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Phenyl hepta cyclopentyl – polyhedral oligomeric silsesquioxane (ph,hcp-POSS)/Polystyrene (PS) nanocomposites: the influence of substituents in the phenyl group on the thermal stability

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Abstract. Some new Polystyrene (PS) nanocomposites were prepared by using two Polyhedral Oligomeric Silsesquioxanes (POSSs), namely $RR'_7(SiO_{1.5})_8$ (where R = 4-methoxyphenyl or 2,4-difluorophenyl and R' = cyclopentyl), as fillers, and their degradation was studied to investigate the effect of the electron-donor or electron-withdrawing character of the phenyl group substituents on thermal stability. Nanocomposites were synthesized by *in situ* polymerization of styrene in the presence of various concentrations of POSS. Proton nuclear magnetic resonance (^{1}H NMR) spectra indicated that the POSS content in the obtained nanocomposites was higher than that in reactant mixtures. Inherent viscosity (η_{inh}) and glass transition temperature (T_g) determinations indicated that the average molar mass of polymer in 4-methoxynanocomposites was the same than neat PS, while it was much lower in 2,4-difluoro derivatives. Degradations were carried out in both flowing nitrogen and static air atmospheres, in the scanning mode, at various heating rates, and temperature at 5% mass loss ($T_{5\%}$) and the activation energy (E_a) of degradation of various nanocomposites were determined. The values obtained for 4-methoxyderivatives were higher than unfilled PS thus indicating higher thermal stability. Conversely, the values found for 2,4-difluoro derivatives were lower, in some cases even than those of neat PS. The results were discussed and interpreted.

Keywords: *nanocomposites, thermal properties, polystyrene, POSS*

1. Introduction

Even though polymers are compounds largely used in many fields owing to the various and excellent chemical properties, the improvement of their physical and mechanical properties is often requested, thus driving researchers towards the synthesis of composite materials, it means of hybrid materials obtained by coupling organic polymers with inorganic fillers [1]. Silica and layered silicates were first used to this purpose [2], so giving rise to composites showing better mechanical and thermal properties than those of conventional polymers [3–7]. Also, the dispersion at nanoscale level of filler in polymeric matrix generally improves physical, mechanical, barrier and flammability properties in comparison with virgin polymer [8–20]. In addition, it leads to a pronounced increase of thermal stability [20–22], it being important feature because nanocomposites so obtained can be subjected to high temperatures during processing and/or in service.

In the last years a new class of inorganic–organic nanoparticles, namely Polyhedral Oligomeric Silsesquioxanes (POSSs), has awaken increasing interest for the use as filler of polymer based nano-

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composites [23–29]. The general formula of POSSs is $(RSiO_{1.5})_n$, or R_nT_n, where organic substituents (R = alkyl, aryl or any other) are attached to silicon cage.

We have in progress a wide research, concerning the synthesis and the characterization of new thermally stable nanocomposites of polystyrene (PS) and polyolefins having POSSs as fillers. Some $RR'_7(SiO_{1.5})_8$ POSSs (where R' = cyclopentyl or isobutyl and R = C_6H_5- or one of its mono-, di- or tri-substituted derivatives) were previously synthesized and characterized [30, 31], owing to their good compatibility and solubility in polymer matrices due to the presence of aliphatic and cycloaliphatic groups linked to silicon cage [32–35].

The results obtained indicated better thermal properties for heptacyclopentyl-POSSs in comparison with the corresponding heptaisobutyl- derivatives, and, in particular, phenyl, heptacyclopentyl-POSS (ph,hcp-POSS) appeared the most thermally stable [30, 31]. Starting from this finding, ph,hcp-POSS/PS nanocomposites were thus prepared by *in situ* polymerization of styrene in the presence of 3, 5 and 10% w/w of filler [36]. The degradation experiments of all obtained nanocomposites showed a significant thermal stability enhancement in respect to neat polystyrene, which was larger for the sample at 5% filler [36].

On continuing our research in this field, we studied here the thermal degradation of PS based nanocomposites having two phenylsubstituted hcp-POSSs as fillers, namely 4-methoxyphenyl hcp-POSS (Figure 1a), and 2,4-difluorophenyl hcp-POSS (Figure 1b). These two fillers were selected among the various hepta cyclopentyl-POSSs investigated in Ref. [30] aiming to check if the presence of substituents (electron-donor as the methoxy group or electron-withdrawing as fluorine atoms) in the phenyl group is able to affect the thermal stability of nanocomposites obtained.

