The effect of polyhedral oligomeric silsesquioxanes (POSSs) incorporation in ethylene-propylene-diene-terpolymer (EPDM): a thermal study

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Abstract

A series of ethylene-propylene-diene-terpolymer (EPDM)/polyhedral oligomeric silsesquioxane (POSS) composites at different percentage of POSS were prepared and subjected to γ -irradiation. Both irradiated and non-irradiated EPDM and composites were investigated by the means of thermal analysis to verify if the presence of POSS molecules is able to reduce the oxidation level of free radicals generated during the degradation and to evaluate the effects of the irradiation. EPDM composites at 1, 3 and 5 mass% of POSS were thus degraded in a thermogravimetric (TG) balance in dynamic heating conditions (25–700 °C), in both inert and oxidative atmosphere by flowing nitrogen and air respectively. Thermal characterization was then completed by carrying out Differential Scanning Calorimetry (DSC) analysis from sub-ambient to better highlight the melting of the polymer and polymer composites occurring just above the room temperature. FTIR spectroscopy was also performed for the prepared samples to check the presence of the molecular filler in the composites and for the TG's residue at 700 °C, in order to evaluate its nature. DSC and TGA parameters were detected and discussed to have information about the effect of the degradation's environment, the effect of irradiation on polymer stabilization and the effect of POSS content in the polymer matrix.

Keywords POSS · EPDM · Thermal stability · Oxidation · FTIR · Thermogravimetric analysis

Introduction

With the acronym EPDM it indicates a family of synthetic rubbers, namely terpolymers obtained from the copolymerization of ethylene (E), propylene (P) and a diene (D). The M is for elastomers having a saturated chain of the polyethylene type [1]. Historically the importance of EPDM is related to their ability in crosslinking via sulfur vulcanization, thus replacing ethylene propylene rubber (EPR), that contains no diene units and can only be crosslinked using radical methods such as peroxides [2]. During the gold age of the petrochemical industry, around the '80 s, EPDM reached the

production of 279,000 metric tons, that means about 6% of the total synthetic rubber production with a higher growth rate than the other ones [3]. For many years EPDM family recorded the fastest growing on the markets, as regards elastomers, due to its outstanding properties. In particular, the absence of double bonds in the polymer chain backbone makes EPDM less sensitive to oxygen, thus allowing its use in outdoor applications [4, 5]. The key of EPDM properties is represented by the easiness of cross-linking process due to the unsaturated sites on the side chain of EPDM [6]. Infact, in this terpolymer, ethylene and propylene monomers provide a saturated backbone interrupted by the incorporation of non-conjugated diene monomers, these latter are responsible for the unsaturated groups in EPDM [7]. The other side of the coin is that polymer's crosslinking leads to different degrees of degradation, thus required further EPDM's stabilization prior to the main applications. The described characteristics allow a widely use of EPDM in automotive sector [5, 8] and as an outdoor electrical insulator [9]. EPDM can be considered the main insulation material in joints and terminals of cable accessories [10,

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[11] but because of the two-phase interface or electric field concentration present in these accessories, it is exposed to easy degradation in both direct or alternating high voltage current [12]. To avoid this degradation, accounted for 21% of the cable systems [13], researchers focused their attempts in the modification of the insulation material by using nanofillers, showing good results in inhibition of the degradation phenomena [14–16]. Coupling with the mentioned properties, more recently EPDM showed also considerable physical characteristics (high elasticity, abrasion and corrosion resistance) thus allowing the extension of its applications to more industrial areas [17] and again, aiming at further expand its useful life in kinds of severe environments, their thermal properties have been widely investigated [6, 7, 18–20].

Polyhedral oligomeric silsesquioxanes (POSSs) have been identified as the ideal class of nanometric reinforcements to restrain electrical degradation, thus improving the lifetime of insulation materials [21] and enhance the resistance to the thermal degradation [22, 23]. In a context of an increasingly frequent use of hybrid materials, POSSs have been covered in the last twenty years a dominant position with respect to the reinforcement of polymeric materials [24]. The incorporation (chemical or physical) of these three-dimensional nanometer size cage structures having Si vertices interconnected by $-O-$ linkages, and substituents organic groups attached to silicon atoms gives rise to polymer nanostructured materials (PNMs) with interesting mechanical and physical properties, thus representing a radical alternative to the traditional filled polymers or polymer compositions [25].

