Isothermal Crystallization Kinetics of Novel Isotactic Polypropylene/MoS₂

Inorganic Nanotube Nanocomposites

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Abstract. Inorganic nanotubes (INT) were used for the first time to prepare advanced polymer nanocomposites by means of the most simple, cost-effective and ecologically friendly way (i.e. melt-processing route). The polymer matrix was isotactic polypropylene (iPP) and the inorganic fillers were molybdenum disulfide nanotubes (MoS₂). The effect of INT-MoS₂ concentration and the crystallization temperature on the isothermal crystallization behaviour of iPP was investigated using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXS). It has been observed that INT-MoS₂ affects the crystallization of nanocomposites remarkably, which can be attributed to the nucleating effect of INT-MoS₂ on the monoclinic α -crystal form of iPP. Other parameters such as the Avrami exponent and the fold surface free energy of crystallization of iPP chains in the nanocomposites were obtained in order to determine the effect of the INT-MoS₂ on them. The addition of INT-MoS₂ remarkably influences the kinetics of nucleation and growth of iPP with a decrease in the fold surface free energy of 11-24%.

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1. Introduction

Nanocomposites can, in principle, incorporate nanoparticles (eg. clays, organoclays, carbon nanotubes, etc.) in a number of ways including various in situ polymerization, solution, and latex methods [1-5]. However, the greatest interest has involved melt processing because this is generally considered more economical, more flexible for formulation, and involves compounding and fabrication facilities commonly used in commercial practice [4]. Compared to conventional micron-sized particles, nanoparticles have a much higher surface-to-volume ratio. As the particle size decreases, the percentage of molecules/atoms present on the surface is tremendously increased. As a result, interparticle forces such as van der Waals and electrostatic forces, as well as magnetic attraction, become stronger. Without proper chemical treatment to reduce the surface energy, it is very common for nanoparticles to form clusters or agglomerates. When this happens, the creation of the nanocomposite is unsuccessful. When using clay fillers, it is necessary to separate the particles at the nanoscale into layers called “exfoliation”. Nevertheless, in the case of the promising carbon nanotube nanoreinforcements, the main approach to solve this problem is through surface functionalization (i.e. covalent and non-covalent pre-treatments), which mediates particle–particle and particle–polymer interactions and significantly influences nanoparticle dispersion [6]. These requirements still pose great difficulties for CNT nanocomposites.

For these reasons synthesis of alternative filler particle types, in particular inorganic nanotubes, becomes increasingly important. Layered metal dichalcogenides such as WS_2 and MoS_2 have shown to form this genuine property. The first synthesis of such nanophases was reported by Tenne in 1992 and 1993, respectively [7, 8]. Since then, the number of articles on successful growth of inorganic nanotubes (INTs) from inorganic compounds has increased rapidly, emphasizing the importance of this field for nanotechnology, with potential applications, in catalysis, rechargeable batteries, drug delivery, solar cells and electronics [9,

10]. Recently, INT like-WS₂ are now routinely synthesized in large amounts by ApNano Materials, Inc. (NanoMaterials, Ltd.) (<http://www.apnano.com>) [11]. The nanotubes are relatively long with respect to their diameter and it is this high aspect ratio that gives them their unique strength and chemical properties. The process does not require a catalyst, and the precursors (tungsten oxide and H₂S or sulfur) are relatively inexpensive. Therefore, the moderate cost of such nanotubes may afford numerous applications in the field of polymer nanocomposites (eg. WS₂ inorganic nanotubes were functionalized with n-octadecyl phosphonic acid by sonication in toluene and blended with mixtures of PS and PMMA to form novel PS/PMMA/INT-WS₂ blend nanocomposites [12]). More particularly, INT like-MoS₂ has a remarkable reinforcing effect on the thermal and mechanical properties of isotactic polypropylene (i.e. the most widely investigated polymer for use in the preparation and application of nanocomposites) [13, 14]. The successful dispersion of INT-MoS₂ into iPP matrix was achieved by means of the most simple, cost-effective and ecologically friendly processing way (i.e. melt-processing route).

