Confinement of iPP crystallites within mesoporous SBA-15 channels in extruded iPP-SBA-15 nanocomposites studied by Small Angle X-ray Scattering

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Abstract

The main objective of this research is the study of different nanocomposites based on isotactic polypropylene (iPP) and mesoporous SBA-15 silica prepared by melt extrusion, analyzing the possible effect of this filler on the polymorphic behavior of iPP and the eventual observation of confinement effects. Thus, simultaneous Small Angle X-ray Scattering/Wide Angle X-ray Diffraction (SAXS/WAXD) synchrotron experiments at variable temperature have been performed on several iPP nanocomposites with different contents of SBA-15 mesoporous particles. Real-time variable-temperature SAXS measurements turned out a very useful tool to analyze the confinement of iPP crystallites within SBA-15 channels, and also to determine the most probable long spacing of chains located outside the SBA-15 nanospaces. Importance of these structural features is assessed by changes in the mechanical response of the final materials, finding that the presence of mesoporous particles leads to a reinforcing effect and contribute to improve the final dimensional stability.

Keywords: iPP-SBA-15 nanocomposites; real-time variable-temperature synchrotron measurements; SAXS/WAXD experiments; depth sensing indentation measurements.

Introduction

Small-angle X-ray scattering (SAXS) probes relatively large-scale structures and includes not only the diffraction of large lattice spacing but also the scattering by perturbed or non-periodic structures of amorphous and mesomorphic materials. The scattering of semicrystalline or amorphous materials is often described in terms of electron density at point $\mathbf{x}$, $\rho(\mathbf{x})$, in reciprocal or Fourier space [1]. Polymeric macrochains can form semicrystalline, mesomorphic, or amorphous structures. A proper structural and morphological evaluation of many polymers requires information attained from combination of SAXS and wide angle X-ray diffraction (WAXD). These simultaneous measurements have become an ideal and essential tool to study the changes that occurs during their crystallization and melting. Furthermore, the SAXS technique offers some unique research opportunities to study, among others: block copolymers either in the solid state or in solution; dimensions of clusters or domains existing in ion-containing polymers (ionomers); mesomorphic structures of liquid crystalline polymers in solutions (lyotropic) and in melts (thermotropic); biopolymers exhibiting some forms of mesoscopic properties in aqueous solutions; small colloidal particles in suspensions as well as microemulsions and micelles with appropriate sizes; polymer blends; polymerization reactions, in solution or in melt, involving electron density changes with the reacting medium during polymer formation; deformation processes of synthetic polymers and biological fibers; and, characterization of nanoparticle dispersion in polymer nanocomposites.

Ordered mesoporous silicas were described [2] for the first time in 1992. Other different ones were prepared years later [3,4]. The best known mesoporous silicas are the MCM-41 and the SBA-15, both with hexagonal arrangements. In particular, SBA-15 particles usually exhibit pore diameters ranging from 5 to 10 nm, although they might reach up to 30 nm if adequate additives are used. Among numerous applications, mesoporous silicas show potential for attaining polymer based nanocomposites with improved performance if macrochains can go

inside those ordered hexagonal channels. An eventual confinement on those polymeric chains within the pores can affect significantly the resulting properties. Presence of semicrystalline macrochains within channels has been recently described by means of Differential Scanning Calorimetry (DSC) for nanocomposites attained by in situ polymerization and based on high density polyethylene (HDPE) with either pristine or decorated MCM-41 particles, as well as on ultra high molecular weight polyethylene and neat SBA-15 silica [5-7] through the appearance of a melting process ranging from 65 to 85 °C in those containing MCM-41 and from 100-115 °C for the ones with SBA-15.

There are also some investigations related to nanocomposites of poly(*N*-isopropylacrylamide)/SBA-15 prepared by in situ polymerization [8] and to polyethylenimine (PEI) based composites with either MCM-41 or SBA-15, where PEI was incorporated to mesoporous silica by the wet impregnation method [9,10]. Authors used SAXS at room temperature to learn the effect of presence of those polymers in the ordered structure of the mesoporous silicas.

The aim of this work consists of going a step further when using SAXS measurements in the characterization of polymeric nanocomposites with mesoporous silica. Thus, evaluation of real-time variable-temperature SAXS experiments is proposed in order to assess eventual confinement effects, by analyzing the presence or absence of a certain amount of polypropylene crystallites within the SBA-15 channels in the nanocomposites based on iPP and SBA-15 prepared by melt extrusion. The results are compared with those derived from DSC experiments. In addition, the most probable long spacing of polypropylene crystals formed in the chains outside SBA-15 pores is analyzed together with the effect on this magnitude of mesoporous silica. The influence of all of these structural aspects on mechanical performance of these materials is also tested.

