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Antioxidant Effects of Rosemary Extract on the Accelerated Degradation of Ethylene-Propylene-Diene Monomer

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The influence of natural antioxidants (rosemary extract, capsaicin, quercetin, or oleanolic acid) in ethylene-propylene-diene-monomer (EPDM) thermal behavior has been investigated by the means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). EPDM and EPDM/rosemary (RM) composite are investigated with a thermogravimetric (TG) balance in dynamic heating conditions (25°C-700°C). DSC analysis is also carried out from subambient to better highlight the melting of the polymer and the composite. The obtained DSC and TG values are discussed to have information about the effect of RM content in the polymer stability.

1. Introduction

Ethylene-propylene-diene monomer (EPDM) is an important class of elastomers, which owe their success to the ability in crosslinking via sulfur vulcanization, thus replacing ethylene propylene rubber[1] and reaching, in the 1980s, 6% of the total synthetic rubber production.[2]

EPDM is probably the main insulation material in joints and terminals of cable accessories, and it is widely used in automotive sector[3] and in outdoor electrical insulator.[4] These outstanding properties are due to the absence of double bonds in the polymer chain and the easiness of cross-linking process due to the unsaturated sites on its side chain,[5] thus giving rise to different degrees of degradation. Among the factors that can be considered in EPDM stabilization, the presence of antioxidants has been widely investigated,[6–9] since the addition of proper molecules can improve the oxidation resistance provided by the interference in the degradation mechanism[7] and the protection of the various intermediate radicals, continuously generated during the polymer aging.[10] The success of these molecules, as in the case of rosemary (RM) extract, is due by the availability of mobile proton of hydroxyl (phenolic) groups. In this work, with the aim to protect EPDM against degradation, we evaluated the thermal behavior of EPDM/RM composites. The prepared composite, prior to be thermally investigated, was subjected to γ-irradiation, since the accelerated degradation caused by the γ-irradiation is an adequate procedure for the evaluation of antioxidant properties of additives because they are able to interfere with the chain intermediates by the breaking of self-catalytic process of oxidation. Considering that the EPDM's melting occurs just above room temperature, the calorimetric investigation was carried out starting from subambient (-40°C), while the resistance to the thermal degradation was evaluated by thermogravimetric analysis (TGA), extrapolating from TG curves the initial decomposition temperature (T_i) and the amount of the solid residue at 700°C. The prepared composites were compared with the pristine EPDM to verify the effect of the rosemary presence and that of the irradiation process.

2. Results and Discussion

DSC analysis was first carried out from -40°C to 125°C, the choice to start scans from such a low temperature was to better highlight the melting that for EPDM occurring just above the ambient temperature. DSC thermograms for unirradiated and irradiated samples are shown in **Figure 1**, while onset melting temperature (T_{onset}), peak melting temperature (T_m), and enthalpy of melting (ΔH_m) values are reported in **Table 1**.

A thermal effect, which was more evident for the irradiated samples than for the unirradiated ones (Figure 1), was observed before the melting temperature range, probably due to the end of the glass transition that for EPDM generally occurs at about -50°C.[11] The lower intensity of this effect for nonirradiated samples could be due to a lower mobility, which then increases following irradiation process. As shown from the data in Table 1, the presence of rosemary in EPDM slightly increases the T_{onset} values, at the same way for the unirradiated and irradiated samples, thus indicating a minimum stabilization effect. The prepared samples were then subjected to TGA, and their TG curves are shown in **Figure 2** for the unirradiated and irradiated EPDM and EPDM/RM composite. No differences have been noticed among the degradation mechanism of EPDM and EPDM with rosemary

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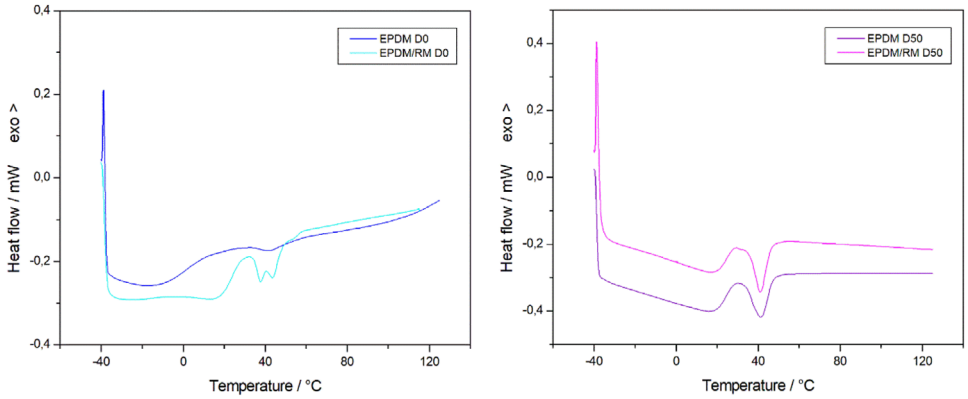

Figure 1. DSC curves, at 10°C min^{-1}, for unirradiated (D0, on the left) and irradiated (D50, on the right) EPDM and EPDM/RM composite.

