Polypropylene-POSS Nanocomposites: Morphology and Crystallization Behaviour

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Summary: Nanocomposites of isotactic polypropylene (PP) with polyhedral oligomeric silsesquioxanes (POSS) $[RSiO_{1,5}]_8$ having different alkyl substituents (R = methyl, isobutyl, isooctyl) were obtained by melt blending and analysed with electron microscopy, optical microscopy and DSC calorimetry. The influence of POSS structure on the morphological characteristics, the crystallization and melting behaviour of PP/POSS composites was investigated with varying the filler amount. The crystallization kinetics of the composites from the melt, examined both in isothermal and non-isothermal conditions, demonstrated that the nucleation activity of the examined POSS can be related to the length of alkyl substituents which, depending on the loading amount, affect the filler dispersion in the PP matrix and the growth of polymer crystals.

Keywords: crystallization; morphology; nanocomposites; polypropylene; POSS

Introduction

In the field of inorganic-organic composite materials, many research interests are oriented to polyhedral oligomeric silsesquioxane (POSS) based materials, both as organic-inorganic hybrids and as polymer nanocomposites. POSS are a family of compounds with general formula $(RSiO_{1,5})_p$ where R is hydrogen or an organic group (alkyl, aryl or any of their derivatives), and are characterized by a size in the range 1–3 nm and by high chemical versatility and capability to form nanostructures with tailored dimensionality.[1]

The dispersion of POSS nanoparticles in polymeric matrices - such as polyacrylates, polyesters, polyimides, polystyrene and its copolymers - allows to obtain advanced composite materials with high thermal, mechanical and oxidative performances.[2] The compatibility of these materials is expected to be markedly enhanced due to the possibility of modifying the chemical/physical interactions at polymer-filler interface through introduction of functional groups on the POSS molecules.

The final properties of polymeric composites are strictly dependent on the morphology generated during their processing when the filler may act as nucleating agent and affect the crystallization behaviour and the supermolecular structure. Therefore, the study of the phase transitions phenomena and polymer-filler interactions is crucial for the control of the processing conditions and the optimization of the end-product properties.

Although the crystallization kinetics of plain polyolefins have been extensively examined, little research has been so far carried out on the crystallization processes and supermolecular organisation of polyolefin/POSS nanocomposites.[3,4]

The preparation and characterization of PP nanocomposites containing various alkyl substituted POSS (Figure 1) was recently reported by some of the authors.[5]

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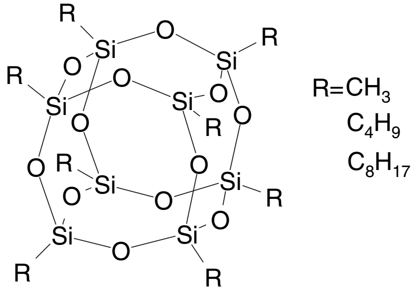

Figure 1.
Chemical structure of alkyl substituted POSS.

In the present paper, the influence of chemical structure and concentration of alkyl substituted POSS on the morphology and crystallization behaviour of PP/POSS nanocomposites is investigated. The crystallization kinetics of these materials were studied both in isothermal and non-isothermal conditions with the aim of analysing the role of the nanoparticles on the nucleation mechanism and growth of the polymer crystals.

Experimental Part

Materials

Isotactic polypropylene was a Moplen HP501L (MFR 6.0 g/10 min at 230 °C/2.16 kg) from Basell (Ferrara, Italy). Fully condensed alkyl substituted POSS ($p = 8$) with different R chain lengths, namely octamethyl (OM-POSS), octaisobutyl (OIB-POSS) and isoctyl (OIO-POSS) (cage mixture: $p = 8\text{-}10\text{-}12$), were provided by Hybrid Plastics (Hattiesburg, USA), and used as received. OM-POSS and OIB-POSS are crystalline solids, whereas OIO-POSS is a liquid at room temperature. PP/POSS composites were prepared via melt blending in a Brabender W50E internal mixer at 180 °C and 60 rpm for 10 min. POSS were loaded into the polyolefin matrix at different weight ratios, from 3 to 10 wt.%. After mixing the samples were cooled in air to room temperature. Samples containing 3, 6 and 10 wt.% OM-POSS were named as PP/OM3, PP/OM6 and PP/OM10 respectively, and so on for PP/OIB and PP/OIO composites. Plain PP was processed in Brabender mixer under the same conditions.

