Polypropylene/polyhedral oligomeric silsesquioxane nanocomposites – study of free volumes, crystallinity degree and mass flow rate*)

Arkadiusz Niemczyk[1], Katarzyna Dziubek[1], **), Krystyna Czaja[1], Roman Szatanik[2], Mariusz Szołyga[3], Michał Dutkiewicz[4], Bogdan Marciniec[4]

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Abstract: Polypropylene/polyhedral oligomeric silsesquioxane (PP/POSS) nanocomposites were prepared by the melt blending method. Positron Annihilation Lifetime Spectroscopy (PALS) was used to study the effects of the structure and of the amount of POSS on the free volumes in PP. The PALS parameters: *o*-Ps lifetime and its intensity, were compared to the crystallinity degree and to the mass flow rate (*MFR*) of nanocomposites. The presence of POSS nanofillers affected the PP microstructure and the size and number of free volumes in the polymer. The crystallinity degree was decreased and the intensity of *o*-Ps component was increased by increasing POSS contents. The *MFR* values increased for nanocomposites, thus POSS nanoparticles can act as plasticizers and generate more free volumes in PP.

Keywords: nanocomposites, polypropylene, polyhedral oligomeric silsesquioxanes (POSS), positron annihilation lifetime spectroscopy (PALS), crystallinity degree, mass flow rate.

Nanokompozyty polipropylen/poliedryczne oligomeryczne silseskwioksany – badania objętości swobodnych, stopnia krystaliczności oraz masowego wskaźnika szybkości płynięcia

Streszczenie: Nanokompozyty polipropylen/poliedryczne oligomeryczne silseskwioksany (PP/POSS) przygotowano metodą mieszania w stanie stopionym polimeru. Wpływ struktury oraz ilości zastosowanych nanonapełniaczy POSS na objętości swobodne w polipropylenie określono z zastosowaniem spektroskopii czasów życia pozytonów (PALS). Ustalono zależności pomiędzy parametrami PALS: czasem życia *o*-Ps (τ_3) i natężeniem (I_3) składowej *o*-Ps oraz wartościami stopnia krystaliczności (X_c) i masowego wskaźnika szybkości płynięcia (*MFR*) badanych materiałów. Obecność nanonapełniaczy POSS wpłynęła na liczbę i rozmiary objętości swobodnych w polimerze, co spowodowało zmianę mikrostruktury osnowy polipropylenowej. Wraz ze zwiększaniem zawartości napełniaczy POSS zmniejszał się stopień krystaliczności kompozytów, zwiększało natężenie składowej *o*-Ps, a dodatkowo wzrastała wartość *MFR* – nanocząstki POSS pełniły w układzie rolę plastyfikatorów.

Słowa kluczowe: nanokompozyty, polipropylen, poliedryczne oligomeryczne silseskwioksany (POSS), spektroskopia czasów życia pozytonów (PALS), stopień krystaliczności, masowy wskaźnik szybkości płynięcia.

The effects obtained after the introduction of filler particles into polymeric matrices on the properties of various polymeric nanocomposites have been extensively studied in recent years. In particular, the determination of the correlation between macroscopic and microscopic properties of these materials is of great interest. It turns out that the thermal, mechanical, rheological and other macroscopic properties of polymers are significantly dependent on the microstructure of the subnanometric local free-volume holes that result from irregular molecular packing in these materials [1, 2]. One of the most useful techniques for studying subnanometer holes in various amorphous and semicrystalline polymers is positron annihilation lifetime spectroscopy (PALS) [1, 2]. The PALS method is also successfully used to study the free-volume properties of polymeric nanocomposites [3–6]. However, the number of literature reports concerning the application of PALS to study the microstructure of polymeric nanocomposites is still limited.

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[1] University of Opole, Faculty of Chemistry, Oleska 48, 45-052 Opole, Poland.

[2] University of Opole, Faculty of Mathematics, Physics and Computer Science, Institute of Physics, Oleska 48, 45-052 Opole, Poland.

[3] Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89B, 61-614 Poznań, Poland.

[4] Adam Mickiewicz University in Poznań, Centre for Advanced Technologies, Umultowska 89C, 61-614 Poznań, Poland.