In this study, we have focused on the analysis of the isothermal melt-crystallization kinetics and crystalline structure of iPP with the presence of INT-MoS₂ using DSC and X-ray diffraction techniques. The parameters of crystallization kinetics, such as the lateral-surface and fold-surface energy of isothermal crystallization as well as the activation energy of isothermal crystallization of iPP and iPP/INT-MoS₂ are also discussed. It is well-known that the properties of a crystalline polymer including the thermodynamic, spectroscopic, physical or mechanical ones depend on the structure and morphology that evolves from the melt. Thus, understanding crystallization mechanism is a key to understanding properties.

2. Experimental section

2.1. Materials and processing. The isotactic polypropylene (iPP) used as matrix was provided by REPSOL and the INT-MoS₂ inorganic nanotubes were kindly supplied by NANOTUL

(Slovenia). All characteristics data of the polymer matrix and inorganic nanotubes were reported in our previous work [13]. Several concentrations of INT-MoS₂ (0.1, 0.5 and 1 wt. %) were introduced in the iPP matrix by melt-mixing using a micro-extruder (Thermo-Haake Minilab system) operated at 210 °C and a rotor speed of 150 rpm for 15 min.

2.2. Characterization techniques. The isothermal crystallization behaviour of the iPP/INT-MoS₂ nanocomposites were investigated by DSC using a Perkin Elmer DSC7/Pyris differential scanning calorimeter, calibrated with indium ($T_m = 156.6$ °C, $\Delta H_m = 28.45$ kJ.kg⁻¹) and zinc ($T_m = 419.47$ °C, $\Delta H_m = 108.37$ kJ.kg⁻¹). The experiments were carried out in a nitrogen atmosphere at a rate flow of 25 ml.min⁻¹, using approximately 10 mg of sample sealed in aluminium pans. Before collecting the data of crystallization, the samples were heated to 210°C and held in the molten state for 5 min to eliminate the influence of thermal history. The sample melts were then subsequently cooled at a rate of 64°C.min⁻¹ to reach the specific temperatures. Partial areas, corresponding to a given percentage of the total transformation, were determined from the data points of the exotherm. For the estimation of the crystallinity of the samples, a value of 190 J.g⁻¹ for the melting enthalpy of 100% crystalline iPP was used [15]. Wide-angle X-ray scattering (WAXS) experiments using synchrotron radiation were performed at the A2 beamline of the HASYLAB synchrotron facility (DESY, Hamburg). The experiments were performed with monochromatic X-rays of 0.15 nm wavelength using a germanium single crystal as the dispersing element. The scattering was detected with a linear Gabriel detector. The methodology used in the isothermal crystallization experiments of the iPP/INT-MoS₂ nanocomposites by WAXS was similar to that described for the calorimetric experiments. Measurements were performed with acquisition time of 30 s (wait time = 20 s and read time = 10 s).

3. Results and discussion

Crystallization, like any phase transformation, is governed by the laws of thermodynamics that determine whether, under specific circumstances, crystals can exist or not. Then, whether crystallization takes place, and its rate, is determined by the kinetics of the process. The crystallization of polymeric materials is generally described in terms of a crystalline nucleation and growth model, where it is assumed that nuclei form from ordered material as a result of thermal fluctuations in the melt. This process can be analyzed by the observation of the growth of a specific crystal face, the growth rate of a crystalline superstructure, or the overall rate of crystallization and is the result of the rate of formation and growth of a stable nucleus and the rate at which the polymer chains are incorporated to the growing crystalline faces. For polymers of sufficient structural regularity, the crystallization can occur in a range of temperatures limited by the glass transition temperature (T_g) and the melting temperature (T_m). All studies show that crystallization rate varies with temperature and the characteristic shape of the curve is a consequence of growth being slowed by increasing viscosity at temperatures close to T_g , and by diminishing thermodynamic drive as the melting point is approached. Or in other words, at low undercooling, that is, at temperatures relatively close to the T_m , and as such, in isothermal experimental conditions, the rate of formation of crystalline nuclei is minimal, the crystallization process is controlled by the nucleation stage, and the rate of the process shows a strongly negative coefficient with the crystallization temperature (T_c). However, in regions where the T_c is low, that is, at high undercooling, and in the majority of cases distant from isothermal conditions, the transport of the polymeric chains at the crystal-melt interface becomes more difficult as it approaches the glass-transition region and, thus, controls the crystallization rate with a positive temperature coefficient. The balance between both processes, nucleation and transport, generates a maximum in the crystallization rate, with antagonistic temperature coefficients, which makes the selection of the interval of T_c 's in polymeric materials extremely important.

