at room temperature in a Gammacell M-38 (USA) irradiator provided with γ -source (^{137}Cs), whose dose rate was calculated starting from the spectroscopic records on a Fricke dosimeter at 0.4 kGy h^{-1} . Acrylic acid (Merck, Germany) and *o*-xylene (Chemopar, Romania) were used as received.

Gel fractions were determined by reflux for 24 h followed by drying in an electrical oven to constant weight after second boiling in ethylic alcohol for 10 h.

The determination of oxidation stability of electron beam (EB)/pre-irradiated samples was performed by two chemiluminescence (CL) methods, isothermal and non-isothermal procedures. LUMIPOL 3 (Slovak Academy of Science, Institute of Polymers, Bratislava) was used for the photon counting of degrading specimens. To accomplish these studies, the EB/pre-irradiated materials were placed into chloroform solutions. After the addition of acrylic acid of 3 phr concentration and stabilizer Irganox 1010 of 0.3 phr, small volumes were evaporated in the round aluminum trays destined to CL investigations, while most part of the solutions were evaporated for the preparation of specimens used in the determination of gel fraction. The non-isothermal measurements were done at the heating rate of $5 \text{ }^\circ\text{C min}^{-1}$, while the isothermal determinations for the calculation of activation energy were carried out over the interval from 200 to 230 $^\circ\text{C}$.

Results and discussion

The action of ionizing radiation (accelerated electrons and gamma rays) on polymer consists in the formation of radicals, hydrocarbon radical intermediates, which further participate in cross-linking or oxidation reactions. They possess enough energy transferred from incident radiation spent for their reactions with available entities like radiolysis products or diffused molecular oxygen. These processes require certain activation energy, which can be globally determined as the threshold condition of processing. The absorbed dose describing the received energy is the main factor in determining the degree of modification. In Fig. 2 the difference between the structural changes reveals a slight increase in the thermal stability of the previously EB-irradiated samples.

The contribution of irradiation is decisive in the accumulation of long life radicals involved in material cross-linking (Fig. 1). The onset oxidation temperature of EPDM containing 50 phr of polymer powder is higher at about 20 $^\circ\text{C}$ in comparison with that of lower powder

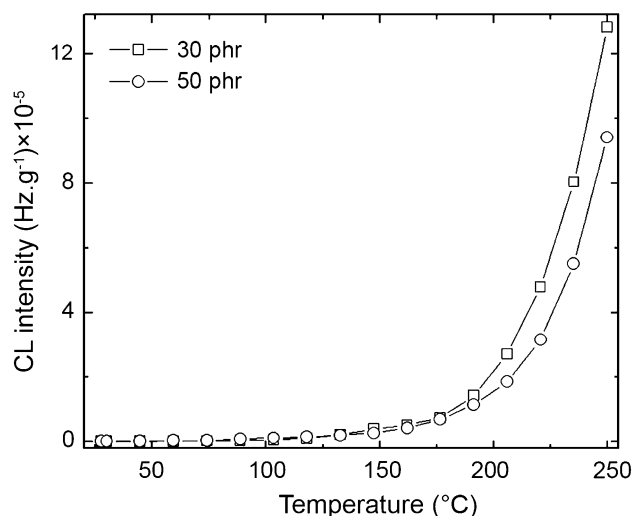


Fig. 2 Non-isothermal CL spectra recorded on samples EB-irradiated at 150 kGy

content. It oxidizes much slower at temperatures exceeding 130 $^\circ\text{C}$. The radiation vulcanization takes place at higher doses according to the saturated structure on EPDM backbones and the low concentration of constitutive tertiary carbon atoms [18]. The waste-polymer phase is the radical source for the random processes, cross-linking and oxidation. The absence of other CL intensity maxima before starting the advanced oxidation explains the lack of other intermediates appeared during radiolysis except the radicals formed by homolytic scissions of C–C bonds of higher substituted carbon atoms. The polymer powder incorporated in EPDM bulk contains also preexisting radicals formed during its manufacture. Their further availability to reactions is the determining feature in the postirradiation concern. The radiation processing is an efficient procedure for the conversion and modification of polymers by their intrinsic fragmentation, but the presence of sensitizers [24], the faster degradation of one of its component [25] or the addition of stabilization agent [26] may deviate mechanisms toward unforeseen directions.

The oxidation vector and peroxy radicals, act similarly in both above formulations at low and medium temperatures up to around 150 $^\circ\text{C}$. At very high temperature range and higher EPDM powder content, the slower oxidation rate indicates a more efficient diffusion of radicals into solid state elastomer. The simultaneous diffusion of reacting moieties, such as radicals and oxygen, feeds the competitive processes, gelation and degradation, which help the radiation processing of elastomer wastes [27–29]. Our results indicate that the grounded elastomer can be successfully used as ingredient in different technologies for the manufacture of thermoplastic blends.