Various nanocomposites were prepared by *in situ* polymerization of styrene in the presence of the appropriate POSS and will be indicated in the text by the corresponding numbers, as follows:

4-methoxyphenyl hcp-POSS/PS at 3% w/w	**1**
4-methoxyphenyl hcp-POSS/PS at 5% w/w	**2**
4-methoxyphenyl hcp-POSS/PS at 10% w/w	**3**
2,4-difluorophenyl hcp-POSS/PS at 3% w/w	**4**
2,4-difluorophenyl hcp-POSS/PS at 5% w/w	**5**
2,4-difluorophenyl hcp-POSS PS at 10% w/w	**6**

where the 3, 5 and 10% values represent the filler percentages in the reactant mixtures.

The actual filler content in the obtained nanocomposites was checked by ^{1}H NMR. Also, inherent viscosity (η_{inh}) determinations were carried out in order to verify if the presence of POSS modified the average molar mass of PS, whilst Fourier Transform Infrared (FTIR) spectra were recorded to evidence the presence of PS-POSS interactions.

The glass transition temperature (T_g) of PS as well as those of the studied nanocomposites were determined by Differential Scanning Calorimetry (DSC). Thermal (in flowing nitrogen) and thermoxidative (in a static air atmosphere) degradations were fol-

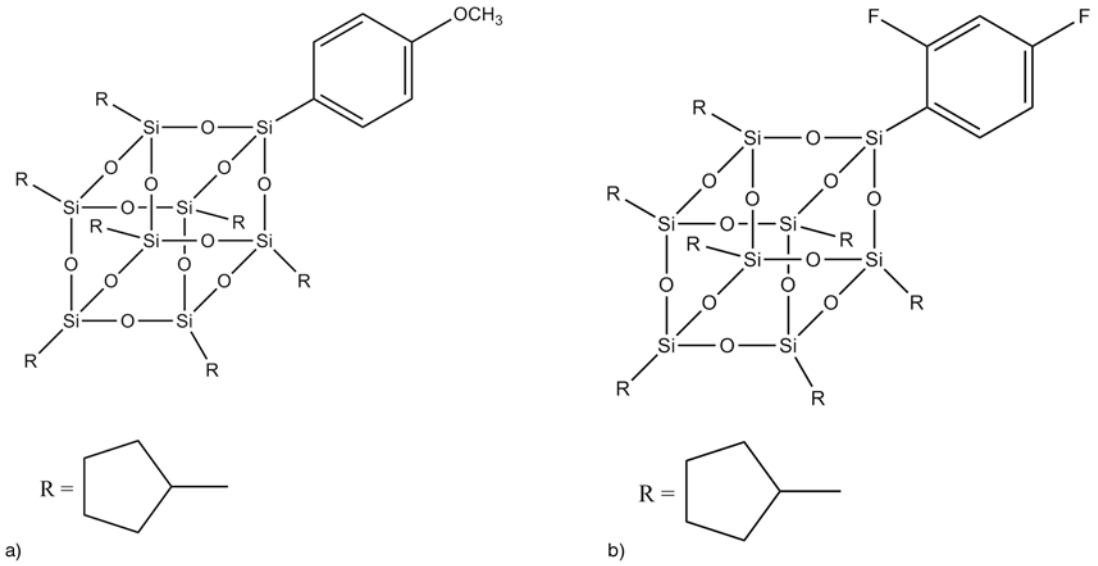

Figure 1. Molecular structure of a) 4-methoxyphenyl hcp-POSS; b) 2,4-difluorophenyl hcp-POSS

lowed by Thermogravimetric (TG) and Differential Thermogravimetric (DTG) analysis, and the parameters associated with the thermal stability, namely temperature at 5% mass loss ($T_{5\%}$) and apparent activation energy (E_a) of degradation, of various nanocomposites were determined and compared with each other and with those of neat PS and of ph,hcp-POSS/PS nanocomposites previously determined [36].

2. Experimental

2.1. Materials

Styrene (Aldrich Co., St. Gallen, CH) was purified by passing it through an inhibitor removal column. 2,2-Azobis(isobutyronitrile) (AIBN) (98% Aldrich Co., St. Gallen, CH) was re-crystallised twice from dry ethanol at temperatures less than 40°C and out of direct light. Toluene was stirred over calcium hydride for 24 h and distilled in a nitrogen atmosphere.