The isothermal crystallization behaviour of neat iPP has been analyzed over a crystallization temperature range between 122 and 128°C. Figure 1.a shows the evolution of the crystallization exotherms of iPP. As the crystallization temperature increased, the exotherms shifted along the time axis. Both the induction time and the width of the exotherms increased, which reflects a reduction in the crystallization rate with decreasing undercooling of the system, ΔT . The influence of T_c on crystallization is similar for both the iPP and the nanocomposites, as shown in Figure 1a and b. However, adding INT-MoS₂ induces a remarkable shift of the crystallization range of iPP by 10°C (e.g. from 129 to 139°C for nanocomposite with 1 wt.% of INT-MoS₂). Also, adding INT-MoS₂ shortens the time to reach the maximum degree of crystallization, which means an increase in crystallization rate. These results indicate that INT-MoS₂ has acted as a nucleation agent for iPP.

The relative degree of crystallinity at time t , $\theta(t)$, can be defined as follows:

$$\theta(t) = \frac{\theta_t(t)}{\theta_c(t_\infty)} = \frac{\int_0^t \frac{dH(t)}{dt} dt}{\int_0^{t_\infty} \frac{dH(t)}{dt} dt} = \frac{\Delta H_c}{\Delta H_\infty} \quad (1)$$

where dH/dt is the rate of heat evolution; ΔH_t is the heat generated at time t ; ΔH_∞ is the total heat generated up to the end of the crystallization process. Figure 2 shows the relative crystallinity at different crystallization time. It can be seen that characteristic sigmoid isotherms shift to the right with increasing isothermal crystallization temperature, and the crystallization rate becomes slower. From these representations, the rate of crystallization (G) was determined using the values of $\tau_{0.1}$ which corresponds to the time necessary to reach a degree of crystalline transformation of 10%. This parameter represents the global crystallization rate for each crystallization temperature considering that $G \sim (\tau_{0.1})^{-1}$. A pronounced change in the crystallization rate was observed as the temperature increased, Figure 3. Also the apparent increase in the isothermal crystallization rate of iPP with the addition of INT-MoS₂ in the nanocomposites, shown previously by comparison of the

crystallization exotherms, was now exhibited over the full temperature range analyzed. In particular, this effect can be seen clearly when the $\tau_{0.1}$ of iPP in the nanocomposites is represented as a function of the concentration of INT-MoS₂ for a particular T_c . The crystallization rate of iPP increased strongly with composition suggesting that the well-dispersed MoS₂ inorganic nanotubes have a remarkable contribution to enhance the nucleation of iPP.

It is well-known that the crystallization rate is an important parameter for industrial processing, just as the modality of the nucleation is of technological importance since it not only contributes to the global crystallization rate, but also affects the size and the size distribution of spherulites and, hence, the solid state properties of polymers. The theories of overall crystallization kinetics are being applied in numerous papers to analyze the crystallization, especially the nucleation. These theories are also widely used to predict crystallization during processing. The crystallization analysis is frequently based on the simplest equations neglecting the possible complexity of the phenomenon, even in quiescent state. The most frequently used analysis of experimental data concerning isothermal crystallization is based on the classic Evans–Avrami (E–A) equation [16, 17]. The general form is:

$$\theta(t) = 1 - \exp(-kt^n) \quad (2)$$

where θ is the crystalline transformation or conversion, n is the Avrami exponent related to the type of nucleation and to the geometry of the growing crystals and k is the overall (macroscopic) rate constant (i.e. it contains contributions from both nucleation and growth).