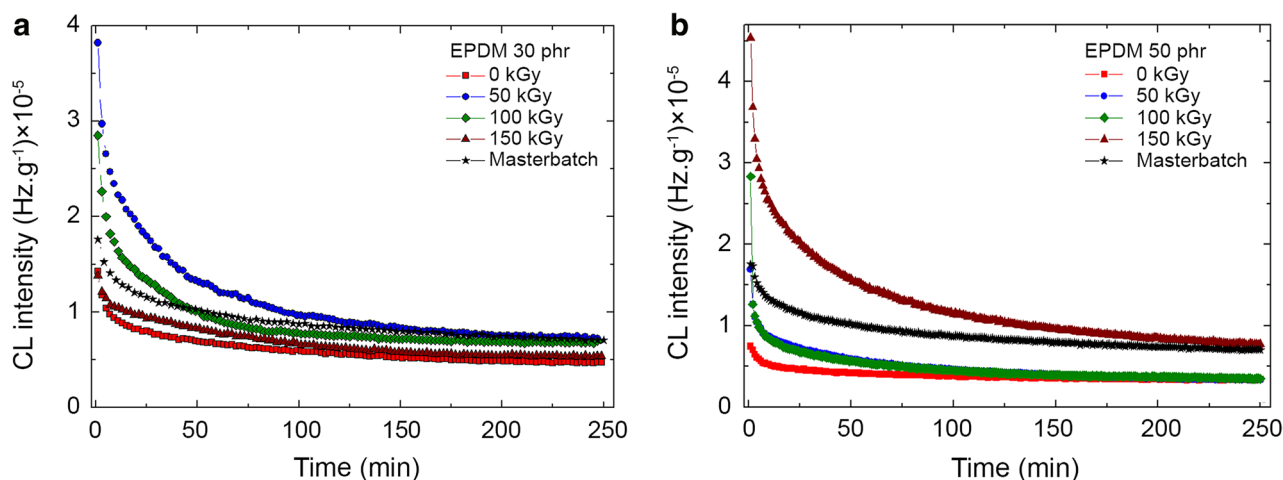


Fig. 3 Isothermal CL spectra recorded at 200 °C on EPDM samples

The isothermal oxidation of EPDM samples consisting of EPDM masterbatch and two concentrations of the same elastomer in powder state illustrates the intrinsic role of powder (Fig. 3a, b). The reverse distribution of curves recorded at increasing EB-dose is the consequence of more consistent contribution involving preexisting radicals to the initiation of oxidative degradation. If the degradation initiated by the radicals contained in powder phase is assured, the tendency to achieve pseudoplateau is the proof for their decay during oxidation. In fact, the levels of CL intensities are similar in the both cases of formulations, but the attenuation of radical concentrations defines the implication of polymer powder in the basic material processing.

The values of initial intensities measured at different doses are indications of the amount of initial quantities of radicals that are oxidized in the first moments of chemiluminescence measurements. The reverse sequences of the two types of compositions are the result of waste component availability to be preferably subjected to oxidation, when no favorable condition exists for cross-linking.

The energies required for the oxidation of the EB-irradiated ethylene-propylene terpolymer can be judged with respect to nonirradiated states (Fig. 4). For a low received dose, 50 kGy, the amount of radicals available for cross-linking is not sufficient and their far separations permit them to react with oxygen rather than with each other or with other macromolecules. The amount of feeding oxygen does not cause critical situation, while an O₂ excess will efficiently block the interradical reactions. Instead of the propagation of cross-linking loop, radicals are involved in a degrading action. For further irradiation, the competition between a drop in soluble fraction and degradation takes place by former process. The thermal stability becomes more relevant and the energy demanded for the aging of

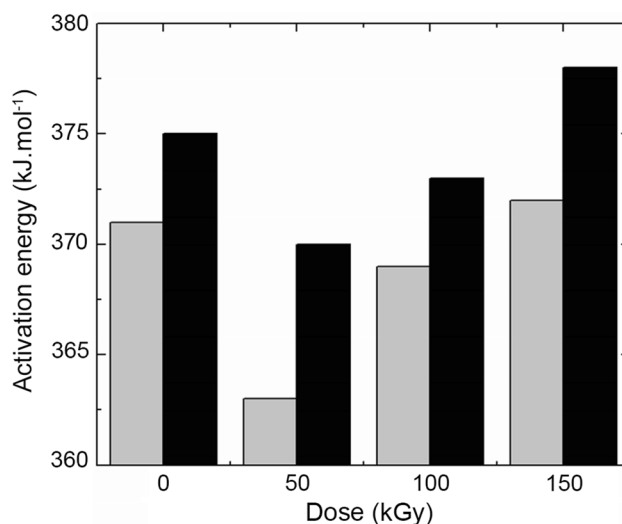


Fig. 4 Activation energies required for oxidation of EPDM γ -irradiated samples:(gray) samples with 30 phr of EPDM powder; (black) samples with 50 phr of EPDM powder

elastomer is higher in comparison with the nonirradiated material.