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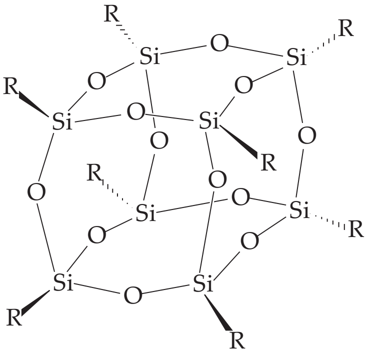
**) Author for correspondence; e-mail: katarzyna.dziubek@uni.opole.pl

POSS are considered a novel group of inorganic-organic hybrid compounds that possess silicon-oxygen cores and external organic substituents [7–9]. POSS compounds have been successfully used for the preparation of various types of polymeric materials, including nanocomposites. The use of POSS nanofillers in such polymers as polyolefins, polyesters, polyamides and polyurethanes makes it possible to obtain composite materials with improved mechanical, rheological, morphological and thermal properties [7–10].

In this work, octakis({*n*-alkyl}dimethylsiloxy)octasilsesquioxane (POSS) nanofillers with long *n*-alkyl substituents on the silicon-oxygen core [Formula (I)] were incorporated into the polypropylene (PP) matrix by melt blending. The PALS technique was for the first time used to study the effect of the POSS nanofiller on the free-volume properties of polypropylene in PP/POSS nanocomposites. The influence of the length of *n*-alkyl substituents in the POSS molecules, and the effect of the weight content of these nanofillers on the number and size of free-volume holes in the PP matrix is discussed. Moreover, the results of PALS measurements for neat PP and PP/POSS composites were compared to the crystallinity degree and processability as characterized by melt flow rate (*MFR*) values.



(I)

POSS8 R = $OSi(CH_3)_2C_8H_{17}$
POSS12 R = $OSi(CH_3)_2C_{12}H_{25}$
POSS18 R = $OSi(CH_3)_2C_{18}H_{37}$

EXPERIMENTAL PART

Materials

– Polypropylene (PP) Moplen HP 400R (*MFR* = 25 g/10 min at 230 °C/2.16 kg, a lot number: RL0173703) was provided by Basell Orlen Polyolefin.

– Octakis({*n*-octyl}dimethylsiloxy)octasilsesquioxane (POSS8), octakis({*n*-dodecyl}dimethylsiloxy)octasilsesquioxane (POSS12) and octakis({*n*-octadecyl}dimethylsiloxy)octasilsesquioxane (POSS18) were synthesized in a two stage process according to procedures well known and described in the literature [11] by the Centre for Advanced Technologies AMU (Poznań, Poland). All chemicals for the synthesis of POSS compounds were used as received from the supplier (Sigma-Aldrich) without any further purification.

Preparation of PP/POSS nanocomposites

PP/POSS nanocomposites were obtained by melt blending in a two step process. In the first step, which was carried out in a HAAKE Polylab Reomixer (180 °C, 50 rpm, 15 min), PP/20%POSS concentrates were prepared. Next, using a laboratory conical twin screw extruder (ZAMAK, type IM-15), with a screw length of 165 mm and screw diameter 8/21 mm (the screw speed was set at 100 rpm), coupled with a laboratory injection molding machine (ZAMAK, type IMM-15), PP/POSS nanocomposites with 1, 3, 5 and 10 wt % of POSS nanofillers were obtained. Samples were prepared in the temperatures range 175–195 °C, in the form of trabeculars according to the ISO 179 standard.

Methods of testing

A fast-fast coincidence spectrometer (Ortec system), based on two γ-ray detectors with BaF_2 crystals as scintillators, was used to record the positron lifetime spectra for the investigated samples. The detectors were placed at the angle of 90° to each other and the time resolution of the spectrometer was ~ 290 ps *FWHM* (Full Width at Half Maximum). The ^{22}Na isotope with activity of 0.9 MBq, prepared from an aqueous solution of $^{22}NaCl$ and enveloped in 8 μm Kapton foil, was used as the source of the positrons, and it was placed between identical polymer samples to form a "sandwich" system. The first detector recorded the 1.28 MeV γ quantum (start signal) and the second detected the 0.511 MeV annihilation γ quantum (stop signal). The positron lifetime was calculated as the time difference between the two detector signals. All positron lifetime spectra were measured at room temperature and they contained $1.5 \cdot 10^6$ counts. The computer Lifetime (LT) software was used to deconvolute the measured lifetime spectra into three lifetime components. Deconvolution of spectra into 3 components was proved by the χ^2 test. However, only the third lifetime (τ_3) value, which represented the *o*-Ps "pick-off" annihilation was analyzed.