The above Eq. 2 can also be rewritten as follows:

$$\log[-\ln(1 - \theta_t)] = \log k_n + n \log t \quad (3)$$

Linear regression of these straight lines at low degrees of crystalline transformation (5–30%) yielded the Avrami exponents n (Figure 4). The values obtained varies with the INT-MoS₂ concentration as follows: $n \approx 3$ for neat iPP, $n \approx 3$ for iPP/INT-MoS₂ (0.1 wt. %), $n \approx 4$ iPP/INT-MoS₂ (0.5 wt. %) and $n \approx 4$ for iPP/INT-MoS₂ (1 wt. %). In the Avrami expression, the exponent n provides qualitative information on the nature of nucleation and the growth processes. They should be integer and from 1 to 4. And, the values of n of heterogeneous nucleation should be less than that of sporadic nucleation under the same crystallization temperature. In most cases, the values of n are noninteger, different from the theoretical prediction [16]. These noninteger values are generally accounted for by mixed growth and/or surface nucleation modes and two-stage crystallization. The values of n reported in the literature are dispersed, ranging from 1.8 to 4.0 [18]. In our case, the increase in the n exponent with increasing the INT-MoS₂ content can be attributed to a change from the instantaneous nucleation to sporadic nucleation with three-dimensional crystal growth [19] or increasing of the dimension of the crystal growth from two-dimensional to three-dimensional crystal growth assuming that the nucleation is homogenous [20].

In addition of these explanations, Bian et al. have reported that the classic heterogeneous nucleation mechanism cannot explain the crystallization kinetics results of polymer materials like PET [21] (i.e variation of the values of n in the Avrami theory). The authors summed up the crystallization modes of PET and proposed that n values relate with the number of growth points in crystal nuclei, namely, the bigger the number is, the larger the n values. Spherulite is formed by the growth of branches of lamellae. However, the lamellar crystals that aggregate to form the spherulite in polymer have an unsymmetrical structure and can not grow isotropically. In this mode of spherulitic evolution, the number of the branching points on the lamellae has a close relationship with the number of growth points, namely, the greater the branching points, the more the growth points are and the bigger the Avrami

exponent n . As the development of new growth points and the end of old points take place at any possible time in the spherulite growth, n values only have an average and statistical meaning. In particular, it was found that the nanoparticles like antimony-doped tin oxide ATO has some physical interaction with the PET chains, and it can improve the order degree of the PET segments [22]. Therefore, the acceleration of the crystallization rate of PET comes from the increasing crystallizing growth points.

The determination of this parameter allowed the analysis of the overall crystallization rate of the crystallization process from the rate constant, k , at each crystallization temperature by the following expression [23]:

$$k_n = \frac{\ln 2}{(\tau_{0.5})^n} \quad (7)$$

where $\tau_{0.5}$ is the time needed to reach 50% crystalline transformation. Values of k_n obtained for each nanocomposite and crystallization temperature are given in Table 1. Additionally, it can be seen that k_n values of iPP are influenced by the INT-MoS₂ content. As an example, neat iPP presented a k_n of around $65 \times 10^{-6} \text{ min}^{-1}$ for T_c of 128°C; in the case of the nanocomposites the k_n values at the same temperature change with the INT-MoS₂ concentration as follows: $239 \times 10^{-6} \text{ min}^{-1}$ for 0.1 wt.%, $2254 \times 10^{-6} \text{ min}^{-1}$ for 0.5 wt.% and $3551 \times 10^{-6} \text{ min}^{-1}$ for 1 wt.%. These results confirm the nucleating activity of the INT-MoS₂ on the crystallization of iPP.

To verify if the variation in the crystallization characteristics is accompanied by the modification of the crystalline structure of iPP, we have monitored the crystallization process by in situ real-time WAXS experiments using synchrotron radiation. As an example, Figure 5 shows the WAXS intensity profiles of iPP/INT-MoS₂ (1 wt.%) nanocomposites. It is well known that the isotactic iPP mainly exhibits three crystalline forms: monoclinic α , the trigonal β and triclinic γ , depending on the crystallization conditions. Five strong peaks at 2θ of 14°, 16.7°, 18.5° and 21.7° corresponding to (110), (040), (130) and (111) planes can be seen in the

integrated WAXS intensity of iPP/INT-MoS₂ nanocomposites, indicating the existence of typical α -form PP crystals. No evidence of the fundamental crystalline reflection at $2\theta = 16.2^\circ$ corresponding to the (300)-plane of the trigonal structure was observed [24]. Similar behaviour was observed for other iPP nanocomposites containing quasi-spherical inorganic fullerene-like WS₂ nanoparticles [20].