Tetrahydrofuran (THF) was distilled over a Na – benzophenone mixture.

2.2. Synthesis of POSSs

POSSs were first prepared as follows: 4-methoxyphenyltrichlorosilane and 2,4-difluorophenyltrichlorosilane were prepared from the appropriate Grignard reagent and $SiCl_4$ [37, 38]. Cyclopentyltrisilanol ($c\ C_5H_9)_7$-$Si_7O_9(OH)_3$ was obtained by literature methods [39, 40].

4-methoxyphenyl hcp-POSS and 2,4-difluorophenyl hcp-POSS were prepared by corner capping reaction of cyclopentyltrisilanol with the suitable aryltrichlorosilane in dry THF, according to our previous work [30].

2.3. Synthesis of nanocomposites

Nanocomposites were obtained by *in situ* polymerization of 3, 5 and 10% w/w POSS/styrene mixtures in toluene. The details of free-radical polymerization procedure are described for compound **2**.

Styrene monomer (3,80 g) and 4-methoxyphenyl hcp-POSS (0,20 g) were dissolved in 40 ml of toluene, and AIBN radical initiator (12 mg) was added; the mixture was frozen in a liquid nitrogen bath, degassed with a vacuum pump, and then thawed. This operation was repeated three times and then tube, sealed under vacuum, was heated at 70°C for 24 h under stirring. The clear solution was poured into a large excess of methanol (600 mL), the precipitated nanocomposite was collected by filtration and dried under vacuum at 40°C. The yield was 3.52 g (88%).

The same polymerization procedure was used to prepare neat PS and compounds **1** (yield 85%), **3** (yield 79%), **4** (yield 84%), **5** (yield 81%) and **6** (yield 86 %).

2.4. ^{1}H NMR spectroscopy

^{1}H NMR spectra were recorded by a Varian (Palo Alto, California, USA) Unity Inova instrument (^{1}H 500 MHz), by using $CDCl_3$ as solvent and TMS as internal standard.

2.5. Viscosity measurements

Inherent viscosities ($\eta_{inh} = \ln\eta_r/C$, where η_r = relative viscosity and C = polymer concentration) at 25±0.1°C were measured with an Ubbelohde suspended-level viscometer, using solutions of polymers in chloroform at the concentration of 0.5 g/dL.

2.6. IR spectroscopy

A Perkin Elmer (Waltham, Massachusetts, USA) Spectrum 100 spectrometer was used to record Fourier Transform Infrared (FTIR), using an universal ATR sampling accessory. Spectra were recorded at r.t. from 4000 to 400 cm^{-1} with a resolution of 4.0 cm^{-1}, directly on compounds, without any preliminary treatment.

2.7. DSC measurements

A Mettler (Greifensee, CH) DSC 20 differential scanning calorimeter, coupled with a Mettler (Greifensee, CH) TC 10 A processor as control and evaluation unit, was employed for the determination of glass transition temperature. The enthalpy and temperature calibrations of equipment were made according to the procedure suggested by the manufacturer and reported in our previous work [36]. Calibrations were repeated every two weeks. Samples of about $5.0\cdot10^{-3}$ g, held in sealed aluminium crucibles, and a heating rate of 10°C·min^{-1} were used for measurements.

2.8. Thermogravimetric analysis

The thermal degradations of the studied compounds were carried out into a Mettler (Greifensee, CH) TA 3000 thermogravimetric analyser, coupled with the

same Mettler TC 10 A processor used for calorimetric measurements. The temperature calibration of the thermobalance was made according to the reliable procedure suggested by the supplier. The temperature calibration was repeated every month.

Degradation experiments were carried out in dynamic heating conditions, from 35 to 700°C, in both flowing nitrogen (0.02 L·min^{-1}) and a static air atmosphere, at various heating rates (Φ = 2, 5, 7.5, 10, 12.5, 15, 17.5 and 20°C·min^{-1}). Samples of about 5·10^{-3} g, held in alumina open crucibles, were used for experiments, and their weights were measured as a function of temperature and stored in the list of data of the appropriate built-in program of processor. The TG and DTG curves were then immediately printed at the end of each experiment, while the list of sample weights at various temperatures was transferred to a PC. These data were afterwards used to plot the percentage of undegraded sample, $(1 - D)$%, as a function of temperature, where $D = (W_0 - W)/W_0$, and W_0 and W were the weights at the starting point and during scanning.

