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## **NANOCOMPOSITES WITH POLYHEDRAL OLIGOMERIC SILSESQUIOXANE NANOFILLERS – CHARACTERIZATION OF MORPHOLOGY, THERMAL AND MECHANICAL PROPERTIES**

### **Abstract**

High-density polyethylene nanocomposites with hydroxy-hepta(*iso*-butyl)-octasilsesquioxane (POSS-(*i*-Bu)<sub>7</sub>OH) and hydroxy-hepta(*iso*-octyl)-octasilsesquioxane (POSS-(*i*-Oct)<sub>7</sub>OH) as nanofillers were prepared by melt blending. The morphological, thermal and mechanical properties as well as processability of obtained nanocomposites were characterized. POSS nanofillers were homogeneously dispersed in polymeric matrix. High compatibility between nanofiller and polymer induced enhanced thermal stability, Charpy impact strength and melt flow rate for composite materials. POSS particles acted also as a nucleating agent for polyethylene crystallization in the nanocomposite.

### **Key words**

nanocomposites, polyethylene, silsesquioxanes

### **Introduction**

Nowadays, the design and development of new functional materials is one of the most intensively expanded research fields. Recently, special attention has been paid to the polymeric nanocomposites containing inorganic fillers. Such materials combine advantageous properties of organic polymers (e.g. processability, toughness, relatively low cost) and inorganic materials (high thermal and oxidative stability, durability), thus they are remarkably promising in various applications [1-4].

Recently, the polyhedral oligomeric silsesquioxanes (POSS) have gained particular popularity, among the all studied and used nanofillers. POSS are large and diverse family of compounds described with (RSiO<sub>1.5</sub>)<sub>n</sub> general formula, where R can be hydrogen or an organic group [5,6]. This class of materials can be considered as unique organic-inorganic hybrid compounds. Silsesquioxanes are consisted of a silicon-oxygen (siloxane) core, often in a cube form, and diverse functional substituents, which can be attached to this inorganic cage. This structure provides opportunities to modify the properties of POSS compounds in wide range [5-8].

POSS were successfully applied as nanofillers in preparation of interesting and useful polymeric nanocomposites, based inter alia on polyolefins, polyesters, polyamides and acrylates matrices [9-13]. In many cases, the introduction of POSS into polymers has a significant influence on their physical and chemical properties [10-12]. It was reported, that POSS particles can act as nucleating agents, plasticizers or fire retardants [14-18]. The application of POSS particles result also in the increase in the thermo-oxidative stability and use temperature, as well as in improving the mechanical, rheological and/or processability of polymeric materials [17-20].

In this work, we present the results of the studies on the effect of introduction hydroxy-hepta(*iso*-butyl)-octasilsesquioxane (POSS-(*i*-Bu)<sub>7</sub>OH) and hydroxy-hepta(*iso*-octyl)-octasilsesquioxane (POSS-(*i*-Oct)<sub>7</sub>OH) as nanofillers into high-density polyethylene (HDPE) matrix, on material's properties. The HDPE-based nanocomposite samples with 2 or 5 wt% POSS content were prepared by melt blending method. The morphological, thermal and mechanical properties, as well as processability of POSS-containing nanocomposites were investigated. It should be noted that in the case of polyolefin composites with POSS nanofillers, octasilsesquioxane derivatives with eight identical alkyl substituents at silicon-oxygen core have

been mainly used [10-12]. Moreover, to the best of our knowledge, hydroxy-hepta(alkyl)-octasilsesquioxanes have not been applied as nanofillers in polyethylene composites, up to date.

### Materials and methods

High-density polyethylene (HDPE) Purell GA 7760 (MFR = 18 g/10 min at 190 °C/2.16 kg) was provided by Basell Orlen Polyolefins. POSS-(*i*-Bu)<sub>7</sub>OH (Fig. 1a) and POSS-(*i*-Oct)<sub>7</sub>OH (Fig. 1b) nanofillers were prepared by Centre for Advanced Technologies AMU (Poznań, Poland) according to well-known literature method described by Caetano *et al.* [21]. All chemicals for the synthesis of POSS compounds were used as received from the supplier (Sigma-Aldrich) without any further purification.