Table 1. Onset melting temperatures (T_{onset}), peak melting temperatures (T_m), and enthalpy of melting (ΔH_m) for unirradiated and irradiated EPDM and EPDM/RM composite.

Samples	T_{onset} [°C]	T_m [°C]	ΔH_m [Jg^{-1}]
EPDM D0	33.3	42.6	0.66
EPDM/RM D0	34.3	37.9	4.36
EPDM D50	33.5	41.4	5.63
EPDM/ RM D50	35.7	40.9	5.38

added, while a different degradation behavior has been observed as a function of the environment of degradation.

In inert atmosphere, both EPDM and EPDM/RM degraded in a single stage with completely weight loss, while in oxidative environment, a second little degradation step, less intensive with respect the main one, is visible at about 500°C (Figure 2). As regards the effect of rosemary content on the composite degradation and related values, we reported the initial decomposition temperatures (T_i), the peak temperatures (T_p), and the percentage residue obtained at 700°C for the studied samples in inert and oxidative atmosphere in Tables 2 and 3, respectively.

From the data reported in **Tables 2 and 3**, it is possible to observe that although for the unirradiated samples, the presence of rosemary in EPDM seems to not positively affect the decomposition temperature, the irradiated samples seem to benefit from the presence of the natural antioxidant. In particular, in oxidative atmosphere, a T_i value 13°C higher with respect that of the pristine polymer has been detected, thus showing an important stabilization effect.

3. Conclusion

EPDM-rosemary composite was prepared and then γ-irradiated with an irradiation dose of 50 kGy to verify the effects on the thermal behavior of both composite and pristine EPDM. DSC analysis showed that the queue of the glass transition is more pronounced for the irradiated samples, while loss intensity for the unirradiated ones, probably due to the restriction of mobility before the induced degradation caused by irradiation process. As regards the melting, it seems that the presence of rosemary leads to a slight increase in the T_{onset} values, thus showing a stabilization effect. A different degradation mechanism was observed for EPDM and EPDM/RM as a function of the environment used for the TGA. In inert atmosphere, the samples degraded in a single stage, while the presence of an oxidative atmosphere caused the presence of two stages of degradation, with the second stage much smaller than the first one. Finally, the initial decomposition temperature for EPDM/RM at 50 kGy of irradiation showed an increase of 13°C with respect that of the pristine polymer, thus confirming the stabilization effect due to the presence of rosemary.

4. Experimental Section

Materials: EPDM was obtained by DSM Elastomers as KELRAN 8550, with the following molecular chain composition: two-thirds of ethylene and one-third of propylene, with a concentration of 5.5 wt% of diene (5-ethylidene-2-norborene). Quercetin, capsaicin, and oleanolic acid were obtained by Sigma Aldrich (USA). About 10 g of Rosemary leaves were first dried and then placed in an Erlenmeyer with ethanol (rosemary/solvent ratio = 1:10 w/v) and permanent shaking. After 5 days, we separated the liquid from the leaves' residue by filtration, while the residue solvent was removed by evaporation under vacuum. The purchased EPDM was placed in a chloroform solution for the removal of insoluble fraction. The clear polymer solution was then loaded with 1 phr of rosemary and 0.5 phr of quercetin, capsaicin, and oleanolic acid, and the final specimens (1 mm thick foils) were obtained by chloroform volatilization at room temperature.