Hereafter, the isothermal crystallization activity energy will be presented in order to understand the dependence of the crystallization rate of iPP with composition. When polymeric materials are crystallized with low undercooling (i.e. high T_c) the crystallization rate is higher the greater the undercooling. This implies that the crystallization process is controlled by the nucleation stage, i.e. by the free energy needed for the formation of a stable crystallite or the free energy of nucleation, ΔG^* .

In agreement with the kinetic theory of crystallization [25-27] depending on the type of regime, the crystallization rate G can be expressed as the following:

$$G = G_0 \exp\left[-\frac{U^*}{R(T_c - T_0)}\right] \exp\left[-\frac{K_g}{fT_c \Delta T}\right] \quad (8)$$

where G_0 is a pre-exponential term, independent on temperature, U^* is the activation energy needed for the chains movement, T_0 represents the temperature at which they are motionless (usually $T_0 = T_g - 30K$), R is the universal gas constant, ΔT is the undercooling and equal to $T_m^o - T_c$ (T_m^o is the equilibrium melting temperature) and f is the corrective factor that takes into account the variation of the equilibrium melting enthalpy (ΔH_m^o) with temperature, defined as $2T_c/(T_c + T_m^o)$.

From T_c (122°–139°C) and T_m^o values, we can determine that the crystallization of iPP and iPP/INT-MoS₂ nanocomposites occurred in crystallization regime III [28], and therefore the nucleation constant, K_g , can be expressed as:

$$K_g = \frac{4b_0 \sigma \sigma_e T_m^0}{k_B \Delta H_m^0} \quad (9)$$

where σ and σ_e are the free energies per unit area of the surfaces of the lamellae parallel and perpendicular to the chain direction, respectively, b_0 is the distance between two adjacent fold planes and k_B is the Boltzmann constant. For the optimization of the linearization of the data within the temperature range the preferred values of U^* , T_0 , R , k_B , T_m^o , b_0 , ΔH_m^o , and σ are 6280×10^7 erg.mol⁻¹ [28], 250 K [29], 8.32×10^7 erg.mol⁻¹.K⁻¹, 1.38×10^{-16} erg.K⁻¹, 469 K [20], 6.26 Å [28], 177×10^7 erg.g⁻¹ [15], and 11.5 erg.cm⁻², respectively [28].

Under these considerations, Figure 6 shows the logarithmic representation of Eq. 8 for iPP/INT-MoS₂ nanocomposites. The growth rate data fit nearly on straight lines, supporting unique regime behaviour of iPP/INT-MoS₂ nanocomposites. From the slope of these plots, the values of K_g were calculated and the values of σ_e were obtained from $\sigma\sigma_e$ by substituting K_g in Eq. 9. The σ_e of iPP is about 123 erg.cm⁻². With the addition of INT-MoS₂, the value of σ_e changed to 109 erg.cm⁻² at 0.1 wt. % INT-MoS₂ content, 95 erg.cm⁻² at 0.5 wt.% INT-MoS₂ content and 94 erg.cm⁻² at 1 wt.% INT-MoS₂ content, respectively. Beck [29] believed a good nucleating agent could reduce σ_e . As it is well known a foreign surface frequently reduces the nucleus size needed for crystal growth because the creation of the interface between polymer crystal and substrate may be less hindered than the creation of the corresponding free polymer crystal surface [30]. So the foreign pre-existing surface could be used to reduce the free energy opposing primary nucleation in a heterogeneous crystal growth. Similar behaviour was observed for iPP nanocomposites incorporating nucleating agents [31-33], nano-sized fillers (e.g. IF-WS₂ [20] or MWCNT [19, 34]) and different types of fibers where transcrystallization takes place [35, 36]. In particular, Marco et al. [34] have also observed a progressive decrease in the fold surface free energy associated with the isothermal crystallization of iPP in iPP/MWCNT nanocomposites up to a nanotube concentration of 1%. The reduction of 27% in σ_e attained at 1 wt.% MWCNT content is similar to this achieved in

iPP/INT-MoS₂ and iPP/IF-WS₂ nanocomposites including 1 wt.% of nanofiller (i.e INT-MoS₂ or IF-WS₂).