The combination of their rigid inorganic skeleton with the organic periphery constituted by functionalized or not vertex groups, makes POSS a perfect hybrid building blocks that, as a function of the number and kind of organic groups, can be chemically built into a polymer structure as a side group of the main chain or terminating end-group [26].

The research focused on POSS-containing polymer has been growing in the recent years achieving important goals in term of thermal and mechanical stability, maintaining non-toxicity and biocompatibility [27–33]. In particular thermal methods are recognized as a very important tool in the characterization of nanoparticles for reinforcement of polymeric matrices [34–37].

Thus, with the aim to protect EPDM against accelerated degradation, we evaluated the thermal behaviour of EPDM and EPDM/POSS composites at different mass percentage (mass%) of octa-vinyl POSS and at different level of irradiation (Fig. 1). First, the prepared composites were investigated by Fourier transform IR (FTIR) in order to verify that they corresponded to what was designed to achieve with the design and preparation. Since the melting behaviour of EPDM occurs just above room temperature, the calorimetric investigation was carried out starting from sub-ambient

Fig. 1 Molecular structure of the octa vinyl polyhedral oligomeric silsesquioxane (POSS)

(40 °C), whilst the resistance to the thermal degradation was evaluated by thermogravimetric analysis (TGA), extrapolating from TG measurements the initial decomposition temperature (T_i) and the amount of the solid residue at 700 °C. The prepared composites and the control EPDM were also subjected to γ -irradiation to verify the effect of the irradiation process on the polymer and polymer composites degradation.

Experimental

Materials

Ethylene-propylene-diene monomer (EPDM) was purchased by DSM Elastomers (The Netherlands) as KELTAN 8550 (average molecular mass 217 kg mol^{-1}). The molecular chains consist of two thirds of ethylene and one third of propylene, with a concentration of 5.5 mass% of diene (5-ethylidene-2-norbornene). Octavinyl—polyhedral oligomeric silsesquioxane (molecular mass $633.04 \text{ g mol}^{-1}$) was purchased by Sigma Aldrich (USA). EPDM were first treated with chloroform to remove possible insoluble fraction. The defined POSS content (1, 3 and 5 mass%) were added to the clear polymer solution, preparing separately each composite formulation. Thus, the specimens were obtained, as 1 mm thick foils, eliminating chloroform by volatilization at room temperature. The accelerated degradation of samples was achieved by the γ -exposure in an irradiation room provided with a ^{60}Co source, whose specific dose rate was 0.6 kGy h^{-1} .

FTIR analysis

Fourier Transform Infrared (FTIR) spectroscopy was carried out in a Spectrum 100 equipment (Perkin Elmer, Waltham, MA, US). FTIR analysis was performed, aiming at verifying the presence of POSSs in the prepared samples, at r.t.

from 4000 to 650 cm^{-1} with a resolution of 4.0 cm^{-1} . An universal ATR sampling accessory was used for measurements, which were made directly on the samples without further treatment.

DSC analysis

A Mettler DSC 1 Star System (Mettler Instrument, Greifensee, Switzerland) was used to evaluate the melting behaviour of EPDM and related composites. The equipment was calibrated, in enthalpy and temperature, following the manufacturer's suggestions reported in the user manual and applied in a previous study [38]. The onset temperature (T_{onset}) and enthalpy (ΔH) of melting were determined performing three scanning for each sample and reporting the averaged value, the deviation remain within $\pm 0.5\%$. Samples of about 6.0 10^{-3} g, held in sealed aluminium crucibles, were heated, with a scanning rate of 10 $^{\circ}\text{C min}^{-1}$, in the range -40 – 125 $^{\circ}\text{C}$.