– The crystallinity degree (X_c) was determined by the differential scanning calorimetry (DSC) analyses, using a DSC1 METTLER TOLEDO instrument. PP/POSS samples were heated to 170 °C under nitrogen, they were held in the molten state for 5 min and then cooled down to 0 °C with heating and cooling rates equal to 10 °C/min. The DSC data were collected for the second melt event to eliminate the previous thermal history of the samples. The crystallinity degree (X_c) was calculated from the ratio $\Delta H_f/\Delta H_0$where ΔH_f is the heat of fusion of a sample and ΔH_0 is the heat of fusion of a 100 % crystallinity sample (209 J/g for PP) [12].

– The melt flow rate (*MFR*) values were measured according to ISO 1133-1:2011 (230 °C; 2.16 kg) using a Zwick Aflow extrusion plastometer.

– The fracture surface of the samples was imaged by a scanning electron microscope (SEM) Hitachi TM3000.

The samples were covered with gold to provide conductivity of the materials to be analyzed. SEM images were taken at a magnification of 2000× with a 15 kV SEM operating voltage.

RESULTS AND DISCUSSION

Free-volume properties – PALS studies

Positron annihilation is a useful and sensitive technique to investigate the characteristics of materials. The positrons emitted from a radioactive source into a polymer after thermalization and diffusion processes can form positroniums (Ps). Ps can exist in two states: as *para*-positronium (*p*-Ps), consisting of e^- and e^+ with antiparallel spin, and as *ortho*-positronium (*o*-Ps), with parallel spin states. In vacuum, *p*-Ps and *o*-Ps annihilate with lifetimes of 0.125 and 142 ns, respectively [2, 13].

Polymers contain local, free-volume holes that appear as a consequence of irregular molecular packing in the amorphous phase. *o*-Ps can be trapped in the free-volume and undergo "pick-off" annihilation during its collisions with molecules, which in turn reduces the *o*-Ps lifetime to a few nanoseconds [1, 2]. The *o*-Ps lifetime therefore may be correlated with the frequency of *o*-Ps collisions with the surrounding molecules and the dimensions of free volumes [13].

By deconvolution of the PALS lifetime spectra, the *o*-Ps lifetime (τ_3) and the intensity (I_3) of *o*-Ps component are determined. These directly correlate with the size and number of free-volume holes, respectively [3]. Tao and Eldrup [14, 15] formulated the correlation between the free-volume hole dimensions in polymers and the experimentally observed *o*-Ps "pick-off" annihilation lifetime. A semiempirical equation was established that relates the *o*-Ps lifetime with the size of the free volume:

$$\tau_3 = 0.5\left[1-\frac{R}{R+\Delta R}+\frac{1}{2\pi}\sin\left(2\pi\frac{R}{R+\Delta R}\right)\right]^{-1} \qquad (1)$$

where: τ_3 (ns) corresponds to a spherical space with the average free volume radius R, ΔR – the empirical constant that is dependent on the shape of the free volume.

In case of polymer nanocomposites, τ_3 and I_3 are dependent mainly on the type and content of the filler in the composite material [3, 4].

Figures 1 and 2 show the τ_3 and I_3 values for neat PP and for PP/POSS nanocomposites. It was found that for PP/POSS nanocomposites, the values of τ_3 and I_3 were higher than for neat PP – irrespective of the type of applied POSS nanofiller. Moreover, the values of those parameters gradually increased with increasing POSS content, especially for small contents of nanofillers.

It can be assumed that the presence of POSS particles and their interactions with the polymer induced changes in the microstructure of polypropylene and affected the free-volume properties of nanocomposite materials. The POSS increased the distances between the polymer chains, thus the size and the number of free-volume holes increased for larger amounts of the POSS filler in nanocomposites.

The values of the PALS parameters were also influenced by the structure of applied POSS nanofillers. The τ_3 and I_3 values generally decreased with lengthening *n*-alkyl groups attached to the POSS core. Thus, the largest values of the PALS parameters were obtained for nanocomposites with POSS8. This can be explained by the lowest compatibility between POSS with *n*-octyl substituents and PP matrix, and the highest POSS8 tendency to aggregate in comparison to POSS12 and POSS18.