The free energy of nucleation, i.e. the free energy necessary for the formation of a nucleus of a critical size, is given by the expression:

$$\Delta G^* = \frac{4b_0\sigma\sigma_e T_m^0}{\Delta H_m^0 \Delta T} \quad (10)$$

ΔG^* , which increases with smaller undercooling, was lower for the INT-MoS₂ nanocomposites than for neat iPP at the same crystallization temperature as shown in Figure 7, which confirms that the energy barrier for nucleation is lowered in the presence of the INT-MoS₂ component, leading to an increase in the overall crystallization rate.

Conclusion

The effect of INT-MoS₂ on the crystal structure and isothermal crystallization behaviour of iPP nanocomposites, obtained by a successfully melt-processing method, has been investigated. The kinetics results from isothermal crystallization of iPP and iPP/MoS₂ showed that the crystallization of iPP in the iPP/MoS₂ nanocomposites was strongly influenced by MoS₂ inorganic nanotubes. Compared with the crystallization process of neat iPP, the value of Avrami exponent n of iPP/MoS₂ nanocomposites increased. However, the crystalline structure of iPP appears unchanged with the addition of INT-MoS₂, as can be observed by in situ real-time WAXS measurements using synchrotron radiation. In addition, in the analysis of the activation energy of crystallization regime III of iPP/MoS₂ nanocomposites, it was determined that the value of fold surface free energy (σ_e) of iPP chains decreased with increasing MoS₂ content. All these results showed that INT-MoS₂ is a nucleating agent for the crystallization of iPP, which plays a relevant effect on the reduction in σ_e during the isothermal crystallization of the nanocomposites. The free energy of nucleation decreased

with the incorporation of INT-MoS₂ into the matrix, which in turn indicates that the nucleation process is facilitated by the presence of INT-MoS₂.

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Figure captions:

Figure 1. Plots of DSC curves of (a) iPP and (b) iPP/INT-MoS₂ (1wt.%) obtained under isothermal crystallization conditions.

Figure 2. Plots of crystalline conversion (θ) *versus* time obtained from isothermal crystallization DSC curves.

Figure 3. Time to attain a 10% degree of transformation ($\tau_{0.1}$) of iPP/INT-MoS₂ nanocomposites as a function of the crystallization temperature.

Figure 4. Avrami plots of the crystallization of (a) iPP and (b) iPP/INT-MoS₂ (1wt.%) as a function of the crystallization temperature.

Figure 5. WAXS diffractograms of iPP/INT-MoS₂ (1wt.%) obtained at 130°C.

Figure 6. Logarithmic plots of Eq. 8 for iPP/INT-MoS₂ nanocomposites.

Figure 7. Variation of the free energy of nucleation (ΔG^*) of iPP/INT-MoS₂ nanocomposites as a function of the crystallization temperature.

Figure 1.

Figure 2.

Figure 3.

Figure 4

Figure 5.

Figure 6.

Figure 7.

Table 1. Values of the isothermal rate constant k of iPP/INT-MoS₂ nanocomposites calculated from Eq. 7.

Crystallization temperature (°C)	$k \times 10^6$ (min ⁻¹)			
	iPP	0.1 wt.% INT-MoS ₂	0.5 wt.% INT-MoS ₂	1 wt.% INT-MoS ₂
122	3209			
123	1737			
124	1110	3211		
125	631	1947		
126	297	981		
127	955	489		
128	65	239	2254	3551
129		120	939	1796
130		56	364	1222
131			154	332
132			59	135
133			23	61
134			10	32
135			5	11
136			3	4
137			2	3
138			0.5	1
139			0.2	0.5