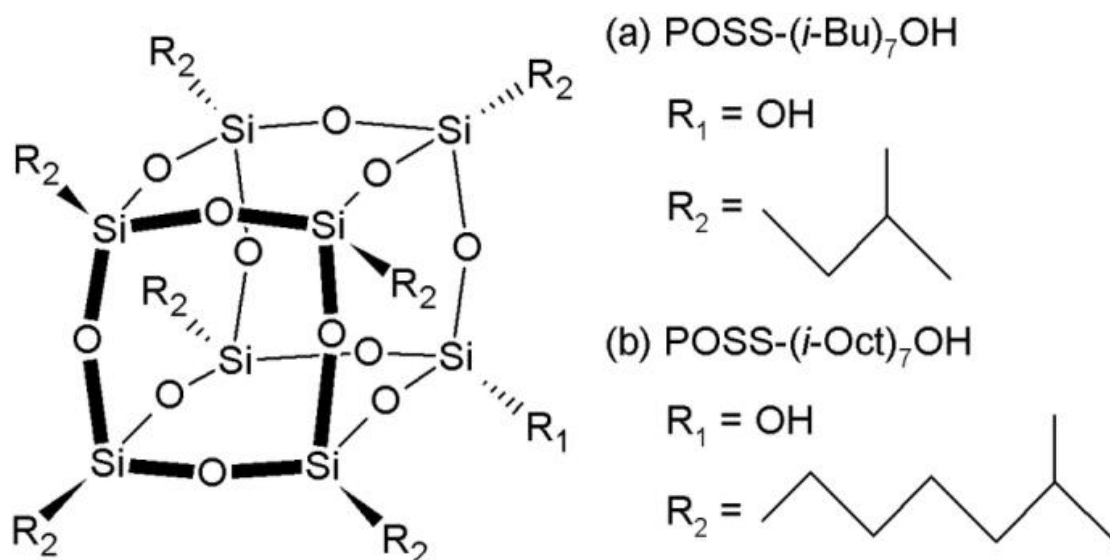


Fig. 1 Chemical structures of (a) POSS-(*i*-Bu)<sub>7</sub>OH and (b) POSS-(*i*-Oct)<sub>7</sub>OH nanofillers.

Source: Author's

The two-step process was used to prepare HDPE with POSS nanofiller. In the first step, the masterbatches containing 10 wt% of POSS were prepared in the HAAKE PolyLab Reomixer (150 °C, 50 rpm, 15 min). In the second step, the HDPE/POSS nanocomposite samples were prepared by melt blending method using ZAMAK IM-15 laboratory conical twin screw extruder (155-170 °C, 100-200 rpm, 3 min) coupled with ZAMAK IMM-15 laboratory injection machine (165 °C, 6 MPa, 6 s). HDPE granulate and appropriate masterbatch were mixed, at suitable weight ratios, to obtain nanocomposites containing 2 or 5 wt% of POSS-(*i*-Bu)<sub>7</sub>OH or POSS-(*i*-Oct)<sub>7</sub>OH.

The Fourier transform infrared spectroscopy (FTIR) was performed on a Thermo Scientific NICOLET 6700 spectrometer using attenuated total reflectance (ATR) technique by recording 32 scans in the 4000-650 cm<sup>-1</sup> range.

The morphology of fractured surface of nanocomposite samples was observed by the scanning electron microscopy (SEM; Hitachi TM3000) equipped with the energy dispersive X-ray spectroscopy system (SEM/EDS). The samples were covered with thin layer of gold, before being examined, to provide their conductivity. SEM images were taken at the magnification of 2000× with the SEM operating voltage of 15 kV.