Microscopical Analysis

Morphological characteristics were analysed by means of imaging scanning electron microscopy (LEO 1450 VP) on cryogenically fractured surfaces of samples obtained from mixer. An optical polarized light microscope (Leitz Ortholux II POL) equipped with a THMSE 600 Linkam hot stage was used to study the crystallization process from the melt. The growth rate $G = dR/dt$ of PP spherulites in the composites was calculated by measuring the radius R of spherulites as a function of time t during isothermal crystallization in the temperature range 125–135 °C. Thin sections of the melt mixed samples, sandwiched between cover glasses, were heated to 190 °C for 3 min to ensure a complete melting, then the samples were quickly cooled (100 °C/min) to the crystallization temperature. The growing crystals were monitored during crystallization using a JVC TK-1085E video camera and a miroVIDEO DC30 capture card. The radius R of several spherulites was measured for each sample on photomicrographs by means of a Scion Image software and G was calculated from the average slope of linear plots of R against crystallization time t. The test was repeated three times with fresh samples.

Calorimetry

The thermal behaviour of the composites was studied by differential scanning calorimetry using a Perkin-Elmer Pyris Diamond DSC, operating under nitrogen flow. Kinetics of crystallization were studied both in isothermal and non-isothermal conditions. For isothermal crystallization studies the samples were first heated from room temperature to 190 °C at 10 °C/min and held there for 3 min to erase any previous thermal history; then they were rapidly cooled (100 °C/min) to the fixed T_{ic} and the heat of crystallization was recorded as function of time until the completion of crystallization. For non-isothermal experiments the samples, after melting to 190 °C for 3 min, were cooled down to 50 °C at different cooling rates (2.5, 5, 10, 20 °C/min). The crystallization peak was recorded as function of temperature which was related to the time t as: $T = T_o - \alpha t$ (where α is the cooling rate and T_o the starting temperature of crystallization for $t = 0$). For all isothermal and non-isothermal processes the relative weight fraction $X(t)$ of material crystallized after time t was evaluated by the ratio of the crystallization area at the time t over the total area. The half-time of crystallization was taken as the time corresponding to $X(t) = 0.5$.

The melting behaviour of the crystallized samples was analysed by heating the samples directly from T_{ic} up to 190 °C in DSC at a rate of 10 °C/min. Melting temperatures and enthalpies were calculated from the maxima and the area of endothermal peaks, respectively. The crystallinity degree X_c was evaluated from the ratio $\Delta H_m/\Delta H_m^\circ$ where $\Delta H_m^\circ = 189$ J/g for PP.[6]

Results and Discussion

Morphology

The POSS dispersion into PP matrix was previously shown to be influenced by the chain length of alkyl groups on the molecules.[5] In the case of composites with OM-POSS the compatibility between POSS and PP was rather low, resulting in the formation of micro-aggregates (Figure 2a) both at low and high filler content. Using OIB-POSS a fine particle dispersion on a sub-micron scale within the polymer matrix was obtained at low filler content. Increasing OIB concentration resulted in some changes of composite morphology; in particular, SEM analysis of fracture surfaces of PP/OIB10 sample revealed the presence of PP crystalline grains that have grown around POSS aggregates (Figure 2b). PP/OIO samples displayed at any composition a very fine filler dispersion with no microscopic evidence of phase separation.