3. Results and discussion

The ^{1}H NMR spectra of the **1**–**6** nanocomposites were first recorded and the actual POSS content in the various compounds was determined through the ratio of aromatic hydrogen atoms of filler and those of polystyrene. The following POSS percentages, which in all cases were higher than those of reactant mixtures, were found, namely 3.6% (sample **1**), 6.8% (sample **2**), 12.0% (sample **3**), 3.7% (sample **4**), 6.9% (sample **5**) and 11.8% (sample **6**).

Inherent viscosity determinations on studied compounds were thus performed. The η_{inh} values obtained with samples **1**, **2** and **3** were the same than those of neat PS and ph,hcp-POSS/PS nanocomposites previously determined [36]. Conversely, all values found for samples **4**, **5** and **6** were lower, and, in particular, those at higher POSS content evidenced a dramatic η_{inh} decrease, thus indicating a lower polymer average molar masses. The values of inherent viscosity are reported in Table 1.

The thermal degradations of samples were carried out into our thermobalance, in both inert and oxidative atmospheres. In order to compare the thermal stabilities of our compounds with each other and with those of neat polystyrene and ph,hcp-POSS/PS nanocomposites previously studied, both temperature at 5% mass loss ($T_{5\%}$), which is correlated with initial decomposition temperature (T_i), and activation energy (E_a) of degradation were determined. Temperature at 5% mass loss was chosen because it appears to us more reliable than initial decomposition temperature, because this last parameter largely depends on the slope of the descending piece of TG curve [30, 36, 41–43]. In addition, since to evaluate the comprehensive thermal stability of a polymer it is necessary, in our opinion, to take into account also the degradation rate, in particular if the compared compounds have close initial decomposition temperatures, the apparent activation energy of degradation was determined.

Degradation experiments were first carried out in inert atmosphere, under dynamic heating conditions, at various heating rates ranging from 2 to 20°C·min^{-1}. $T_{5\%}$ values were drawn from the curves traced at the rate of 10°C·min^{-1}, which was selected because it is a medium scanning rate among those used for thermal degradations. The studied nanocomposites degraded completely in flowing nitrogen at all used heating rates. The corresponding TG degradation curves at 10°C·min^{-1} for methoxy- and difluoro- derivatives are reported in Figures 2 and 3,

Table 1. Inherent viscosity (η_{inh}), glass transition temperature (T_g), temperature at 5% mass loss ($T_{5\%}$), apparent activation energy (E_a) of degradation of **PS** and various nanocomposites in static air atmosphere and in flowing nitrogen

Compounds	Air static atmosphere				Nitrogen flow	
	η_{inh} [dL·g^{-1}]	T_g [K]^a	$T_{5\%}$ [K]^a	E_a [kJ·mol^{-1}]	$T_{5\%}$ [K]^a	E_a [kJ·mol^{-1}]
PS	0.17	372	511	141 (±6)	573	206 (±11)
1	0.17	372	546	155 (± 8)	581	221 (± 7)
2	0.17	373	569	168 (± 8)	588	242 (± 13)
3	0.17	372	558	164 (± 7)	583	238 (± 13)
4	0.16	369	555	155 (± 7)	579	225 (± 8)
5	0.12	368	550	152 (± 8)	570	224 (± 10)
6	0.12	368	530	150 (± 8)	567	221 (± 11)

^{a}determined at 10°C·min^{-1}

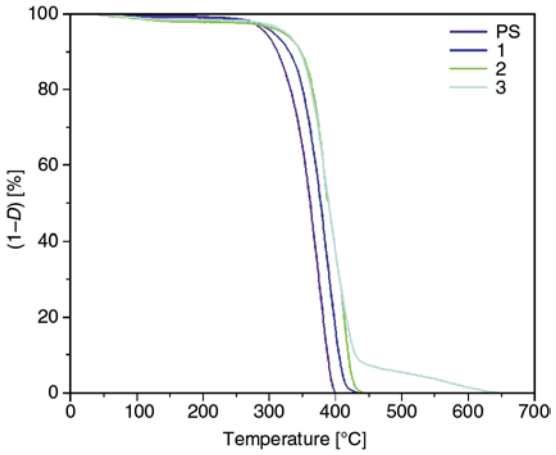

Figure 2. TG degradation curves, at 10°C·min^{-1}, under nitrogen flow of PS and various 4-methoxyphenyl hcp-POSS/PS nanocomposites