Experimental part

Materials and chemicals

A commercially available metallocene-catalyzed isotactic polypropylene (Metocene HM562P: melt flow index of 15 g/10 min, ISO 1133, kindly supplied by LyondellBasell) has been used in the present research as polymeric matrix. The SBA-15 particles were purchased from Sigma-Aldrich (specific surface area, $S_{\text{BET}} = 517 \text{ m}^2/\text{g}$; total pore volume, $V_t = 0.83 \text{ cm}^3/\text{g}$; average mesopore diameter [11], $D_p = 6.25 \text{ nm}$) and were used as received.

(Nano)composite and film preparation

Composites with different contents in SBA-15 particles (1, 4, 8 and 13% in weight, labeled as iPP-SBA1, iPP-SBA4, iPP-SBA8 and iPP-SBA13 respectively) were processed by melt extrusion in a corotating twin-screw microextruder (Rondol). Both polymer and SBA-15 were dried previously for 24 h under vacuum at 110 °C. A screw temperature profile of 190, 185, 180, 170 y 115 °C was used from the die to the hopper, being the length-to-diameter ratio 20:1. Then, films were obtained by compression molding at 190 °C and at 30 bar for 6 minutes in a hot-plate Collin (model 200x200) press. A relatively slow cooling process was applied to the different films from their melt to room temperature at the inherent cooling rate of the press (after switching off the power, cooling rate around 1.5 °C/min) between plates under pressure (30 bar).

Scanning electron microscopy

Experiments of scanning electron microscopy (SEM) were carried out in the SBA-15 particles at room temperature in a XL30 ESEM PHILIPS equipment. The particles were dispersed in acetone in an ultrasonic bath for 5 min and then deposited in a holder prior to observation.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed in a Q500 equipment of TA Instruments under air or nitrogen atmosphere at a heating rate of 10 °C/min. Determination of the SBA-15 amount in the nanocomposites prepared by extrusion has been carried out as an average of the values obtained under the two atmospheres. The resulting values of the SBA-15 content are listed in Table 1.

Differential Scanning Calorimetry

Calorimetric analyses were carried out in a TA Instruments Q100 calorimeter connected to a cooling system and calibrated with different standards. The sample weights were around 3 mg. A temperature interval from -40 to 180 °C was studied at a heating rate of 20 °C/min. For the determination of the crystallinity, a value of 160 J/g was used as the enthalpy of fusion of a perfectly crystalline material [12-14].

X-ray experiments with synchrotron radiation

Real-time variable-temperature simultaneous SAXS/WAXD experiments were carried out with synchrotron radiation in beamline BL11-NCD at ALBA (Cerdanyola del Valles, Barcelona, Spain) at a fixed wavelength of 0.1 nm. An ADSC detector has been used for SAXS (off beam, at a distance of 294 cm from sample) and a Rayonix one for WAXD (at about 19 cm from sample, and a tilt angle of around 30 degrees). A Linkam Unit, connected to a cooling system of liquid nitrogen, was employed for the temperature control. The calibration of spacings was obtained by means of silver behenate and Cr₂O₃ standards. The initial 2D X-ray images were converted into 1D diffractograms, as function of the inverse scattering vector, $s = 1/d = 2 \sin \theta / \lambda$. Film samples of around 5×5×0.1 mm were used in the synchrotron analysis.

Depth sensing indentation measurements

Depth sensing indentation (DSI) experiments were performed at 20 °C with a Shimadzu tester (model DUH211S) equipped with a Berkovich-type diamond indenter. At least 10 distinct indentations were carried out at different regions on the surface for the different materials analyzed, iPP homopolymer and its nanocomposites with SBA-15 particles. The experimental protocol consisted in several stages: a) application of a load of 10 mN at a loading speed of 1.46 mN/s; b) maintenance of this constant load for 5 s; and c) release of the load at an unloading speed equal than the one used along the loading stage. Finally, indentation depth was registered for 5 additional seconds after reaching the minimum load (0.02 mN).

Martens hardness (HMs) as well as indentation hardness (H_{it}) and the modulus (E_{it}) were calculated according to Oliver-Pharr method [15]. These two hardness values are given by the ratio of the maximum load to either the contact area under load or after releasing the indenter, respectively. Consequently, HMs is related to elastic, viscoelastic and permanent strains, whereas H_{it} only depends on viscoelastic and plastic strains.