The presence of crosslinkable monomer, in our case acrylic acid, provides the cross-linking of radicals by scission of vulnerable double bonds. The accumulation of reactive units in the sample volume allows the increase in the gel fraction (Fig. 5). Acrylic acid creates intermolecular bridges, which increase the molecular order, decrease the diffusion rate of oxygen and improve the oxidation strength. The gel fraction is grown faster in the elastomer with higher content of polymer powder. The augmentation of gel fraction is not too extended, even though the applied γ -dose is high enough. The low dose rate is the main reason

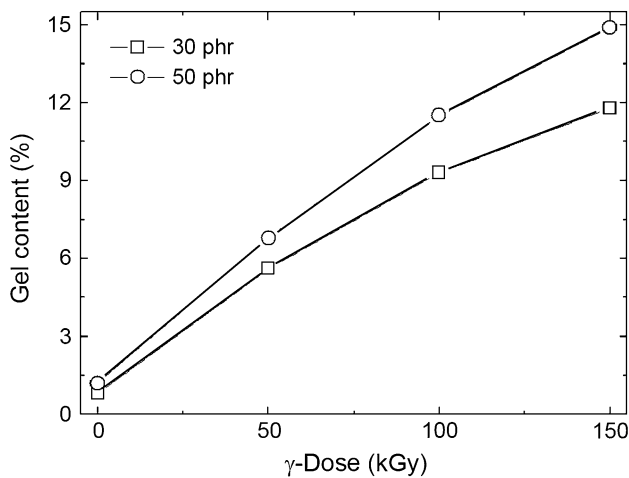


Fig. 5 Modification in gel dose in γ -irradiated EPDM/AAC systems

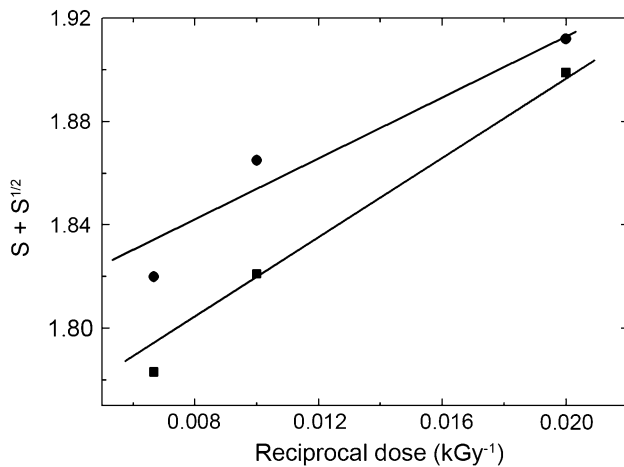


Fig. 6 Charlesby–Pinner representation for γ -irradiated EPDM/AAC systems

which promotes a larger contribution of the radical decay by oxidation. The consumption of cross-linking initiators diminishes the chance of the interaction between them and polymer chains.

However, the depletion of free hydrocarbon radicals in the interaction with acrylic acid leads to a buildup of macromolecular network when the ratios between the radiochemical yield of cross-linking and radiochemical yield of scission [$G(X)/G(S)$] become higher than unit. This feature demonstrates the availability of EPDM wastes for the generation of more stable EPDM product and the background for the extension of radiation processing onto the polymer recycling. In Fig. 6, the representation of Charlesby–Pinner dependency is linear. The intercepts are 1.73 and 1.78 for the EPDM blends containing 30 and 50 phr of polymer powder, respectively.

The mathematical relationships obtained for these dependencies are:

$$30\text{phr} : S + S^{1/2} = 1.72 + 8.59 \times (1/D) \text{ correlation factor} : 0.0895$$

$$50\text{phr} : S + S^{1/2} = 1.78 + 6.39 \times (1/D) \text{ correlation factor} : 0.0985.$$

The comparison of intercepts highlights the possibility of EPDM recycling in powder form. The values exceeding unit depicts that our procedure can be proper for the embedding wastes as micronized phase in the pristine materials. The optimal processing with accelerated electrons creates a satisfactory concentration of cross-linking intermediates. Acrylic acid is effectively consumed for macromolecular bridging offer convenient $G(X)/G(S)$, values with 1.75 times much higher than 1. The described procedure can be extended to other polymers, whose waste amounts represent a real pollution factor.

Conclusion

This study demonstrates the possibility of radiation processing to recover polymeric wastes by the addition of a crosslinker in the irradiating formulations by which the pollution by polymer product wastes can be efficiently diminished. The powdered aged material is a suitable alternative for the embedding waste fraction in the pristine fraction. The favorable ratios between the radiochemical yields of cross-linking and scission prove the participation of acrylic acid for the buildup of gel fractions. Chemiluminescence method as isothermal and non-isothermal procedures can characterize the preexisting radicals which contribute to the homogenization of processed materials. The conversion of pre-irradiated polymers into useful materials is a practical option for the recovery of materials by clean technologies; the recovery being useful for expanding the diversity of commodities, anticorrosive materials, thermal insulations in buildings, computer cases and plastic bags.

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