All samples exhibited the characteristic spherulitic morphology of isotactic polypropylene with α-monoclinic crystal structure as confirmed by WAXS analysis.[5] Traces of β and γ crystal phases were found only for PP/OIB10 sample. No change of spherulitic texture was detected with varying the blend composition, and straight boundaries between impinged spherulites in melt crystallized samples were generally observed, which are typical of crystallization process initiated by athermal heterogeneous nucleation.[7]

Observation by polarized optical microscopy (POM) showed that for composites with OM-POSS the growth of PP spherulites occurred preferentially on the particle surfaces (Figure 3a). Similar effects were observed for the sample with 10 wt.% OIB-POSS (Figure 3b).

The spherulite growth rates G of PP and PP/POSS composites, measured during isothermal crystallization at

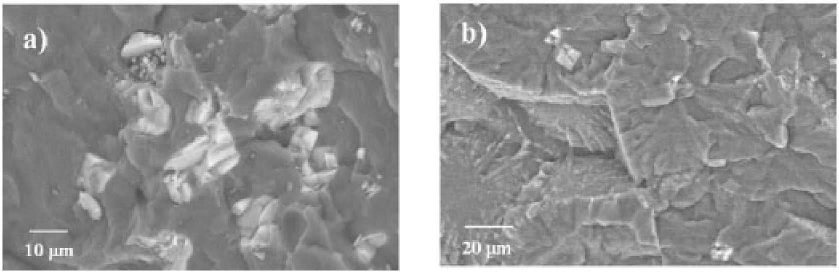

Figure 2.
SEM micrographs of fracture surfaces of (a) PP/OM10 and (b) PP/OIB10 samples.

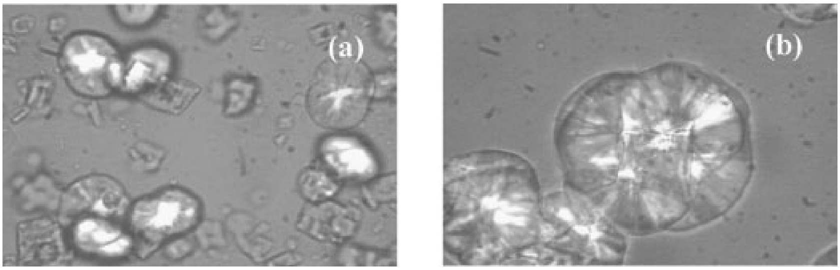

Figure 3.
POM micrographs of growing spherulites in (a) PP/OM3 and (b) PP/OIB10 molten samples during isothermal crystallization at $T_{ic} = 130\ ^{\circ}C$.

$T_{ic} = 130\ ^{\circ}C$, are plotted in Figure 4 as function of POSS content. For all samples the spherulite radius increased linearly with time before the spherulites contact each other. At all examined temperatures the growth rate of PP appeared to increase for OM-POSS content higher than 3 wt.% while in the presence of OIB-POSS and OIO-POSS it resulted almost unaffected by the filler content. This suggests that the nucleation and the growth process of the spherulites from the melt is influenced by the type of alkyl substituent on the POSS cage-structure and, in particular, by the interactions at the surface of POSS aggregates, which in turn depend on the filler concentration as evidenced by the microscopic analysis for PP/OM and PP/OIB samples.

Thermal Behaviour

The results of DSC analysis of PP/POSS composites are summarized in Table 1. It was found that on cooling from the melt the crystallization onset, T_{ons}, and peak temperature, T_c, of PP increased after the addition of OM-POSS (3–10 wt.%) supporting a nucleating effect of this filler as reported by other authors.[3] Otherwise, the addition of OIB-POSS and OIO-POSS resulted in a shift of T_c towards lower temperatures than that of plain PP, with exception of the sample PP/OIB10 which showed a crystallization behaviour similar to PP.