Thermogravimetric analysis

EPDM and EPDM/POSS composites were thermally characterised in a Mettler Thermogravimetric Analyzer TGA 1 Star System. Following the procedure reported in the User's manual the TG equipment was calibrated by using the change of magnetic properties of three metal samples (Isatherm, Nickel-alloy and Trafoperm 86) at their Curie points (148, 355 and 750 $^{\circ}\text{C}$, respectively). The degradations

were performed in the range 25–700 $^{\circ}\text{C}$ in dynamic mode (10 $^{\circ}\text{C min}^{-1}$), in inert (nitrogen flow at 0.06 L min^{-1}) and oxidative (air flow at 0.06 L min^{-1}) environments respectively. Before performing TG measurements, a blank run with an empty pan was carried out, in the same experimental conditions used for the samples, to correct the error in the mass determination due to the reduction of the buoyancy force on increasing temperature [39]. The blank curve obtained with the empty pan was subtracted from those containing, from time to time, about 5×10^{-3} g of samples.

Results and discussion

FTIR spectroscopy of the control EPDM and the prepared composites were performed to check the presence of POSS in the composites. As expected, in Figs. 2 and 3, the band at about 1100 cm^{-1} related to the asymmetric Si–O–Si stretching and associated to the POSS cage [40], is clearly visible for the composites and not for neat EPDM, thus confirming, at least qualitatively, the presence of POSS molecules in the EPDM composites. It is worth to note that the band associated with the presence of POSS molecules is clearer for the composites irradiated at 50 kGy (Fig. 3), whilst for the non-irradiated composites the greater or lesser presence of POSS molecules seems to influence the intensity of the band (Fig. 2).

Fig. 2 FTIR spectra of pristine EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 0 kGy

Fig. 3 FTIR spectra of pristine EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 50 kGy

Fig. 4 DSC curves, at 10 °C min⁻¹, under nitrogen flow for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 0 kGy

Fig. 5 DSC curves, at 10 °C min⁻¹, under nitrogen flow for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 50 kGy

Control EPDM and composites, irradiated and not, were calorimetric characterised by carrying out DSC scans from 40 to 125 °C in flowing nitrogen. This range was chosen to better highlight the melting, that for EPDM occurring at a temperature just above the ambient one. DSC curves for non-irradiated and irradiated samples are shown in Figs. 4 and 5 respectively, whilst the characteristic DSC parameters, namely onset melting temperature (T_{onset}), peak

melting temperature (T_m) and enthalpy of melting (ΔH_m), are reported in Tables 1 and 2. A thermal effect was observed for the investigated compounds before their melting, probably due to the end of the glass transition that for EPDM generally occurs at about 50 °C [41]. This effect is more pronounced for EPDM whilst it loss intensity by increasing the POSS content in the composites, probably due to the restriction of mobility for the presence of the POSS cage in the matrix

Table 1 Onset melting Temperatures (T_{onset}), peak melting Temperatures (T_m) and Enthalpy of melting (ΔH_m) for non irradiated EPDM and composites

Samples	$T_{\text{onset}}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$\Delta H_m/\text{Jg}^{-1}$
EPDM D0	33.3	42.6	0.66
EPDM/POSS1 D0	32.8	37.6	5.45
EPDM/POSS3 D0	33.4	42.8	5.56
EPDM/POSS5 D0	32.1	43.9	4.51

Table 2 Onset melting Temperatures (T_{onset}), peak melting Temperatures (T_m) and Enthalpy of melting (ΔH_m) for irradiated EPDM and composites

Samples	$T_{\text{onset}}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$\Delta H_m/\text{Jg}^{-1}$
EPDM D50	33.5	41.4	5.63
EPDM/POSS1 D50	35.6	41.3	5.28
EPDM/POSS3 D50	34.3	41.2	3.71
EPDM/POSS5 D50	34.7	41.0	4.42

[42]. As regards the data in Table 1, seem to indicate that the presence of POSS does not influence the melting behaviour of the composites with respect the control polymer. The irradiated composites seem to show a slight increase in the T_{onset} , which is maximum at 1% of POSS, thus indicating a minimum stabilization effect. For the irradiated composites an endothermic phenomenon was recorded just above 100 °C, whose intensity increase as a function of POSS content in the polymer. Similar endothermic phenomena were observed in the past on similar symmetric POSS and were attributed to not reversible solid–solid transitions, due to the cleavage of weak secondary bonds [25]. This hypothesis seems confirmed considering that the phenomena is detected here only for the γ -irradiated samples, suggesting that the irradiation has favored this cleavage.