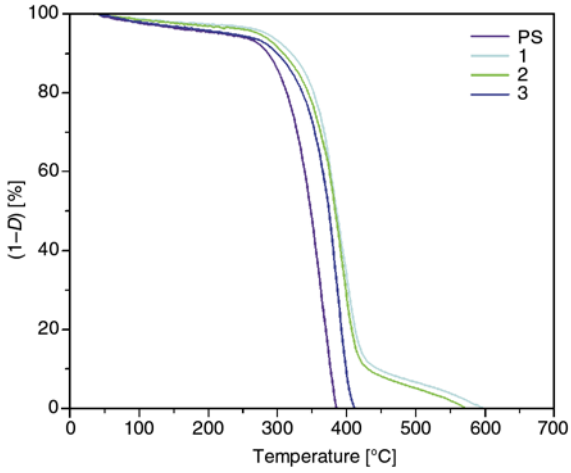

Figure 4. TG degradation curves, at 10°C·min^{-1}, in static air atmosphere of PS and various 4-methoxyphenyl hcp-POSS/PS nanocomposites

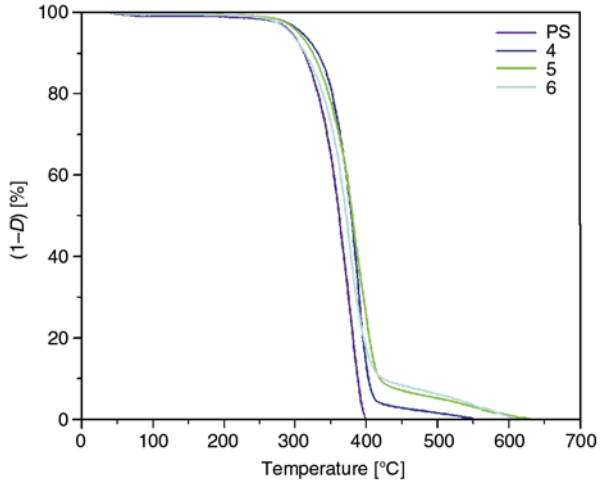

Figure 3. TG degradation curves, at 10°C·min^{-1}, under nitrogen flow of PS and various 2,4-difluorophenyl hcp-POSS/PS nanocomposites

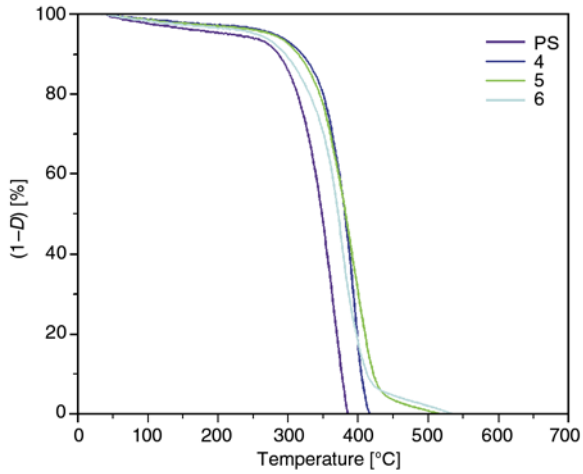

Figure 5. TG degradation curves, at 10°C·min^{-1}, in static air atmosphere of PS and various 2,4-difluorophenyl hcp-POSS/PS nanocomposites

respectively, while the determined $T_{5\%}$ values are listed in Table 1. The behaviour of our compounds in oxidative atmosphere (Figures 4 and 5) was similar to that under nitrogen and the corresponding $T_{5\%}$ values are listed in Table 1.

The nanocomposites degraded up to complete mass loss at all used heating rates, but, differently than PS, which completely degraded in a very sharp single stage, they showed a first quick degradation stage, followed by a slow second one in the last piece of TG curve, more evident for the high filler content samples. This behaviour was the same as that of the ph,hcp-POSS/PS nanocomposites previously studied [36], for which it was there demonstrated that during the second low rate degradation stage both polymer and filler were present at temperatures largely higher than that of the complete decomposition of neat PS, thus indicating a thermal stabilisation of polymer.