Melting thermograms on the 2nd heating run showed a single melting peak ($T_m \approx 166\ ^{\circ}C$) for PP and PP/OM samples and a double peak at lower Tm for the other composites, due to PP crystals with lower

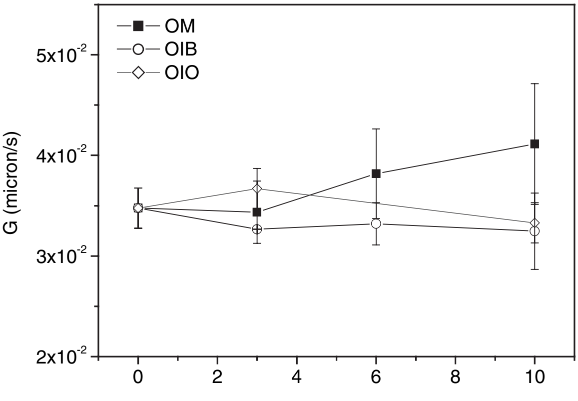

Figure 4.
Spherulite growth rate as function of POSS content for PP and PP/POSS samples isothermally crystallized at $T_{ic} = 130\ ^{\circ}C$.

Table 1.
DSC data for PP/POSS composites (cooling and heating rate: 10 °C/min).

Sample	Cooling			2nd heating		
	T_{ons} (°C)	T_c (°C)	ΔH_c (J/g PP)	T_m (°C)	ΔH_m (J/g PP)	X_c (%)
PP	120.9	115.5	95.8	166.7	88.5	46.8
PP/OM 3	123.5	118.9	97.0	165.9	91.7	48.5
PP/OM 6	123.9	120.5	97.8	162.4	85.8	45.4
PP/OM 10	123.4	119.8	98.1	165.2	91.1	48.2
PP/OIB 3	117.4	112.3	94.5	159.8	88.3	46.7
PP/OIB 6	115.0	110.1	89.9	162.5	77.2	40.9
PP/OIB 10	122.6	115.2	98.1	162.5	89.7	47.5
PP/OIO 3	118.8	113.8	91.7	161.0	80.2	42.5
PP/OIO 10	117.3	111.9	96.0	159.4	84.3	44.6

perfection and stability which can reorganise during heating.

Isothermal Crystallization Kinetics

The isothermal crystallization behaviour of PP and composites was examined in the T_{ic} range 120–138 °C. Plots of the relative weight fraction $X(t)$ vs. time indicated that the overall crystallization rate of PP increased in the composites containing OM-POSS, while decreased in the case of samples with OIB-POSS and OIO-POSS. The analysis of the isothermal kinetics was made according to the Avrami equation:

$$X(t) = 1 - \exp -K_n t^n \qquad (1)$$

where n is the Avrami exponent which depends on both the mechanism of nucleation and morphology of crystals growth, and K_n, the rate costant.[8] The slope and the intersection of logarithmic plots of $-\ln[1-X(t)]$ vs. t were used to estimate n and K_n, respectively: these plots generally showed a linear trend up to a high conversion degree ($X(t) \approx 80$–90%), followed by a change of slope which can be attributed to secondary crystallization phenomena. The Avrami exponent of the composites showed average values in the range $n = 3 \div 4$ for PP/OM and $n = 2.5 \div 3$ for PP/OIB3 and PP/OIO as compared to neat PP and PP/OIB10 with $n = 3$. This result confirms that the nucleation and growth of PP crystals in the matrix are strictly affected by the type and content of POSS, and the observed value of n for PP/OM is in agreement with a spherulitic growth initiated by heterogeneous nucleation.

In Figure 5 the overall crystallization rate of PP and PP/POSS, expressed as the

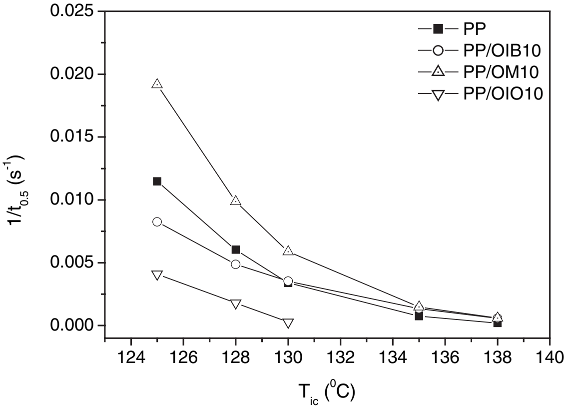

Figure 5.
Temperature dependence of the overall crystallization rate ($1/t_{0.5}$) of isothermally crystallized PP and PP/POSS composites (10 wt.% POSS).