Results and discussion

Figure 1 shows SEM micrographs of the SBA-15 silica used for this investigation. The left picture displays the characteristic vermicular elongated shape of these particles with an average size of 350 nm wide and 0.9 μ m long. The magnification shown in the right picture depicts their interior structure based on well-defined uniform and ordered rods.

Figure 2 depicts the WAXD diffractograms at room temperature of the different slowly cooled films for the several materials. Two distinct crystalline lattices are developed in the metallocene iPP matrix under these crystallization [16] conditions: the monoclinic and orthorhombic polymorphs. Presence of monoclinic α crystals is deduced from the (130) reflection

at around 2.11 nm^{-1} while the γ crystallites are characterized by the diffraction peak (117) at about 2.28 nm^{-1} .

Total WAXD crystallinity, f_c^{WAXD} , of the iPP polymeric component can be assessed from these WAXD profiles after subtracting both the SBA-15 contribution and the amorphous polymeric component. The pattern of the original SBA-15 powder is also shown in Figure 2. It is clearly noticeable that the mesoporous silica particles are completely amorphous and its halo is overlapped in this range with the iPP profile. The amorphous polymeric component for the room-temperature profiles of Figure 2 can be easily obtained from the diffractograms of the melt, with an appropriate shifting to account for the thermal expansion [14]. After those two subtractions, the total crystallinity values attained are detailed in Table 1, together with those for each individual crystalline lattice.

The crystallinity values are practically inside the experimental error. Moreover, there is a rather good agreement with those attained from the DSC results, also shown in Table 1 (corrected for the actual iPP content in the nanocomposites).

A small, but appreciable, effect of the mesoporous silica on the polymorphic behavior of iPP is observed, and the relative amount of orthorhombic crystals decreases slightly as the SBA-15 content is increased in the composites. Thus, the orthorhombic proportion is reduced from 81% of total crystals for pristine iPP to 78% for the sample iPP-SBA13 (see all the values in Table 1, and the profiles in the right part of Figure 2).

As aforementioned, the existence of polymeric crystallites within mesoporous channels has been assumed in literature up to now through the observation by DSC of a secondary melting process in nanocomposites prepared by in situ polymerization and based on different types of polyethylene and particles of MCM-41 or SBA-15 [5-7]. This synthetic approach is considered as a methodology more favorable for confinement, since mesoporous silica was also used as catalytic carrier, in contrast to the present method of extrusion where the polymeric chains have

to be pushed into the channels. Then, they could crystallize if the conditions were appropriate. Figure 3 shows the DSC results obtained during the first melting run for the several materials. Different endothermic processes are observed: two at high temperature involving the greatest amount of heat flow and other small ones within the 90-120 °C interval. The former are related to the melting of the two polymorphs existing in the different nanocomposites: γ and α , in order of increasing temperatures [17,18]. The two main melting temperatures ($T_{m\gamma}$ and $T_{m\alpha}$, respectively) can be estimated and their values are represented in Figure 4. A small shift to lower temperature is observed in both $T_{m\gamma}$ and $T_{m\alpha}$ as SBA-15 is incorporated, this variation being more noticeable for the orthorhombic crystallites. These two endothermic processes are rather evident because the amount of γ crystallites is high enough. In fact, they are majority as revealed by the just commented WAXD results.

On the other hand, the small endotherms observed in Figure 3, and amplified in the inset of that figure, appear in the interval around 90-120 °C. These endothermic events are assigned to the melting of the thinner crystals confined inside the SBA-15 pores. The melting temperature of such thin crystals is considerably lower than those of the main endotherms for the iPP crystals outside the channels. The reason can be found by considering the Gibbs-Thomson equation. A simplified equation is used [19-21] in the case of "regular" lamellar crystals but a more general version [22,23] is necessary for the thin crystals confined in the SBA-15 channels, presenting, supposedly, very low values in their lateral size because of the pore diameter. As a consequence, the corresponding melting temperatures are considerably depressed.

Much more detailed information can be obtained from the real-time variable-temperature synchrotron experiments. Figure 5 shows the WAXD profiles during the first melting process for the iPP (left) and for iPP-SBA13 nanocomposite (right). The separate melting of the γ and α polymorphs can be clearly observed. In fact, the values of the corresponding melting temperatures for the different samples are represented in Figure 4, together with the results

attained by DSC. The agreement between both techniques is excellent, again with small shift to lower temperature in both T_m^γ and T_m^α as SBA-15 is incorporated, although the values for the monoclinic α crystallites are all practically inside the experimental error. The decrease on going from iPP to iPP-SBA4 is much more evident for the orthorhombic γ crystals.