The presence of small aggregates in the sample of PP/POSS8 nanocomposites was proved by SEM images (Fig. 3a). For comparison, particles of POSS with longer *n*-alkyl substituents on the core were more uniformly dispersed in the polypropylene matrix (Fig. 3b).

Crystallinity degree vs. free-volume properties

The incorporation of POSS may affect the crystallization behavior of the polymeric matrix. The observed changes are usually attributed to the effect of POSS dispersion, mainly in the amorphous regions of the polymer [9, 10, 16, 17]. POSS nanoparticles can act as nucleating agents, increasing the crystallinity degree [17]. On the other hand, they can disturb the packing of polymer chains in some

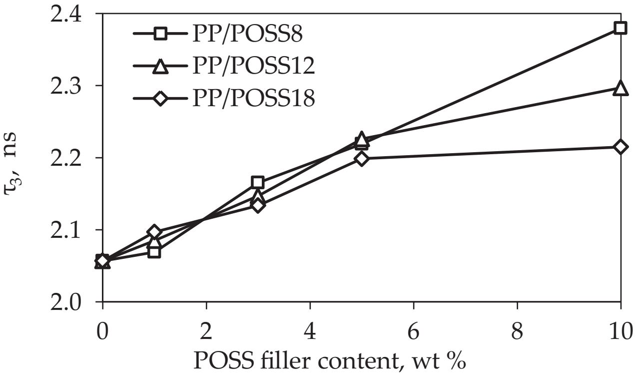


Fig. 1. *o*-Ps lifetime (τ_3) versus weight content of POSS nanofillers in PP/POSS nanocomposites

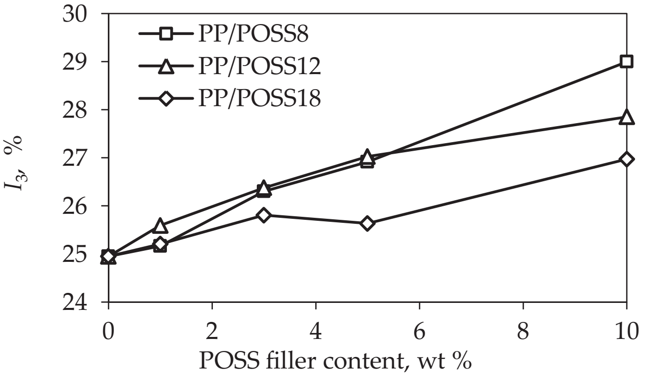


Fig. 2. Intensity (I_3) of *o*-Ps component versus weight content of POSS nanofillers in PP/POSS nanocomposites