Methods: A 50 kGy irradiation was carried out γ-exposure in an irradiation room provided with a ^{60}Co source, whose specific dose rate was 0.6 kGy h^{-1}. Calorimetric measurements were performed in a Mettler DSC 1 Star System, which was calibrated following the manufacturer's suggestions reported in the user manual and applied in previous studies.[12] Sealed aluminum crucibles, containing about 6.0 10^{-3} g, were heated from -40°C to 125°C, with a scanning rate of 10°C min^{-1}. Multiple experiments were performed, and the considered values were averaged from those of three runs (being ±1°C the difference between the average and the experimental values). Thermal behavior was evaluated with a Mettler Thermogravimetric Analyzer TGA 1 Star System, which was calibrated in agreement with previous work.[13] About 5•10^{-3} g of samples was placed in alumina pan and heated from room temperature up to 700°C, in dynamic

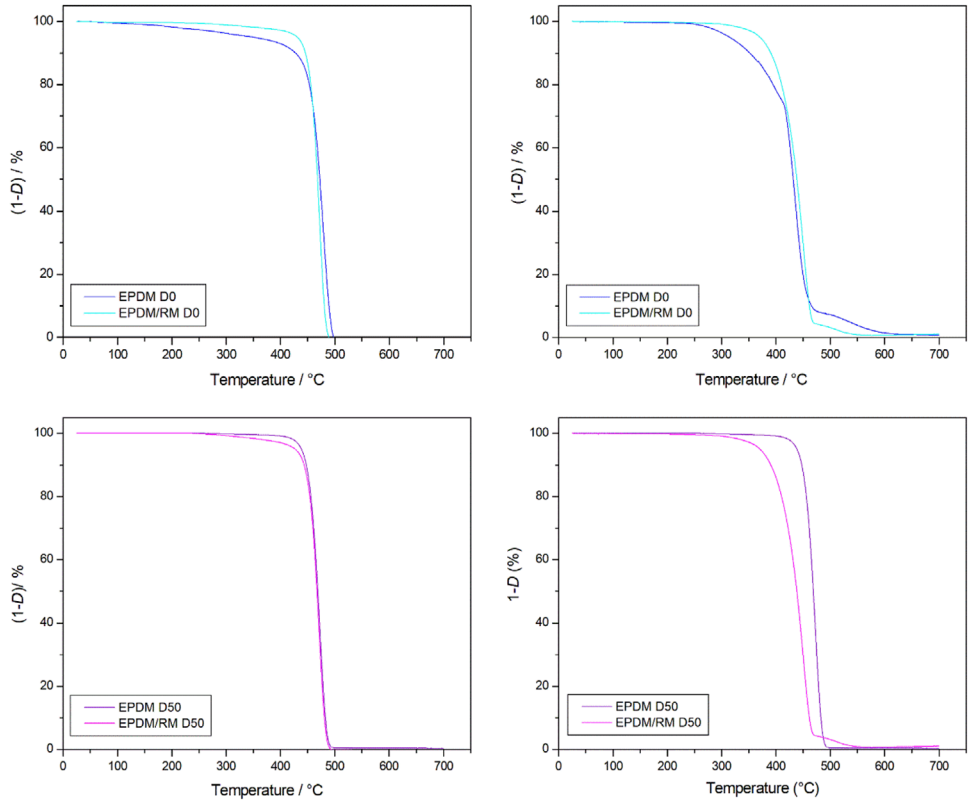

Figure 2. TG degradation curves, at 10°C min^{-1}, under nitrogen (top left) and air (top right) flow for unirradiated samples, and under nitrogen (lower left) and air (lower right) flow for the irradiated ones.

Table 2. Initial decomposition temperatures (T_i), peak temperatures (T_p), and residue % at 700°C for unirradiated and irradiated EPDM and EPDM/RM composite in inert atmosphere.

Samples	T_i [°C]	T_p [°C]	Residue [%]
EPDM D0	450.6	476.3	0
EPDM/RM D0	448.7	469.0	0
EPDM D50	453.7	469.3	0
EPDM/ RM D50	452.2	468.2	0

Table 3. Initial decomposition temperatures (T_i), peak temperatures (T_p), and residue % at 700°C for unirradiated and irradiated EPDM and EPDM/RM composite in oxidative atmosphere.

Samples	T_i [°C]	T_p [°C]	Residue [%]
EPDM D0	406.8	435.7	0
EPDM/RM D0	386.9	444.3	1.05
EPDM D50	382.4	423.5	0
EPDM/ RM D50	395.8	441.3	0

mode (10°C min^{-1}), in nitrogen and oxidative flows (0.06 L min^{-1}). The obtained thermogravimetric (TG) data were plotted as percentage of undegraded sample, (1-*D*) % against temperature, where $D = (Wo\text{-}W)/Wo$, and Wo and W were the weights at the starting point and during measurement.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The study did not report any data.

Keywords

antioxidant activity, EPDM, rosemary, stabilization, γ-irradiation

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