Coming back to the DSC results, the small endothermic peak observed in the 90-120 °C interval is associated, as mentioned above, with those small crystals generated within a confined space. These crystallites are developed from the iPP chains that were pushed in the SBA-15 channels during extrusion by the action of shear forces. These small endotherms have been previously observed in nanocomposites, prepared by in situ polymerization, based on distinct types of polyethylene and mesoporous silicas but, to the best of our knowledge, they have been never described in materials prepared by melt extrusion. They involve a small amount of enthalpy since reptation of iPP chains within SBA-15 channels is not specially boosted in the molten state. In fact, their actual crystallinity values estimated for iPP-SBA1, iPP-SBA4, iPP-SBA8 and iPP-SBA13 are rather low: 0.2, 0.7, 1.3 and 2.2 %, respectively, compared with the total crystallinity (around 68 %). Accordingly, the SBA-15 channels are filled with polymeric chains that are able to crystallize in this constrained space. But how is it truly known that the assumption of filling the SBA-15 pores is correct and that the ordered hexagonal arrangements of SBA-15 channels are maintained and they are not damaged by the shear forces during extrusion?

Figure 6 shows for the iPP-SBA13 composite, represented as an example, that the ordering of the mesoporous particles has been kept throughout extrusion for the distinct composites, since the characteristic reflections (100), (110), (200), (210) and (300) of its hexagonal $p6mm$ symmetry [4,24] are observed in the real-time variable temperature SAXS profiles obtained during the first melting process. In addition to the diffractions ascribed to SBA-15, a broad peak is also noticeable in the region of low values of s . This is related to the variation of the electron density existing in the iPP matrix as consequence of its semicrystalline nature and

its lamellar crystallites, i.e, ascribed to its most probable long spacing. This latest peak disappears once iPP melts, but a rather evident lamellar thickening is undergone on increasing temperature prior to the melting process is complete.

Figure 7 depicts a narrower s interval, which only implies the long spacing region of iPP and the first order of the hexagonal arrangement from the SBA-15 particles, and displays an unexpected feature. Let's first focus the attention in the variable-temperature profiles of the pristine SBA-15. The characteristics of its (100) reflection (position, intensity and width) are not altered in the iPP melting interval, i.e., from 20 °C to 180 °C. On the contrary, all the different composites show a clearly noticeable discontinuity in the intensity of the (100) diffraction. The magnitude of this step is evidently dependent on SBA-15 content and it takes place for all of them at temperatures ranging from 95 to 120 °C. This temperature interval is identical to that observed in the DSC endotherm of small intensity at low temperature, which was ascribed to the melting of those thin crystals confined in the space of SBA-15 channels. This means that the first order of the hexagonal arrangement of SBA-15 is able of sensing the presence of iPP crystallites in the interior of its pores. These crystals possess an electronic density distinct than that in the amorphous regions of those confined macrochains. These electronic density differences disappear when they melt (at temperature lower than those iPP crystals from the outside chains because their smaller size) and, then, the intensity of the (100) SBA-15 reflection becomes constant.

Figure 8 shows the variation in area of the (100) diffraction from the SBA-15 for the distinct materials under study. Constancy of this area for the neat SBA-15 is again seen in the whole temperature interval, while a step is observed for the different nanocomposites. The magnitude of this step increases as the SBA-15 content does, having into account that the Y axis of Figure 8 is in logarithmic scale.

It was reported in the case of PEI based composites [10] with SBA-15 that the intensities of the SBA-15 diffraction peaks changed with increasing PEI content. This fact was interpreted [25,26] by suggesting that the intensity of the SBA-15 diffraction depended both on the degree of pore filling and on the scattering contrast between the walls and the inside of the SBA-15 channels. It was concluded, therefore, that those intensity variations were indicative of the PEI molecules being inside the SBA-15 pores. Analogous conclusions were reached in the case of MCM-41 and KIT-6 materials [9,27]. Therefore, in the present case, the step in the area of the SBA-15 diffraction observed in Figures 7 and 8 shall be related to the change in the scattering contrast before and after the melting of the iPP molecules confined inside the SBA-15 pores.