Table 2.
Nucleation density (nuclei/cm^3) for isothermally crystallized PP/POSS samples.

T_{ic} (°C)	PP	PP/OM3	PP/OM6	PP/OM10	PP/OIB3	PP/OIB6	PP/OIB10
125	$8.8\ 10^9$	$1.9\ 10^{10}$	$2.0\ 10^{10}$	$2.3\ 10^{10}$	$3.3\ 10^8$	$1.0\ 10^8$	$4.0\ 10^9$
130	$1.5\ 10^9$	$8.3\ 10^9$	$2.9\ 10^{10}$	$2.0\ 10^{10}$	$6.0\ 10^7$	$2.5\ 10^7$	$3.9\ 10^9$

reciprocal of the half-time of crystallization $t_{0.5}$, is plotted as function of T_{ic}. Composites PP/OM displayed a higher rate than PP at same crystallization temperature and the rate increased with increasing the filler amount. For samples PP/OIO and PP/OIB (3–6 wt.%) a marked decrease of rate was recorded, while composite with 10 wt.% OIB showed a similar behaviour to PP. The temperature dependence of crystallization rate was thus related to the activation energy for the formation of critical nuclei, which was evaluated from the slope of linear plots of $\ln(1/t_{0.5})$ or $\ln K_n$ vs. $1/(T_{ic}\Delta T)$, according to the kinetic theory.[9] The data obtained indicate that the activation energy for PP/OM and PP/OIB10 samples was lower than that found for PP and other composites.

For a crystallization process determined by heterogeneous nucleation and three-dimensional growth, the kinetic constant (K_3) can be expressed as

$$K_3 = (4\pi\rho_c/3\rho_a)\cdot N_h\, G^3 \qquad (2)$$

where ρ_c and ρ_a are the density of crystalline and amorphous PP phases respectively and N_h the number of nuclei per unit volume.[10] By assuming for ρ_c and ρ_a literature values[8] and calculating $K_3 = (K_n)^{3/n}$ from the experimental values of K_n and n, as reported by Bartczak et al.,[11] N_h was determined for the various samples (Table 2). It can be noticed that the nucleation density, which decreases with increasing T_{ic}, generally displays larger values for PP/OM as compared to PP and PP/OIB (3–6 wt.%).

Melting thermograms of isothermally crystallized samples are shown in Figure 6. A higher melting peak (and enthalpy) was always observed for PP and PP/OM with respect to other composites, supporting the existence of more perfect and stable crystals in accordance with the morphological effects of spherulite growth above reported. In some cases a smaller peak was recorded at lower temperature (≈152 °C), which could likely be associated with the occurrence of β-form crystals of PP.[12]

The melting temperature of crystallized samples increased with T_{ic} according to a linear trend as described by the Hoffman-Week relation.[9] The equilibrium melting

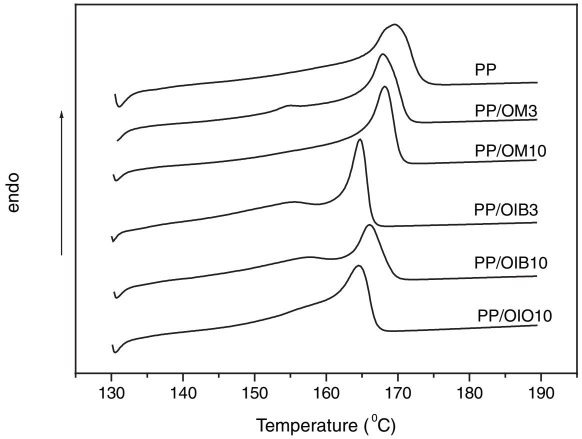

Figure 6.
DSC melting thermograms of PP and PP/POSS composites crystallized at $T_{ic} = 130$ °C.

