Kinetics of the Non-isothermal Degradation of POSS/EPDM Hybrids Composites

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Polyhedral Oligomeric Silsesquioxane (POSS)/Ethylene-propylene-diene monomer (EPDM) composite, at 3% wt of POSS, is prepared by the evaporation of solvent ($CHCl_3$) from polymer/filler system at room temperature and is investigated, by the means of thermogravimetric analysis (TGA), and the obtained TGA data are treated by the Kissinger method to get the apparent activation energy (E_a) of degradation. The results obtained for the composites, at different levels of irradiation, are discussed and compared with each other and with those obtained for pristine EPDM. A good improvement of the thermal stability, with respect to the neat polymer, is found showing the effect of the POSS molecules on the degradation rate. A classification among the samples at different levels of radiations is also drawn up, showing also in this case, the beneficial effect of the POSSs presence.

1. Introduction

Ethylene-propylene-diene monomer (EPDM) was largely investigated by Academia, showing excellent electrical, thermal and mechanical properties, light weighting, ease-of-installation, and handling properties such as high elasticity, abrasion, and corrosion resistance.[1–3] Thanks to the listed properties, EPDM performed very well in various fields,[4] but its highly filled feature[5] pushed the research towards the design and characterization of EPDM composites, aiming at expanding its useful life in severe environments. The long-term durability of high-quality materials[6] may be achieved following different roads, such as antioxidants addition,[7,8] nanophase formation,[9,10] or dispersion of inorganic filler.[11,12]

The extending applications of hybrid materials, especially over drastic environmental conditions, require the investigations on stabilization effects brought about by the filler nature in polymeric materials.[13,14] During the last two decades, Polyhedral Oligomeric Silsesquioxanes (POSS) became interesting molecular filler that provides the broadening lifetime of several polymers.[15,16] The chemically modified forms of POSS may improve the prevention activities due to the modification of electronic densities of POSS configurations. Accordingly, in this work, we evaluated the kinetics of degradation of an upgraded EPDMPOSS composite in comparison to the control polymer, at different levels of irradiation. Thus, EPDM and EPDM filled with 3% of POSS were analyzed by thermogravimetric analysis (TGA); the obtained data were used to calculate the apparent activation energy (E_a) of degradation, by the means of kinetics literature method in order to evaluate how the different levels of irradiation influence their thermal degradation.

2. Experimental Section

Ethylene-propylene-diene monomer, commercially branded as KELTAN 8340/A, was purchased by DSM Elastomers (The Netherland), including 5% wt 5-ethylidene-2-norbornene, with an ethylene/propylene ratio of 3:1. Polyhedral Oligomeric Silsesquioxane (**Figure 1**) was prepared by Corner Capping Reaction of isobutyltrisilanol with the suitable aryltrimethoxysilane, following a consolidated procedure reported in our previous work.[17]

Before starting with the preparation of the hybrid composites, EPDM pellets were brought into a $CHCl_3$ solution. Then, the saturated mother solution with 3% wt of POSS nanoparticles was mixed, extracted from the solvent, and dried at room temperature. A hybrid film of 100 μm in thickness was thus obtained, named as **P0** (EPDM sample) and **P1** (EPDM-POSS sample).

The γ-exposure was carried out, in air at room temperature, in an Ob Servo Sanguis (Hungary) irradiation apparatus with ^{60}Co source and a dose rate of 0.6 kGy h^{-1}. Both EPDM (**P0**) and EPDM-POSS composite (**P1**) were subjected to 0, 25, 50, 75, and 100 kGy of radiations. A Mettler Thermogravimetric Analyzer TGA 1 Star System (Switzerland) was used to acquire the thermal degradation data. TGA apparatus was calibrated following the procedure suggested by the manufacturer and reported in our previous work.[18] Thermal degradations were carried out