The degradation E_a values of various compounds, in both flowing nitrogen and static air atmosphere, were thus determined by using the data from DTG degradation curves at the various heating rates. The classical Kissinger method [44] was used to this aim, which is based on Equation (1):

$$\ln\left(\frac{\Phi}{T_m^2}\right) = \ln\left(\frac{n\mathrm{RA}W_m^{n-1}}{E_n}\right) - \frac{E_a}{\mathrm{R}T_m} \qquad (1)$$

where 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 the maximum rate of mass loss. We used as T_m values the temperatures of DTG peaks. The E_a value was obtained through the linear dependence of $\ln(\Phi/T_m^2)$ on $1/T_m$ at various heating rates.

The least square treatment of T_m values was then performed according to the Equation (1). Single linear $\ln(\Phi/T_m^2)$ vs $1/T_m$ relationships were obtained for all samples in both studied environments. The corresponding regression coefficients and the calculated degradation E_a values are reported in Tables 2 and 3 for nitrogen and air, respectively.

The glass transition temperatures of the considered compounds were lastly determined by DSC measurements, and the values found are reported in Table 1 together with η_{inh}, $T_{5\%}$ and degradation E_a values.

Some comments about the results reported in Table 1:

– the ^{1}H NMR spectra indicated that the POSS content in nanocomposites is higher than that in the reactant mixtures. This finding is in agreement with the results obtained for ph,hcp-POSS/PS nanocomposites [36];
– the much lower η_{inh} values of difluoro- compounds **4**, **5** and **6** in respect to those of both neat PS and methoxy-compounds **1**, **2** and **3** here studied, as well as to those of the previously investigated ph,hcp-POSS/PS nanocomposites, indicate lower average molecular weight, and then a lower polymerization degree of PS. Also, the dramatic η_{inh} decrease observed on increasing the fluorinated POSS concentration suggests that this filler behaves as polymerization inhibitor;
– also glass transition temperatures exhibited different behaviour between the two series of studied compounds: no difference was observed for methoxy-derivatives with each other as well as in respect to neat **PS** and ph,hcp-POSS/PS nanocomposites [36]. Conversely lower T_g values were found for the difluoro- derivates, which decreased on increasing POSS percentage. Since it is well known that glass transition temperature increases with the increase of molecular weight [45], these results appear to be in agreement with viscosimetric measurements and confirm the lower average molar mass of **PS** in the **4**, **5** and **6** nanocomposites;
– as regards degradation experiments, the picture of results in both inert and oxidative environments (Table 1) did not show any substantial difference of behaviour between the 4-methoxyphenyl hcp-POSS/PS nanocomposites (samples **1**, **2** and **3**) here studied and the unsubstituted ph,hcp-POSS/PS nanocomposites previously investigated [36]. Both $T_{5\%}$ and degradation E_a values determined for **1**, **2** and **3** samples were quite higher than those of neat polystyrene, and slightly, but not significantly, different from those found for ph,hcp-POSS/PS nanocomposites [36]. The best values were found for the sample at 5% of POSS, thus suggesting a similar overall thermal stability of the two groups of compounds, in every case better than that of pure polymer. A different behaviour was observed with fluorinated nanocomposites: both $T_{5\%}$ and degradation E_a values of **4**, **5** and **6** samples were lower than those of **1**, **2** and **3** samples. Also, they decreased with the increase of POSS content and, in some cases ($T_{5\%}$ values of samples **5** and **6**

Table 2. Regression coefficients and apparent activation energy (E_a) of degradation by the Kissinger equation for **PS** and nanocomposites in flowing nitrogen

Compounds	a[a)]	b·10^{-3} [K][b)]	r[c)]	E_a [kJ·mol^{-1}]
PS	27.3 (± 2.0)	24.8 (± 1.3)	0.9919	206 (± 11)
1	29.5 (± 1.2)	26.6 (± 0.8)	0.9975	221 (± 7)
2	31.9 (± 2.4)	29.1 (± 1.6)	0.9906	242 (± 13)
3	31.3 (± 2.3)	28.6 (± 1.6)	0.9909	238 (± 13)
4	30.3 (± 1.5)	27.1 (± 1.0)	0.9962	225 (± 8)
5	30.4 (± 1.8)	27.0 (± 1.2)	0.9940	224 (± 10)
6	30.2 (± 2.0)	26.6 (± 1.3)	0.9927	221 (± 11)

[a)] $a = \ln(n\mathrm{R}A W_m^{n-1}/E_a)$
[b)] $b = E_a/\mathrm{R}$
[c)] product moment correlation coefficient