Thermal properties of nanocomposites were studied by the differential scanning calorimetry (DSC) method using a DSC1 Mettler Toledo device. Three successive runs (heating-cooling-heating) were performed at the 10 °C × min<sup>-1</sup> rate under nitrogen flow with ca. 3-10 mg of samples. The presented data were taken from the cooling run (crystallization process) and second heating run (melting process). The crystallinity degree ( $X_c$ ) was calculated from the ratio:

$$X_c = \frac{\Delta H_f}{w \cdot \Delta H_0} \cdot 100\% \quad (1)$$

where  $\Delta H_f$  is the heat of fusion of the analyzed sample and  $\Delta H_0$  is the heat of fusion of the 100 % crystallinity sample (293 J × g<sup>-1</sup> for HDPE [22]), and  $w$  is the mass fraction of polymer in the nanocomposite.

Thermogravimetric analyses (TGA) were performed on a TG/DSC1 Mettler Toledo device. The samples (3–10 mg) were put into alumina pans and heated under nitrogen from the room temperature to 500 °C at the 10 °C × min<sup>-1</sup> rate.

The melt flow rate (MFR) values were measured according to ISO-1133-1:2011 (190 °C/2.16 kg) using a Zwick Aflow extrusion plastometer.

Charpy impact strength tests were performed using the Zwick HIT 50P machine according to PN-EN ISO 179-1. Notched bars were broken using a pendulum with the nominal energy of 0.5 J.

## Results and discussion

### ATR-FTIR studies

The presence of POSS nanofiller particles within the HDPE matrix was proved by ATR-FTIR technique. Figs 2a and 2b show ATR-FTIR spectra for neat HDPE and HDPE/POSS nanocomposites.

In the ATR-FTIR spectra of all samples, the absorbance bands with maximum intensity at 2914 and 2850 cm<sup>-1</sup> were observed, which were assigned to asymmetric and symmetric stretching vibrations of –CH<sub>2</sub> groups. The bands at 1472 and 1461 cm<sup>-1</sup> from deformation and scissoring vibrations of –CH<sub>2</sub> groups were also visible [23,24]. However, in the case of HDPE/POSS nanocomposites, the band with maximum intensity at 1120 cm<sup>-1</sup>, which is associated with stretching vibrations of Si–O–Si bonds in the POSS cage, was also identified [25,26]. Moreover, the intensity of this band increased with the increasing content of the POSS nanofiller in composite materials, what confirmed the successful incorporation of POSS particles into polyethylene matrix.

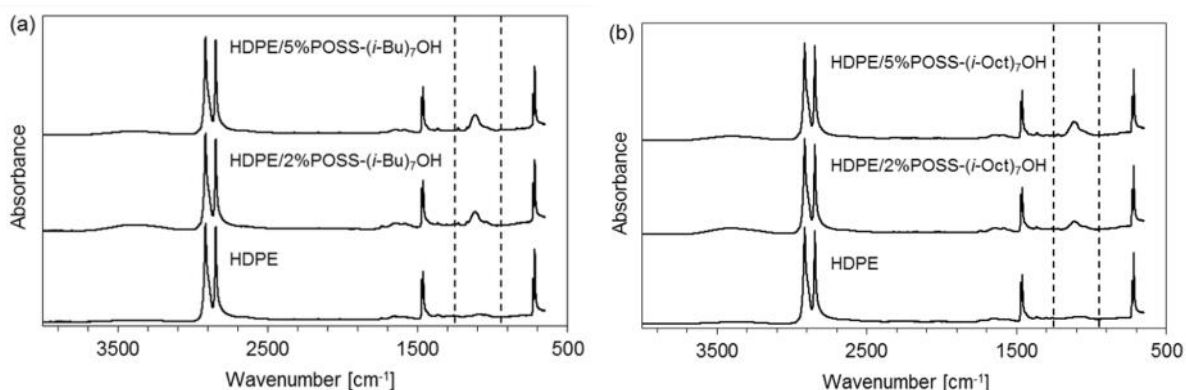


Fig. 2 ATR-FTIR spectra of neat HDPE and (a) HDPE/POSS-(*i*-Bu)<sub>7</sub>OH as well as (b) HDPE/POSS-(*i*-Oct)<sub>7</sub>OH nanocomposites.