EPDM and EPDM/POSS composites were then degraded, in dynamic heating conditions (r.t.—700 °C), into the TGA equipment in both inert and oxidative environment, and their TG curves are shown in Figs. 6 and 7 for the non-irradiated samples and in Figs. 8 and 9 for the irradiated ones, reporting the percentage of un-degraded sample ($1-D\%$) as a function of the temperature. In Tables 3 and 4 we reported the initial decomposition temperatures (T_i), the peak temperatures (T_p) and the residue % at 700 °C for the non-irradiated EPDM and composites in inert and oxidative atmosphere respectively. Analogously, In Tables 5 and 6 we reported T_i , T_p and the residue % at 700 °C for the irradiated EPDM and composites in inert and oxidative atmosphere respectively.

In the considered temperature range (25–700 °C) it has been observed a different degradation mechanism for the control EPDM and the EPDM/POSS composites. The

Fig. 6 TG degradation curves, at 10 °C min⁻¹, under nitrogen flow for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 0 kGy. $D = (W_o - W)/W_o$, W_o and W were the masses at the starting point and during scanning **Fig. 7** TG degradation curves, at 10 °C min⁻¹, in static air atmosphere for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 0 kGy. $D = (W_o - W)/W_o$, W_o and W were the masses at the starting point and during scanning

virgin polymer degraded in a single stage whilst EPDM/POSS composites, irradiated and not, showed two different stages of degradation in both used atmospheres (Figs. 6–9). Three differences are worth to highlight: the effect of the degradation's environment, the effect of irradiation on polymer stabilization and the effect of POSS content in the polymer matrix. In inert atmosphere the first degradation stage is more evident than in oxidative environment at the same dose of irradiation, whilst the

Fig. 8 TG degradation curves, at $10\text{ }^{\circ}\text{C min}^{-1}$, under nitrogen flow for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 50 kGy. $D = (W_o - W)/W_o$, W_o and W were the masses at the starting point and during scanning

Fig. 9 TG degradation curves, at $10\text{ }^{\circ}\text{C min}^{-1}$, in static air atmosphere for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 50 kGy. $D = (W_o - W)/W_o$, W_o and W were the masses at the starting point and during scanning

Table 3 Initial decomposition temperatures (T_i), peak temperatures (T_p) and residue % at 700 $^{\circ}\text{C}$ for non irradiated EPDM and composites in oxidative atmosphere

Samples	$T_i/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_{i2}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	residue/%
EPDM D0	n.p.*	n.p.*	406.8	435.7	0
EPDM/POSS1 D0	239.7	n.d.**	396.6	423.8	1.10
EPDM/POSS3 D0	276.7	298.7	464.0	484.3	0.54
EPDM/POSS5 D0	238.9	272.2	402.6	451.0	15.7

*n.p. = not present

**not detectable

Table 4 Initial decomposition temperatures (T_i), peak temperatures (T_p) and residue % at 700 $^{\circ}\text{C}$ for non irradiated EPDM and composites in inert atmosphere

Samples	$T_i/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_{i2}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	residue/%
EPDM D0	n.p.*	n.p.*	450.6	476.3	0
EPDM/POSS1 D0	240.0	256.0	449.9	467.0	4.26
EPDM/POSS3 D0	238.9	266.2	447.1	467.7	0.35
EPDM/POSS5 D0	242.3	279.0	452.0	469.2	8.69

*n.p. = not present

Table 5 Initial decomposition temperatures (T_i), peak temperatures (T_p) and residue % at 700 $^{\circ}\text{C}$ for irradiated EPDM and composites in oxidative atmosphere

Samples	$T_i/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_{i2}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	Residue/%
EPDM D50	n.p.*	n.p.*	382.4	423.5	0
EPDM/POSS1 D50	242.2	252.6	407.6	433.7	0.17
EPDM/POSS3 D50	223.2	251.0	413.5	435.3	5.20
EPDM/POSS5 D50	248.2	255.7	424.4	452.0	11.11