Table 3. Regression coefficients and apparent activation energy (E_a) of degradation by the Kissinger equation for **PS** and nanocomposites in static air atmosphere

Compounds	a[a)]	b·10^{-3} [K][b)]	r[c)]	E_a [kJ·mol^{-1}]
PS	15.5 (± 1.1)	17.0 (± 0.7)	0.9950	141 (± 6)
1	17.4 (± 1.5)	18.7 (± 1.0)	0.9915	155 (± 8)
2	19.9 (± 1.3)	20.2 (± 0.9)	0.9944	168 (± 8)
3	19.3 (± 1.2)	19.7 (± 0.8)	0.9950	164 (± 7)
4	17.1 (± 1.4)	18.6 (± 0.9)	0.9927	155 (± 7)
5	16.9 (± 1.5)	18.3 (± 1.0)	0.9916	152 (± 8)
6	17.0 (± 1.5)	18.1 (± 1.0)	0.9911	150 (± 8)

[a)] $a = \ln(n\mathrm{R}A W_m^{n-1}/E_a)$
[b)] $b = E_a/\mathrm{R}$
[c)] product moment correlation coefficient

under nitrogen), were lower than neat PS. These results suggest a negative influence of our fluorinated POSS on the thermal stability of nanocomposites.

In order to interpret the different behaviour of the two groups of compounds, the IR spectra of neat PS, of both 4-methoxyphenyl hcp-POSS and 2,4-difluorophenyl hcp-POSS, as well as those of compounds **3** and **6**, were carried out. Compounds **3** and **6** were selected for these experiments because they are those with the most high filler content. The IR spectra of methoxy- POSS and methoxy- nanocomposite, as well as those of fluorinated- POSS and fluorinated- nanocomposite, are reported in Figures 6 and 7, respectively, together with that of PS. The spectra of nanocomposites, if compared with those of PS and corresponding POSSs, show the shift of the characteristic sharp band attributable to Si–O bonds from 1082 cm^{-1} (of 4-methoxyphenyl hcp-POSS) and 1078 cm^{-1} (of 2,4-difluorophenyl hcp-POSS), to 1090 cm^{-1} and 1096 cm^{-1} in the IR spectra of compounds **3** and **6**, respectively, thus suggesting the presence of filler-polymer interactions in both series of nanocomposites, to which the Si–O bond of POSS cage is assigned.

The thermal degradations in air of both **3** and **6** samples were then carried out from r.t. up to 450°C. This temperature, at which the mass of samples is 10% about of initial mass, was chosen because it is roughly the starting temperature of the low rate degradation stage.

The IR spectra of the residues so obtained were compared with the IR spectrum of residue at 380°C (10% about of initial sample mass) from the degradation of neat PS (Figures 8 and 9 for methoxy- and fluorinated- derivatives, respectively).

The presence in both the IR spectra of the residues from samples **3** and **6** of the band at 697 cm^{-1} as well as of some weak bands in the 2900–3100 cm^{-1} range, which are characteristic of PS, clearly indicates that when nanocomposites degrade polymer is still present at temperatures largely higher than that at which the complete mass loss of neat PS is observed (Figure 4).

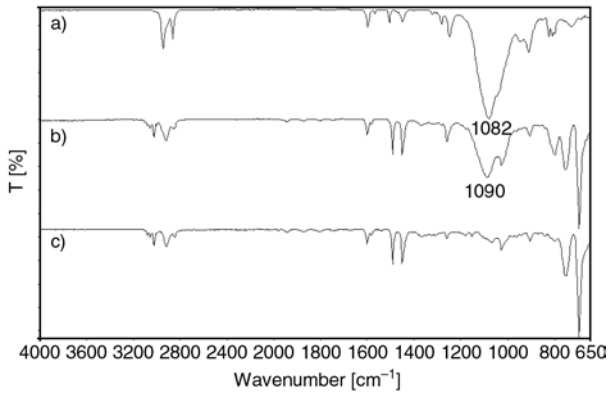

Figure 6. FTIR spectra of 4-methoxyphenyl hcp-POSS (a), sample **3** (b) and PS (c)