Source: Author's

### Morphology

The homogenous dispersion of nanofiller particles in polymeric matrix is one of the key factors determining the favorable and unique properties of nanocomposites. However, in the case of nanocomposites, the aggregation of nanofiller particles gains special significance, because contribute to an unsatisfactory reinforcing/improving effect of nanofiller [2, 27].

The dispersion of POSS particles in HDPE matrix was evaluated using SEM/EDS method. Fig. 3a-d show SEM micrographs and SEM-EDS Si-mapping micrographs of fracture surface of HDPE nanocomposites containing 2 and 5 wt% of POSS-(*i*-Bu)<sub>7</sub>OH or POSS-(*i*-Oct)<sub>7</sub>OH nanofiller. It was found that the POSS particles were uniformly dispersed throughout the polymer matrix, regardless to the kind of POSS nanofiller used. Moreover, no aggregates of nanofillers were observed even at higher content of POSS in nanocomposite materials. It could be explained by favorable interactions between the POSS nanofiller particles and polymer. Similar observations were reported in the case of polypropylene composites with POSS nanofillers which contained *iso*-butyl or *iso*-octyl groups attached to the silicon-oxygen cage [14, 19] as well as for polyethylene composites with *n*-hexadecyl-substituted POSS [20]. Thus, it could be concluded that the presence of hydroxyl group in the POSS molecule does not worsen the dispersion of POSS in HDPE matrix.

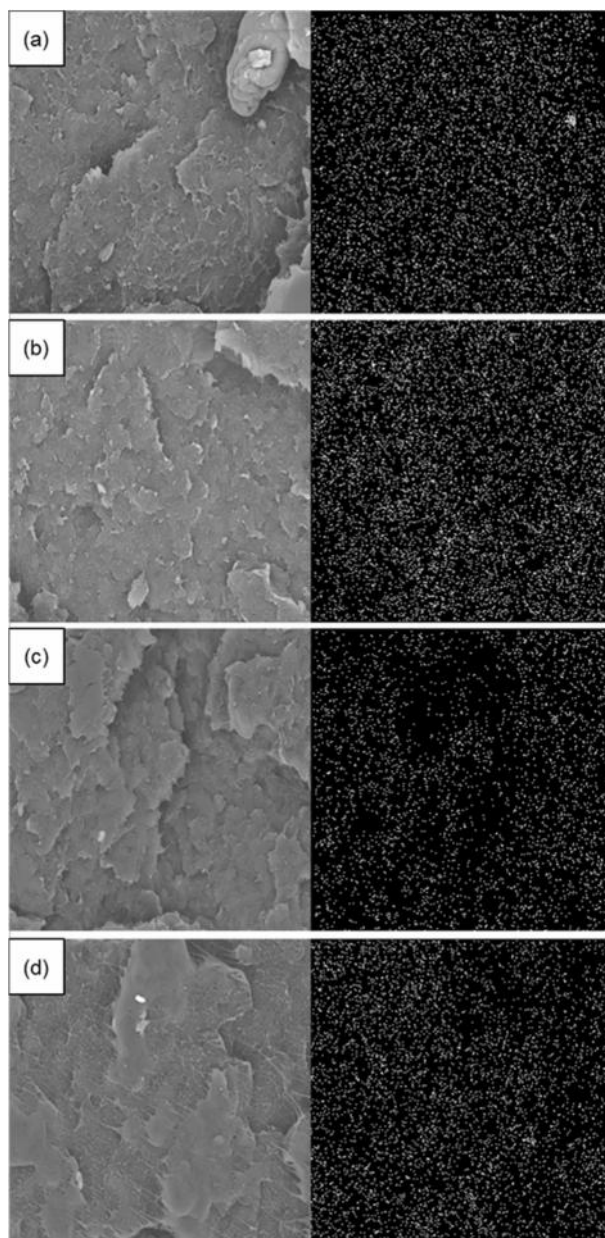


Fig. 3 SEM micrographs (left column) and SEM/EDS Si-mapping micrographs (right column) for the (a) HDPE/2%POSS-(*i*-Bu)<sub>7</sub>OH, (b) HDPE/5%POSS-(*i*-Bu)<sub>7</sub>OH, (c) HDPE/2%POSS-(*i*-Oct)<sub>7</sub>OH and (d) HDPE/5%POSS-(*i*-Oct)<sub>7</sub>OH nanocomposites.