On the other hand, the position of the SBA-15 main diffraction, in the temperature range when the melting of those small confined crystals takes place by DSC, is rather independent of SBA-15 weight content, while its area depends strongly on it. These features point out the relevance of these real-time variable-temperature SAXS experiments as a very useful tool to determine the presence of polymeric crystals in nanocomposites within the channels of the SBA-15 mesoporous silica. It is also interesting to indicate the good correlation existing in the normalized initial value of the area with the SBA-15 weight content determined as average value of TGA experiments performed under inert and oxidative environments.

As aforementioned, the region of low s values (in between the beam stop and the first order in the hexagonal arrangement of the SBA-15) in the SAXS experiments provides information about the most probable long spacing of iPP lamellar crystalline structure. The results show (see Figure 7) that the SAXS peak is quite symmetric for the iPP and the several composites, in spite of two polymorphs are coexisting in this matrix under the applied processing conditions. Thus, most probable long spacings involve crystallites from both crystalline structures, indicating that no large differences in size exist between them.

The temperature dependence of the most probable long spacing (L) values for iPP and

the nanocomposites with different SBA-15 content is shown in Figure 9. A small but noticeable decrease of the long spacing at high temperatures is observed with the increase in the content of SBA-15. In that temperature interval, significant thickening of the iPP crystallites takes place through melting-recrystallization processes [16,28] as temperature rises.

There are not many articles dealing with polyolefins and mesoporous silicas, as mentioned in the Introduction, and even less investigating the most probable long spacing [5,29]. These two articles studied HDPE and MCM-41, the latest neat or decorated with undecenoic acid. In both of them, long spacing values increased when mesoporous content did. Nevertheless, long spacing remains almost constant in these iPP based nanocomposites with SBA-15. It should be considered that characteristics of the polymeric matrix and silica used are rather distinct. On one hand, long spacing in HDPE is around 32 nm at room temperature while it is less than half in iPP and, on the other hand, the pore size is more than double in the SBA-15 compared with that in the MCM-41. Other difference is the preparation methodology: these iPP based materials have been obtained by extrusion and those from HDPE were by in situ polymerization. The importance of the approach used is not really known at present time since there is not information in the literature. Another variation is the protocol applied during films processing: a fast crystallization in the HDPE samples while a slow cooling has been imposed to the present nanocomposites since it was attempted to provide favorable crystallization conditions because of the melt extrusion approach chosen for preparation.

The influence of all the previous structural aspects (and of the SBA-15 content) on the mechanical performance of these materials has been tested from indentation measurements. Figure 10 shows the results achieved with this technique. Figure 10a displays the effect of mesoporous SBA-15 silica in the capability of the indenter to penetrate within the surface of these materials. The depth reached at a given load is reduced as SBA-15 content rises, although differences between iPP and iPP-SBA1 are within the experimental error, because of the small

amount in SBA-15. These data are associated with the stiffness characteristics, either in the bulk or in the surface, as shown in Figure 11a where modulus (E_{it}) and hardness (H_{it}) of indentation have been represented. It is noticeable that the effect of SBA-15 in the bulk is greater than in the surface. Both mechanical parameters change rather linearly with SBA-15 content. Its reinforcement role is, then, remarkable because SBA-15 particles are the rigid component [29,30,31] in these materials.

Figure 10b allows focusing the attention in the creep region at a constant 10 mN load. It can be observed that the indenter is able to reach in the homopolymer a depth larger than those achieved in the several nanocomposites. This depth is also dependent on SBA-15 content. This feature is displayed in Figure 11b where h_{max} , which is the depth at the end of the maintenance interval at constant load (creep process), decreases with SBA-15 content. The parameter h_{max} is associated with the dimensional stability of the ultimate materials, this magnitude becoming, therefore, improved with the presence of mesoporous SBA-15. Its role is, then, very important and the presence of mesoporous particles leads to a positive mechanical effect since they exert, even at small compositions, a reinforcing effect and contribute to improve the final dimensional stability.

Conclusions

Nanocomposites, prepared by melt extrusion, based on iPP and different amounts (ranging from 1.4 to 12.8 wt.%) of mesoporous SBA-15 silica have been studied and the possible influence of this filler on the iPP polymorphic behavior and on the eventual observation of confinement effects has been evaluated.

Overall crystallinity values for the different nanocomposites have been found to be very similar (around 68%), practically inside the experimental error. Moreover, there is a rather good agreement between the DSC and WAXD determinations. A small, but appreciable, effect of the

mesoporous silica on the polymorphic behavior of iPP is observed, and the relative amount of orthorhombic crystals decreases slightly as the SBA-15 content is increased in the composites.