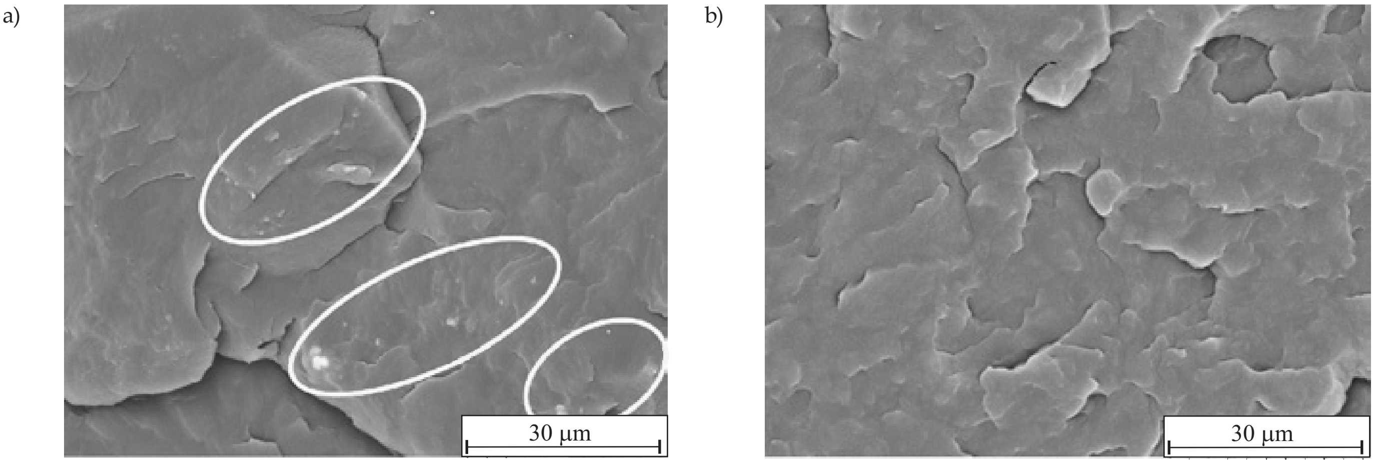


Fig. 3. SEM micrographs of: a) PP/5%POSS8, b) PP/5%POSS18 nanocomposites

cases and reduce the polymer crystallinity by contributing to the growth of the free-volume holes [4, 18].

The influence of POSS in the polypropylene matrix on the crystallization behavior of POSS-containing nanocomposites has been studied elsewhere [9, 10, 16, 17]. However, there are no reports available for changes in the free-volume parameters for polyolefin/POSS nanocomposites versus crystallinity. Generally, the *o*-Ps lifetime intensity (I_3) increases with lower crystallinities of the polymeric material, which suggests that *o*-Ps are more easily formed in regions of low electron density [1, 2].

Figure 4 shows the crystallinity degree (X_c) for neat PP and PP/POSS nanocomposites. The values of X_c for POSS-containing polypropylene nanocomposites were generally lower than that for the neat PP matrix. Moreover, the increase in the weight content of the POSS nanofiller resulted in lower X_c values for the nanocomposites, irrespective of the type of the POSS used. The results suggest that the POSS nanoparticles may induce the hindering of the molecular motion of the polymer chain, and retard the crystallization process in polypropylene [9, 10, 17]. The crystallinity degree values were also influenced by the structure of the POSS nanofiller. The most significant decrease in X_c values (from 46.0 % to 42.0 % with the increasing weight content of POSS) was observed when POSS8, *i.e.*, the structure containing the shortest alkyl substituents on the silicon-oxygen POSS, was used as a nanofiller. For the PP/POSS12 and PP/POSS18 nanocomposites, the changes of X_c were in the range from 46.5 % to 44.0 %, and from 46.4 % to 43.2 %, respectively. This may be explained by the occurrence of stronger POSS-POSS interactions between POSS8 molecules, and by lower compatibility between POSS particles and polypropylene, in comparison with the performance of POSS12 and POSS18.

A correlation between the X_c and I_3 parameter values for nanocomposites was also found. I_3 was observed to increase as the X_c decreased with the increasing weight content of POSS in the nanocomposites, irrespective of the POSS type. The POSS molecules distributed among the polymer chains may be assumed to perturb the packing in PP, resulting in the higher number of free-volume holes in the polymeric material, and in the decrease of the crystallinity degree.

Mass flow rate vs. free volume properties

The determination of the flow behavior of polymeric nanocomposites is important from both the scientific and practical points of view. The flow properties of polymers are characterized mainly by melt flow tests, such as mass flow rate test that provide a valuable information about the processability of a material. The *MFR* is an important parameter that is widely used in the industry, due to the ease of operation, low cost and repeatability of the results [19, 20]. Recently, a significant interest has been also paid on the study of the relationship between *MFR* values and the physicochemical properties of polymers, such as molecular weight or viscosity [20, 21].

The presence of POSS nanoparticles in the polymeric matrix may result in changed melt flow properties and thus in the processability of the nanocomposite material versus those of neat polymer. POSS-POSS and polymer-POSS interactions may retard the polymer chain movements. However, polymer chain disentanglements and formation of more free volumes in the melt may occur, depending on the weight content of POSS in a nanocomposite [18].