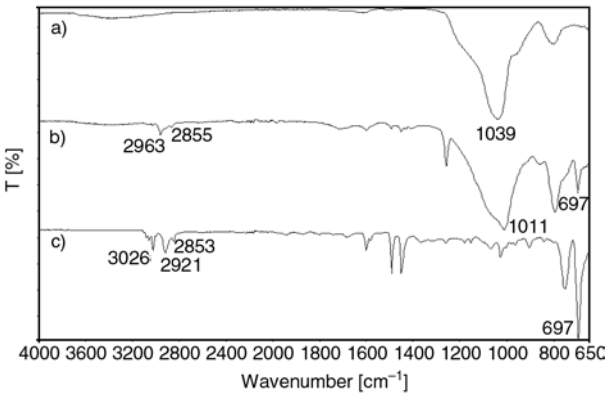

Figure 8. FTIR spectra of the residues of 4-methoxyphenyl hcp-POSS (a), sample **3** (b) and PS (c) after thermal degradation in static air atmosphere

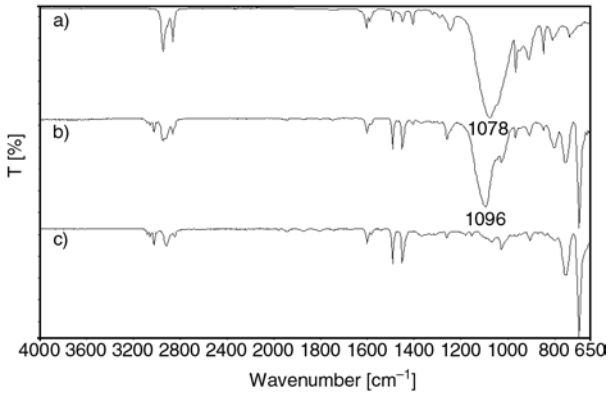

Figure 7. FTIR spectra of 2,4-difluorophenyl hcp-POSS (a), sample **6** (b) and PS (c)

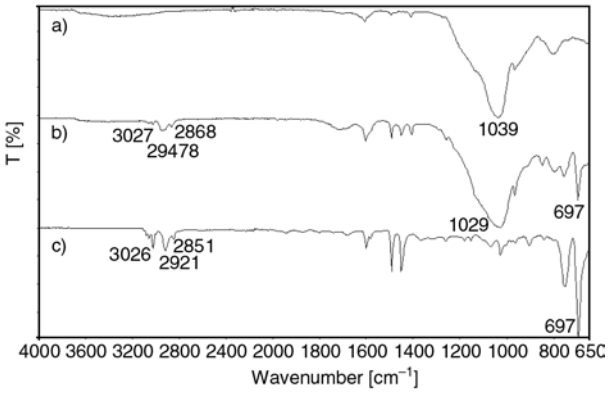

Figure 9. FTIR spectra of the residues of 2,4-difluorophenyl hcp-POSS (a), sample **6** (b) and PS (c) after thermal degradation in static air atmosphere

Since no qualitative difference was found in the IR behaviour of both methoxy- and difluoro- nanocomposites before degradation as well as in the final stage of degradation, the worse thermal behaviour of fluorinated nanocomposites can not be due, on the basis of spectrophotometric experiments, to the lack of filler-polymer interactions. It could be thus attributed, in our opinion, to lower average molar mass of PS in fluorinated nanocomposites, as evidenced by both viscosity and glass transition temperature determinations. This hypothesis agrees very well with literature data showing that the onset temperature of PS pyrolysis (which corresponds at $T_{5\%}$ about) in air decreases on decreasing the polymer average molar mass [46].

4. Conclusions

In a previous work we synthesized some ph,hcp-POSS/PS nanocomposites by the direct polymerization *in situ* of styrene in the presence of different amounts of filler, and the obtained results indicated a much higher thermal stability of nanocomposites than that of the virgin polymer. On continuing our research in this field, we would verify, in the present work, if the substitution of hydrogen atoms of POSS phenyl group with electron-donor (methoxy-) or electron-withdrawing (fluorine-) groups was able to affect the thermal stability of nanocomposites through the formation of differently strong (or through the lack of) POSS-polymer interactions. We expected some changes of the characteristic parameters of thermal stability in respect to unsubstituted ph,hcp-POSS/PS nanocomposites, but opposite for the two groups of studied compounds. The results until now obtained drive us to suppose that no significant difference of filler-polymer interactions occurs between the two groups of compounds. The decrease of thermal stability observed for difluoro-nanocomposites appears due to the lower polymerization degree of PS which could be attributable to the presence of fluorinated POSS during the *in situ* polymerization process.

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