A separate melting process has been clearly observed for the γ and α polymorphs, both by DSC and real-time WAXD experiments. The agreement between both techniques is excellent, showing a small shift to lower temperature in both T_m^γ and T_m^α as SBA-15 is incorporated, although the values for the monoclinic α crystallites are all practically inside the experimental error. The decrease is much more evident for the orthorhombic γ crystals. Besides these main melting peaks, other endothermic events appear in the interval around 90-120 °C. These endotherms are assigned to the melting of the thinner crystals confined inside the SBA-15 pores, whose melting temperatures are considerably lower than those of the main endotherms for the iPP crystals located outside the channels.

Real-time variable-temperature SAXS experiments turned out a very useful and conclusive tool to analyze the confinement of iPP crystallites within SBA-15 channels. It is believed (although it has to be proved) that these measurements can be valid and definite for characterizing presence of confined crystallites in similar materials based on semicrystalline polymeric matrices, either polyolefins or other different ones. The results show a discontinuity at temperatures ranging from 95 to 120 °C in the intensity of the (100) diffraction of the SBA-15, whose magnitude is strongly dependent on SBA-15 content. This variation in the area of the SBA-15 diffraction seems to be related to the change in the scattering contrast before and after the melting of the iPP molecules confined inside the SBA-15 pores.

Moreover, SAXS allows also determining the most probable long spacing of chains located outside the SBA-15 mesostructure. The dependence on temperature of the most probable long spacing values shows a small but noticeable decrease as the SBA-15 content increases in the region of high temperatures, where considerable thickening of iPP crystallites takes place through melting-recrystallization processes.

All of these structural aspects as well as the SBA-15 content significantly affect the mechanical performance of these materials, which has been preliminary tested from indentation measurements. It is noticeable that the effect of SBA-15 on the stiffness in the bulk is greater than in the surface. Indentation modulus and hardness change almost linearly with SBA-15 content. The reinforcement role of SBA-15 is, then, very important, and the presence of mesoporous particles leads to a positive mechanical effect either in rigidity or in the final dimensional stability of the materials under study.

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Table 1. Average SBA-15 wt.% content, and crystallinity values determined by WAXD and DSC.

sample	SBA-15 wt.% by TGA	f_c^{WAXD}	Percent γ	Percent α	f_c^{DSC}
iPP	0	0.68	81	19	0.69
iPP-SBA1	1.4	0.68	81	19	0.67
iPP-SBA4	3.9	0.66	79	21	0.68
iPP-SBA8	8.0	0.65	79	21	0.68
iPP-SBA13	12.8	0.67	78	22	0.68

Figure captions

Figure 1. SEM image of SBA-15 particles at a scale bar of (a) 2 μm and (b) 1 μm .

Figure 2. (a) Synchrotron WAXD 1D diffractograms at room temperature (left); and, (b) amplified baseline-subtracted region (right) of the diffractions characteristic for the monoclinic and orthorhombic polymorphs in the different materials analyzed.

Figure 3. DSC curves for the first heating process in the iPP based materials with distinct SBA-15 content. Inset: amplification of the small endothermic processes observed in the 90-120 $^{\circ}\text{C}$ range.

Figure 4. Variation with the SBA-15 content of melting temperatures for the γ and α polymorphs determined from both WAXD and DSC measurements.

Figure 5. WAXD profiles during the first melting process for iPP (left) and for the iPP-SBA13 nanocomposite (right). Only one of every two frames is plotted for clarity.

Figure 6. SAXS profiles during the first melting process for iPP-SBA13. Only one of every two frames is plotted for clarity.

Figure 7. SAXS profiles during the first melting process for the different materials at the s interval corresponding to the first order of SBA-15 hexagonal arrangement. Curves have been shifted for a better understanding.

Figure 8. Temperature dependence of the area for the main SBA-15 SAXS peak in the neat SBA-15 and the different iPP nanocomposites during the melting experiments of Figure 7. The results have been normalized to a relative area of 100 for pure SBA-15 powder.

Figure 9. Temperature dependence of the most probable long spacing (L) values for the different samples.

Figure 10. (a) Load–maintenance-unload vs. depth curves; and (b) Indenter depth dependence on experimental time for the iPP homopolymer and the nanocomposites with different SBA-15 contents.

Figure 11. Mechanical parameters determined from indentation measurements: (a) related to stiffness: modulus, E_{it} (left axis), and hardness, H_{it} (right axis); and, (b) related to creep: maximum depth at constant load (h_{max}) for the iPP homopolymer and nanocomposites with different SBA-15 contents

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11