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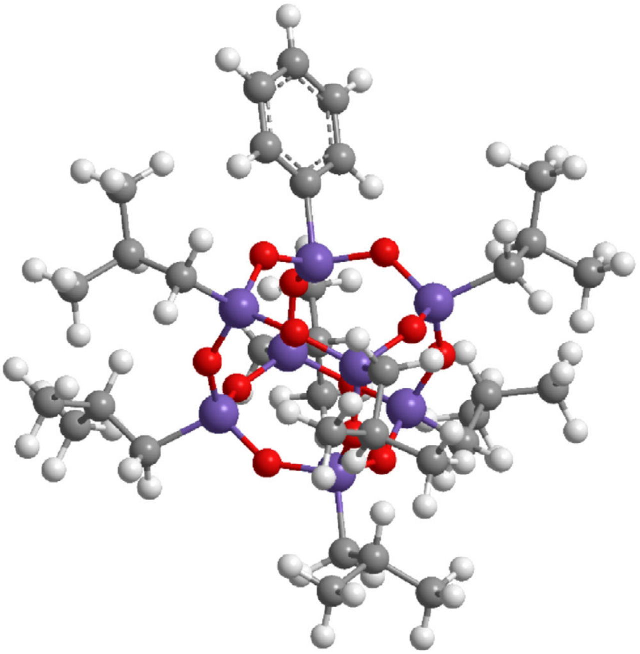

Figure 1. Molecular structure of the used hepta isobutyl mono phenyl polyhedral oligomeric silsesquioxanes.

at various heating rates (Φ = 2, 5, 7.5, 10, 12.5, 15, 17.5, and 20 $K \cdot min^{-1}$), in the temperature range 298 – 973 K in both inert (flowing nitrogen 0.02 $L \cdot min^{-1}$) and oxidative (static air) atmosphere. Samples of about $10•10^{-3}$ g, placed in a 40 μL alumina open pan, were used for experiments. The sample mass as a function of temperature was monitored and the temperature at maximum rate of weight loss (T_m) was recorded to be used in kinetics calculation. All the T_m values were averaged from those of three runs, the maximum difference between the average and the experimental values being within ± 1°C.

Table 1. Temperatures at maximum rate of weight loss (T_m), in oxidative atmosphere, for the degradation of **EPDM** exposed to various γ-irradiation total doses.

Φ /(°C·min^{-1})	P0 0 kGy T_m /K	P0 25 kGy T_m /K	P0 50 kGy T_m /K	P0 75 kGy T_m /K	P0 100 kGy T_m /K
2	719	714	713	710	709
5	733	728	726	723	723
7.5	738	736	735	731	732
10	745	743	741	739	739
12.5	753	749	748	745	744
15	754	755	753	750	750
17.5	758	756	755	753	753
20	762	761	760	758	759

Table 2. Temperatures at maximum rate of weight loss (T_m), in oxidative atmosphere, for the degradation of **EPDM-POSS** composite exposed to various γ-irradiation total doses.

Φ /(°C·min^{-1})	P1 0 kGy T_m /K	P1 25 kGy T_m /K	P1 50 kGy T_m /K	P1 75 kGy T_m /K	P1 100 kGy T_m /K
2	722	718	718	715	713
5	733	731	732	729	725
7.5	740	737	737	735	732
10	744	741	739	740	738
12.5	751	745	745	744	743
15	753	753	752	750	745
17.5	758	756	755	753	751
20	762	758	759	757	755

3. Results and Discussion

The evaluation of the pristine EPDM and composite thermal behavior was carried out by performing TGA scans and thus completed by the kinetics elaboration of the obtained data. The T_m values of **P0** and **P1** samples, at all heating rates and different levels of irradiation, are reported in **Tables 1** and **2** (oxidative atmosphere) and **Tables 3** and **4** (inert atmosphere).

The least square treatment of the data in Tables 1 and 4 was made to calculate the E_a of degradation, by using the Kissinger equation[19]

$$\ln(F/T_2^2) = \ln\left(nRAW_m^{n-1}/E_a\right) - E_a/RT_m \tag{1}$$

in which Φ is the heating rate, T_m is the temperature at maximum rate of weight loss, n is the apparent reaction order, R is the universal gas constant, A is the pre-exponential factor, and W_m is the weight of sample at T_m. Verified the constancy of conversion (α) as a function of the heating rate, the activation energies of degradation were calculated by the slope of the straight lines obtained reporting ln ($\Phi/T_m{}^2$) versus $1/T_m$ at the various heating rates. In **Figure 2**, Kissinger straight lines for the P1 sample in air atmosphere at the various irradiation dose are shown as example.