temperature (T_m°) of the composites, calculated by extrapolation of T_m lines to $T_{ic} = T_m$, was found at a value of about 189 °C, in satisfactory agreement with that usually observed for PP homopolymer.[6]

Non-isothermal Crystallization Kinetics

The onset and the crystallization peak temperature (T_{nc}) on the DSC thermograms of PP/POSS recorded at various cooling rates ($2.5 \div 20$ °C/min) resulted to change with type and content of POSS. The addition of OM-POSS shifted the crystallization temperature to higher values whereas addition of OIB and OIO-POSS moved T_{nc} to lower values as compared to plain PP at same cooling conditions. The values of reciprocal of crystallization half-time, as determined from plots of $X(t)$ vs. time, are reported in Figure 7 as a function of cooling rate α. In all the examined range the crystallization rate of PP is higher for PP/OM and lower for PP/OIB (3–6 wt.%) and PP/OIO, as already observed for the isothermal crystallization. However, these effects are depending on the cooling rate: for $\alpha < 10$ °C/min the difference of crystallization rate among the composites is progressively reduced and when $\alpha = 2.5$ °C/min all samples display a quite similar behaviour with little effect of filler approaching the equilibrium conditions.

The kinetics were analysed by using both the Avrami and the Ozawa theory. According to the Avrami model (see eq. 2), plots of $\log[-\ln(1 - X(t))]$ vs. $\log t$ were used to obtain values of the kinetic parameters n and K_n from the slopes and the intercepts, respectively.

The plots are characterized by the presence of three regions and the linear middle portions were chosen for the determination of the parameters. However, the linearity of these plots is generally limited with values of $n = 4 \div 5$ for PP and $n = 4 \div 6$ for the composites, which could be accounted for on the basis of branching crystallization mechanism controlled by athermal and thermal nucleation modes.[8]

According to Ozawa model, the relative crystallinity $X(T)$ at a temperature T can be calculated as:

$$X(T) = 1 - \exp -K(T)/\alpha^m \tag{3}$$

where α is the cooling rate, m is the Ozawa exponent which depends on the dimension of crystal growth and $K(T)$ is the cooling function related to the overall crystallization rate.[13] Accordingly to eq. (3) plots of $\log[-\ln(1 - X(T))]$ vs. $\log\alpha$ should give straight lines from which the values of m and $K(T)$ can be determined. The resulting plots for PP/POSS samples did not show linear trends indicating that m is not

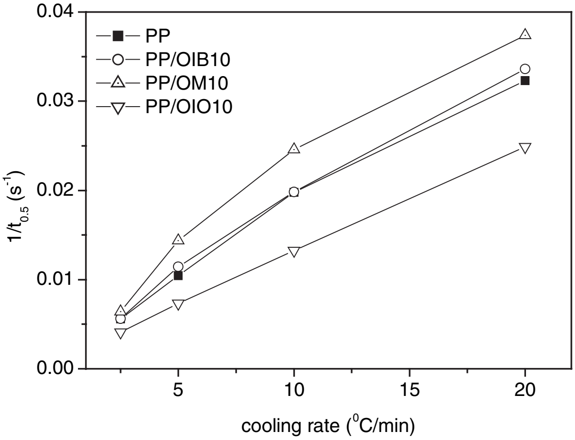

Figure 7.
Cooling rate dependence of non-isothermal crystallization rate ($1/t_{0.5}$) for PP and PP/POSS samples.