The influence of POSS in the PP matrix on the processability of the obtained nanocomposites was characterized in the mass flow rate test. Figure 5 shows *MFR* values for neat PP and for PP/POSS nanocomposites. The *MFR* values for PP/POSS nanocomposites were found to be significantly higher in comparison with those for neat PP, irrespective of the type of the POSS nanofiller used. Moreover, the increasing weight content of POSS nanofillers in those materials resulted in an increase of their *MFR* values. The POSS nanofillers added to the PP matrix may be assumed to improve the polymer chain mobility by loosening the chain packing and to affect plasticization of the polymer. It should also be noted that

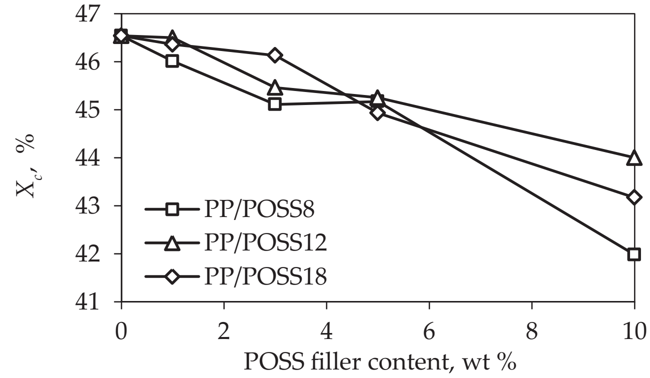


Fig. 4. Crystallinity degree (X_c) versus weight content of POSS nanofillers in PP/POSS nanocomposites

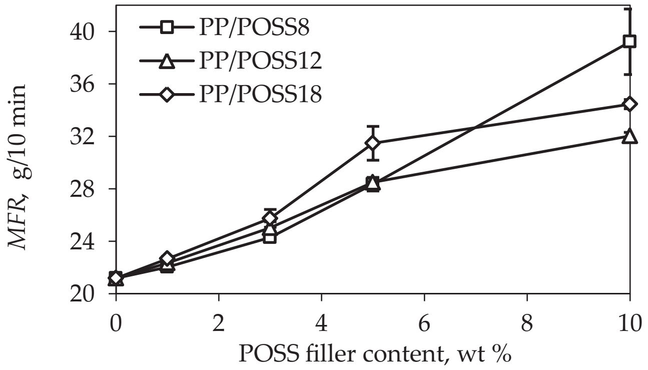


Fig. 5. Melt flow rate (*MFR*) versus weight content of POSS nanofillers in PP/POSS nanocomposites

the *MFR* values were dependent on the length of *n*-alkyl substituents on the POSS core and they increased as follows: PP/POSS8 < PP/POSS12 < PP/POSS18. The highest *MFR* values for nanocomposites with POSS18 may result from the greater compatibility between the PP matrix and POSS that contain a long *n*-alkyl substituent on the silica-oxygen core. Thus, it may be concluded that the presence of long *n*-alkyl chains as substituents in the POSS molecules promotes the plasticization effect of these nanofillers.

A correlation was found for the studied PP/POSS nanocomposites between *MFR* and values of the intensity (I_3) of *o*-Ps component, which is interesting. It was apparent that higher I_3 values (Fig. 2) increased the *MFR* values, too (Fig. 5). Moreover, the values of both parameters increased with the increasing weight content of the POSS particles in the PP matrix. The obtained results confirmed that the POSS nanofillers can act as plasticizers and they can generate more free volumes in a polymer [22].

CONCLUSIONS

The PALS technique was used for the first time to investigate the influence of the structure and weight content of a POSS nanofiller on the free-volume properties of PP/POSS nanocomposites. Octakis({*n*-alkyl}dimethylsiloxy)octasilsesquioxanes with *n*-octyl, *n*-dodecyl and *n*-octadecyl substituents were used as nanofillers.

Incorporation of POSS into PP affected the microstructure of the polymeric matrix. The PALS parameters: *o*-Ps lifetime (τ_3) and intensity (I_3) of the *o*-Ps component were higher when POSS nanofillers were added to the polymer. It can thus be concluded that the size and number of free-volume holes in polypropylene were increased in the presence of POSS nanoparticles probably because of a perturbation in the PP chain packing. The values of the PALS parameters gradually increased with the increasing weight content of POSS. However, the values of τ_3 and I_3 generally decreased with the lengthening *n*-alkyl substituents on the silicon-oxygen core of POSS particle.

Correlations between the PALS parameters (τ_3 and I_3) and crystallinity degree (X_c), as well as the melt flow rate (*MFR*) values for PP/POSS nanocomposites, were observed. Incorporation of POSS particles into the PP matrix reduced the crystallinity degree for those materials due to disorder in the polymer chain packing. However, the *MFR* values for PP/POSS nanocomposites were significantly higher than for neat PP. The results suggest that POSS particles act as plasticizers that generate more free volumes in polypropylene.

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