Degradation E_a values with their corresponding regression coefficients are reported in **Tables 5** and **6** and **Tables 7** and **8** for oxidative and inert environment, respectively. Where a = ln ($nRAW_m{}^{n-1}$ / E_a); $b = E_a$ / R and r is the product moment correlation coefficient.

Table 3. Temperatures at maximum rate of weight loss (T_m), in inert atmosphere, for the degradation of **EPDM** exposed to various γ-irradiation total doses.

Φ /(°C·min^{-1})	P0 0 kGy T_m /K	P0 25 kGy T_m /K	P0 50 kGy T_m /K	P0 75 kGy T_m /K	P0 100 kGy T_m /K
2	722	721	719	717	715
5	736	733	732	729	726
7.5	742	740	738	736	737
10	747	747	746	745	743
12.5	752	751	751	748	749
15	758	756	755	753	752
17.5	760	760	758	756	755
20	765	763	762	761	758

Table 4. Temperatures at maximum rate of weight loss (T_m), in inert atmosphere, for the degradation of **EPDM-POSS** composite exposed to various γ-irradiation total doses.

Φ /(°C·min^{-1})	P1 0 kGy T_m /K	P1 25 kGy T_m /K	P1 50 kGy T_m /K	P1 75 kGy T_m /K	P1 100 kGy T_m /K
2	724	721	720	719	716
5	733	733	732	730	726
7.5	741	739	737	735	734
10	747	745	743	743	740
12.5	752	750	748	747	745
15	755	754	753	753	749
17.5	759	757	756	755	753
20	761	760	759	757	754

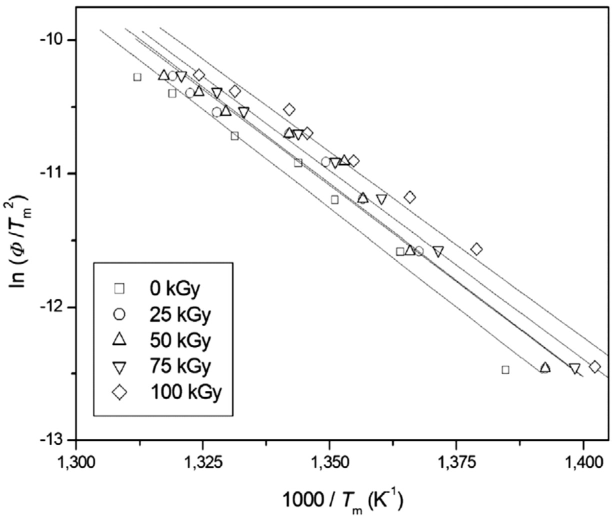

Figure 2. Kissinger straight lines for EPDM-POSS, at various irradiation doses, in static air atmosphere at various degrees of conversion (α).

Two important results can be derived by the analysis of the kinetics results:

- E_a values for the EPDM-POSS composites are considerably higher than those of the control polymer, both in oxidative (Tables 5 and 6) and in inert (Tables 7 and 8) environment, showing an increase of 20 kJ·mol^{-1} for the nonirradiated samples;

Table 5. Regression coefficients and apparent activation energies (E_a) of degradation by the Kissinger equation for **EPDM** exposed to various γ-irradiation total doses in oxidative atmosphere.

Irradiation level	a	$b \cdot 10^{-3}$ /K	r	E_a /(kJ·mol^{-1})
0 kGy	25.5 (± 2.0)	27.2 (± 1.5)	0.9905	226 (± 12)
25 kGy	21.9 (± 1.6)	24.4 (± 1.2)	0.9927	203 (± 10)
50 kGy	21.7 (± 1.8)	24.3 (± 1.3)	0.9912	202 (± 11)
75 kGy	20.8 (± 1.9)	23.5 (± 1.4)	0.9895	195 (± 12)
100 kGy	20.2 (± 1.7)	23.1 (± 1.2)	0.9914	192 (± 10)

Table 6. Regression coefficients and apparent activation energies (E_a) of degradation by the Kissinger equation for **EPDM-POSS** composite exposed to various γ-irradiation total doses in oxidative atmosphere.