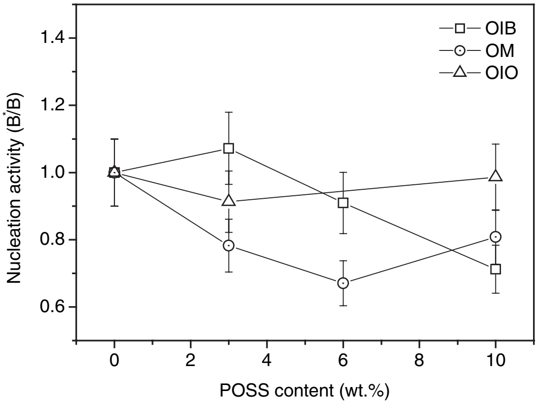

Figure 8.
Nucleation activity of alkyl substituted POSS in PP/POSS composites as a function of filler content.

constant with temperature and the cooling function could not be evaluated. According to several authors,[14,15] the failure of the Ozawa model to describe the non-isothermal behaviour of polymer systems is most likely due to the fact that this theory ignored the effect of secondary crystallization and the dependence of the lamellar thickness on temperature.

The above results indicate that both Avrami and Ozawa model are not adequate to describe the non-isothermal kinetics of the examined materials. It should be taken into account that other kinetic equations based on a combined approach of the two models, as proposed by Liu et al.,[16] have been more satisfactorily applied to nanocomposite systems to relate the crystallinity change with cooling rate and crystallization time (or temperature).[4]

The nucleation activity Φ of the various POSS samples was evaluated according to the model proposed by Dobreva *et al.*[17] Values of Φ were experimentally calculated on the basis of non-isothermal crystallization kinetics at various cooling rates (α) from the slopes (B, B^*) of the linear relations:

$$\ln\alpha = \text{constant} - B/\Delta T_p^2 \tag{4}$$

$$\ln\alpha = \text{constant} - B*/\Delta T_p^2 \tag{5}$$

where $\Delta T_p = T_m^\circ - T_c$ is the supercooling and $\Phi = B^*/B$. Values of B and B^* were measured for plain PP and PP/POSS composites respectively. For particles with no nucleation activity $\Phi = 1$, while for very active substrates Φ approaches zero. The effect of the various POSS on the nucleation activity is shown in Figure 8 as function of filler content. It can be seen that OM-POSS displays a higher activity ($\Phi \approx 0.7$–0.8) at all examined compositions, whereas OIO-POSS is uneffective for nucleation ($\Phi \approx 1$) and OIB-POSS results to be effective only at a content of 10 wt.% ($\Phi \approx 0.7$). It is interesting to notice that very similar results have been reported for composites of HDPE with OM-POSS [4] which showed nucleation activity for a POSS amount of 10 wt.% ($\Phi \approx 0.8$).

Conclusions

The melt crystallization behaviour of PP composites containing various alkyl substituted POSS has been examined to gain insights into the effect of POSS structure and concentration on the morphological characteristics and properties of these materials.

The results indicated that the length of alkyl groups on POSS molecules plays a fundamental role in determining the dispersion degree and the interactions with the polypropylene matrix during the cooling process from the melt. The microscopic analysis showed that octamethyl-POSS gave mainly rise to crystalline aggregates on micron-size scale, whereas isooctyl-POSS and, partially, octaisobutyl-POSS were well dispersed in the PP matrix likely owing to a more favourable interaction of the long alkyl groups with the polymer chains, as compared to that between the same POSS molecules.

OM-POSS resulted to be a nucleating agent for PP at all explored compositions and cooling conditions, while OIO-POSS retarded the crystallization kinetics, which can be ascribed to the high dispersion of this filler as liquid phase component. OIB-POSS showed a different behaviour depending on the loading amount in PP: at low content (3 wt.%) the nano-dispersion of OIB likely hinders the PP crystal growth, thus resulting in a retarded crystallization; at higher content (10 wt.%) this effect is counterbalanced by the presence of OIB crystal aggregates which behave as nucleants for PP.

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