Source: Author's

### Crystallization and melting behavior studies

The introduction of POSS particles into polyolefin matrices may improve crystallization and melting behavior of polymer, thus POSS can act as nucleating agent. Moreover, in the case of POSS-containing nanocomposites, the structure and the amount of applied POSS nanofillers have a great influence on the melting and crystallization process of polymeric matrices [14,15].

In this study, the influence of addition of POSS-(*i*-Bu)<sub>7</sub>OH and POSS-(*i*-Oct)<sub>7</sub>OH nanofillers particles on the crystallization and melting characteristic of HDPE matrix was evaluated by DSC analysis. The DSC results, such as crystallization temperature ( $T_c$ ), melting temperature ( $T_m$ ) and crystallization degree ( $X_c$ ) for neat HDPE and HDPE/POSS nanocomposite samples are shown in Tab. 1. It was found, that introduction of POSS particles into HDPE matrix resulted in a slight decrease of  $T_c$  and  $T_m$ , regardless to the type and amount of applied nanofiller. Similar changes were also observed for other polyethylene composites with POSS nanofillers as reported in previous works [28-31]. Worth mentioning is that Perrin *et al* [28] suggested that small amounts of POSS

nanofiller does not significantly influence the crystalline structure of PE, regardless to the structure of substituents in POSS molecules.

In turn, values of  $X_c$  increased with increasing POSS content in composite materials. Moreover, somewhat higher increase of crystallinity degree values was observed in the case of nanocomposites with the POSS-(*i*-Bu)<sub>7</sub>OH particles, which contain shorter (*iso*-butyl) substituents attached to the POSS cage, in comparison to the materials with POSS-(*i*-Oct)<sub>7</sub>OH nanofiller (with *iso*-octyl substituents). It may be assumed that the arrangement of high-density polyethylene polymer chains in the presence of POSS-(*i*-Bu)<sub>7</sub>OH and POSS-(*i*-Oct)<sub>7</sub>OH nanofillers was more ordered. This observation is in agreement with results described in the literature [28,31] where the slight increase in the polymer crystallinity after addition of POSS particles was also demonstrated.

Tab. 1 DSC results of neat HDPE and HDPE/POSS nanocomposites.

Sample	$T_c$ [°C]	$T_m$ [°C]	$X_c$ [%]
HDPE	118.4	132.1	73.9
HDPE/2%POSS-( <i>i</i> -Bu) <sub>7</sub> OH	118.0	131.7	74.7
HDPE/5%POSS-( <i>i</i> -Bu) <sub>7</sub> OH	117.7	131.5	75.6
HDPE/2%POSS-( <i>i</i> -Oct) <sub>7</sub> OH	118.1	131.4	72.7
HDPE/5%POSS-( <i>i</i> -Oct) <sub>7</sub> OH	118.2	131.4	75.0

Source: Author's

### Thermal stability studies

The type and amount of POSS nanofiller introduced into polymer matrix strongly affect the thermal stability of the nanocomposites obtained. This can be explained by the high rigidity and thermal stability of silicon-oxygen structure of POSS core [9]. It was determined that during the thermal decomposition of POSS-containing nanocomposites, a silica-like residues, which are produced on the surface of material, can act as protective barrier [28,32].