Irradiation level	a	$b \cdot 10^{-3}$ /K	r	E_a /(kJ·mol^{-1})
0 kGy	28.7 (± 3)	29.6 (± 2.0)	0.9864	246 (± 17)
25 kGy	27.7 (± 3)	28.8 (± 2.0)	0.9863	239 (± 17)
50 kGy	28.0 (± 3)	28.9 (± 2)	0.9807	240 (± 17)
75 kGy	27.2 (± 1.9)	28.3 (± 1.4)	0.9927	235 (± 12)
100 kGy	26.7 (± 2)	27.8 (± 1.7)	0.9895	231 (± 14)

Table 7. Regression coefficients and apparent activation energies (E_a) of degradation by the Kissinger equation for **EPDM** exposed to various γ-irradiation total doses in inert atmosphere.

Irradiation level	a	$b \cdot 10^{-3}$ /K	r	E_a /(kJ·mol^{-1})
0 kGy	26.6 (± 2.0)	28.2 (± 1.5)	0.9916	234 (± 12)
25 kGy	26.1 (± 2.0)	27.7 (± 1.5)	0.9909	230 (± 12)
50 kGy	25.4 (± 1.9)	27.1 (± 1.4)	0.9921	225 (± 12)
75 kGy	24.5 (± 2.1)	26.4 (± 1.6)	0.9892	219 (± 13)
100 kGy	23.9 (± 1.9)	25.9 (± 1.4)	0.9915	215 (± 12)

- a reduction of the E_a values was observed by increasing the irradiation dose from 25 to 100 kGy, thus showing a faster degradation for the irradiated samples (Tables 5–8). Anyway, it is worth to note that whilst for EPDM (Table 5) we observed a reduction in the apparent activation energy of degradation of 34 kJ·mol^{-1}, when the POSS molecule is added to the polymer matrix (Table 6), the reduction recorded was more than halved (15 kJ·mol^{-1}). This finding confirms the active role of the POSSs in the thermoxidative degradation process of the hybrid system prepared. Thus, the presence of POSS molecule not only enhances the resistance to the thermal degradation, in agreement with literature report,[20] but also slows the degradation rate increasing the overall thermal stability of the EPDM-POSS composite.

Another important aspect highlighted by our kinetics study was the role of the environment in the degradation behavior. In fact, whilst the atmosphere plays a key role in the degradation of the control polymer, with the inert environment that halves the degradation rate with increasing the radiation dose (Table 7),

Table 8. Regression coefficients and apparent activation energies (E_a) of degradation by the Kissinger equation for **EPDM-POSS** composite exposed to various γ-irradiation total doses in inert atmosphere.

Irradiation level	a	$b \cdot 10^{-3}$ /K	r	E_a /(kJ·mol^{-1})
0 kGy	29.9 (± 3)	30.6 (± 2.0)	0.9877	254 (± 17)
25 kGy	29.3 (± 1.9)	30.0 (± 1.4)	0.9931	249 (± 12)
50 kGy	29.0 (± 2)	29.8 (± 1.8)	0.9891	248 (± 15)
75 kGy	28.4 (± 3)	29.2 (± 2.0)	0.9861	243 (± 17)
100 kGy	28.1 (± 2)	28.9 (± 1.7)	0.9893	240 (± 14)

compared to the behavior in oxidative environment (Table 5). For the EPDM composite, the effect of the atmosphere on the degradation seems to be canceled by the presence of POSS, 15 kJ·mol^{-1} for **P1** in air, by passing from 0 to 100 kGy (Table 6) and 14 kJ·mol^{-1} for **P1** in nitrogen in the same radiation dose range (Table 8).

4. Conclusion

EPDM-POSS composite was prepared by an effective, and quite simple and fast method. The TGA experiments, in inert and oxidative atmosphere, and the kinetics analysis on the Ethylene-propylene-diene monomer/polyhedral oligomeric silsesquioxanes showed a good improvement of the resistance to the degradation with respect to neat EPDM. It was possible to observe how the presence of the POSS molecules lowers the degradation rate generally, halving the radiation effects. Furthermore, the presence of POSS in the EPDM composites seemed to make uniform the degradation in oxidative and inert environment.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

EPDM, kinetics of degradation, POSS, radiation

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