*n.p. = not present

Table 6 Initial decomposition temperatures (T_i), peak temperatures (T_p) and residue % at 700 $^{\circ}\text{C}$ for irradiated EPDM and composites in inert atmosphere

Samples	$T_i/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_{i2}/^{\circ}\text{C}$	$T_{p2}/^{\circ}\text{C}$	residue/%
EPDM D50	n.p.*	n.p.*	453.7	469.3	0
EPDM/POSS1 D50	244.9	294.0	473.0	493.7	0
EPDM/POSS3 D50	253.7	280.3	465.0	483.3	1.18
EPDM/POSS5 D50	257.6	282.3	451.2	476.7	12.64

*n.p. = not present

Fig. 10 DTG curves, at $10\text{ }^{\circ}\text{C min}^{-1}$, under nitrogen flow for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 0 kGy

Fig. 11 DTG curves, at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, under nitrogen flow for EPDM and EPDM/POSS 1%; EPDM/POSS 3%; EPDM/POSS 5% at irradiation dose of 50 kGy

samples irradiated at 50 kGy presents a shift of this first degradation stage to higher temperature. As regards the effect of POSS content on the composites degradation, it is clearly visible a direct relationship among the intensity of the first degradation stage and the POSS content, Derivative Thermogravimetric Curves (DTG) for EPDM and composites, irradiated and not, in inert environment are shown in Figs. 10 and 11 as examples. Focusing

our attention on the main degradation stage, occurring just above $400\text{ }^{\circ}\text{C}$, if for the non-irradiated composites the presence of POSS seems to not affect particularly this degradation, from Tables 5 and 6 reporting the TG parameters for the irradiated samples, it is possible to observe a consistent increase in T_i , which was higher in air than in nitrogen. By looking at the data reported in Tables 3–6 the solid residue obtained at $700\text{ }^{\circ}\text{C}$ from the TG degradations increase as a function of POSS content in the composites, and its amount seems not influenced by the atmosphere used during the degradation. In order to confirm its siliceous nature, the residue was subjected to FTIR analysis. We reported, as an example, the FTIR plot for the residue of EPDM/POSS 3 irradiated sample (Fig. 12), from which it is possible to observe the typical band associated with the presence of silica [43].

Conclusions

EPDM- octa vinyl POSS composites at different mass percentage (mass%) of POSS were prepared and characterised by FTIR to check the effective presence of POSS in the obtained composites. The prepared composites were thus γ -irradiated with an irradiation dose of 50 kGy and investigated by TGA and DSC. The thermal behaviour of the irradiated samples were compared each other to verify the effect of POSS content on the thermal properties and with respect the virgin EPDM and the non-irradiated composites. DSC

Fig. 12 FTIR spectra of the residues at $700\text{ }^{\circ}\text{C}$, under nitrogen flow, of EPDM/POSS 5% at irradiation dose of 50 kGy

analysis showed that the queue of the glass transition is more pronounced for EPDM whilst it loss intensity by increasing the content of POSS in the composites, probably due to the restriction of mobility for the presence of the POSS cage in the matrix. As regards the melting, it seems that the presence of POSS does not influence those of the composites with respect that of control polymer, but for the irradiated composites a slight increase in the T_{onset} was recorded, thus indicating a minimum stabilization effect. For the irradiated composites an endothermic phenomenon was recorded above the melting and it was attributed to not reversible solid–solid transitions, due to the cleavage of weak secondary bonds. A different degradation mechanism was observed for EPDM and the composites, which degraded in two stages whilst the control polymer showed a single stage of degradation. The environmental condition of degradations seem to affect the first degradation stage, that is more evident in inert atmosphere than in oxidative one at the same dose of irradiation. A direct relationship among the intensity of the first degradation stage and the POSS content was recorded, showing an increase of this stage on increase the content of molecular filler. Finally, the main degradation stage, occurring just above 400 °C, for the irradiated samples, showed an increase in the initial decomposition temperature, which was higher in air than in nitrogen.

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