Fig. 4 shows the values of the maximum mass loss rate temperature ( $T_{max}$ ), which defines the temperature at which thermal decomposition of sample take place with the highest rate [33]. It was found that introduction of 2 wt% of POSS nanofillers into HDPE matrix improved the thermal stability of nanocomposites, irrespective to the kind of nanofiller applied. However, further increase in content of POSS nanofillers led to slight decrease of  $T_{max}$  values. Interestingly, HDPE/POSS-(*i*-Oct)<sub>7</sub>OH nanocomposites had higher thermal stability, than HDPE/POSS-(*i*-Bu)<sub>7</sub>OH nanocomposites. It should be noted that the lack of significant changes of thermal stability (in nitrogen atmosphere) after incorporation of POSS particles into polyethylene matrix was also reported in literature [28,32].

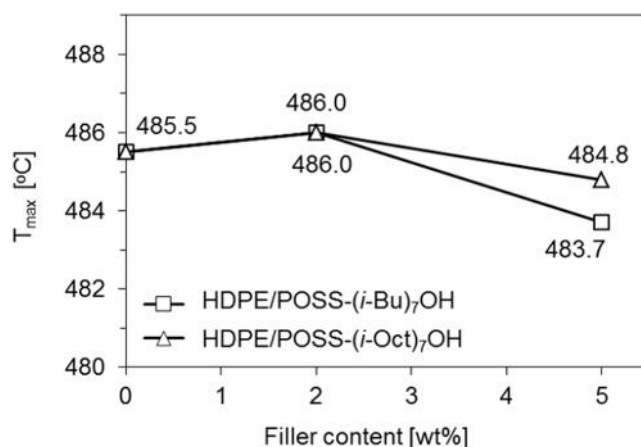


Fig. 4 The maximum mass loss rate temperatures ( $T_{max}$ ) of HDPE and HDPE/POSS nanocomposites.

Source: Author's

### MFR studies

The ease of operation, low cost and repeatability of the results make the MFR an important parameter that is widely used in the industry [34]. Moreover, the determination of MFR values gives valuable information about the materials processability and allows the estimation of changes in rheological properties, due to e.g. changes in the material's microstructure [34,35].

Fig. 5 shows the MFR values of neat HDPE and HDPE/POSS nanocomposites. The introduction of POSS particles into HDPE matrix caused increase in MFR values, in comparison with neat polymer. Moreover, the MFR values increased with the increasing content of nanofiller. It should be noted that the addition of POSS-(*i*-Oct)<sub>7</sub>OH with *iso*-octyl substituents on silicon-oxygen core to the HDPE resulted in larger improvement of MFR, in comparison with HDPE/POSS-(*i*-Bu)<sub>7</sub>OH nanocomposites. It could be explained by higher compatibility between POSS-(*i*-Oct)<sub>7</sub>OH molecules containing longer *iso*-octyl substituents with HDPE, than POSS-(*i*-Bu)<sub>7</sub>OH with shorter *iso*-butyl substituents attached to the POSS core. Thus, this indicates that POSS molecules with long alkyl substituents attached to the POSS cage could act more efficiently as plasticizers. This is probably caused by disengagement in the polymer chain packing in presence of POSS nanofiller particles, what affects the microstructure of nanocomposite materials obtained. It should be emphasized that *Huang et al* [30] and *Joshi et al* [36] also indicated on the formation of free volumes in the melt after introduction POSS particles into polyethylene matrix.

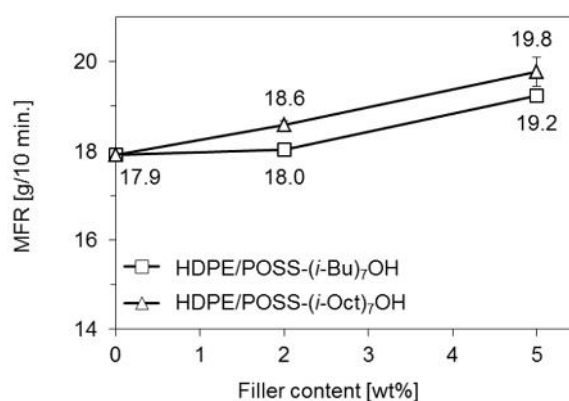


Fig. 5 MFR values of HDPE and HDPE/POSS nanocomposites.

Source: Author's

### Charpy impact strength

Fig. 6 shows the values of Charpy impact strength as a function of POSS content. It was observed that the increasing content of POSS-(*i*-Oct)<sub>7</sub>OH in HDPE matrix resulted in clear improvement of this parameter. In turn, addition of POSS-(*i*-Bu)<sub>7</sub>OH particles caused only slight enhancement of impact strength of HDPE/POSS-(*i*-Bu)<sub>7</sub>OH nanocomposite. The better results obtained in Charpy impact strength tests in the case of HDPE/POSS-(*i*-Oct)<sub>7</sub>OH nanocomposites confirm more uniform dispersion of POSS-(*i*-Oct)<sub>7</sub>OH particles in HDPE and their high compatibility with HDPE polymer chains.

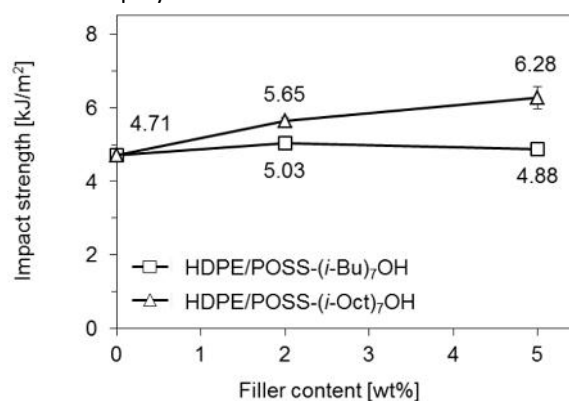


Fig. 6 Charpy impact strength values of HDPE and HDPE/POSS nanocomposites.

Source: Author's

## Conclusions

The effect of introduction of POSS-(*i*-Bu)<sub>7</sub>OH and POSS-(*i*-Oct)<sub>7</sub>OH particles as nanofillers into HDPE matrix on morphology, thermal and mechanical properties as well as processability of obtained nanocomposites was investigated. The influence of the structure and wt% content of the POSS nanofillers in the nanocomposites was also studied.

The application of POSS as nanofillers for polymer nanocomposites give opportunities to develop the interesting and unique materials, because material's properties could be modified by structural control of POSS derivatives used. The presence of POSS particles in HDPE/POSS nanocomposites was proved by ATR-FTIR spectra. Moreover, it was found that the POSS particles were uniformly dispersed in polyethylene matrix, regardless to the kind and wt% content of nanofillers, as determined by SEM/EDS analysis. The structure of the substituents attached to the POSS cage (*iso*-butyl or *iso*-octyl) had a significant influence on the properties of HDPE/POSS nanocomposites. Interestingly, crystallization and melting behaviors of prepared nanocomposites were almost unchanged, in comparison to the neat HDPE. However,  $X_c$  values were increased, especially in the case of HDPE/POSS-(*i*-Bu)<sub>7</sub>OH nanocomposites. This could prove that POSS with short alkyl substituents (such as POSS-(*i*-Bu)<sub>7</sub>OH) could act as nucleating agents which contributed to the increase in the polymer chains arrangement. The thermal stability of POSS-containing materials was slightly improved after introduction of 2 wt% of POSS nanofillers. Somewhat higher  $T_{max}$  values were observed for materials with POSS-(*i*-Oct)<sub>7</sub>OH than in the case of HDPE/POSS-(*i*-Bu)<sub>7</sub>OH. This is the result of better compatibility between HDPE and POSS containing *iso*-octyl substituents. HDPE-based nanocomposites with POSS were characterized by higher MFR values, and thus by better processability, than neat polymer. Moreover, the increasing POSS wt% content resulted in increase of MFR values for nanocomposites. Such behavior may be related to the POSS role as plasticizers in HDPE. Mechanical properties determined by Charpy impact strength were improved after introduction of POSS nanofillers into HDPE and better results were obtained in the case of HDPE/POSS-(*i*-Oct)<sub>7</sub>OH nanocomposites.

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