

Crystallization behavior of iPP/LLDPE blend filled with nano kaolin particles

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Abstract:

The crystallization kinetics of isotactic polypropylene (iPP/LLDPE) blends, and iPP composite containing nano kaolin particles has been investigated. The addition of nano kaolin and LLDPE to iPP affects both its nucleation and spherulitic growth rate. With the addition of the nano filler particles, significant increase in the nucleation and maximum growth rate were observed. To improve the dispersion in the matrix, the filler particles were treated with silane. An experimentally determined value for the Avrami exponent was calculated. The Scanning electron microscopy indicates that the nano particles cause a finer dispersion of the LLDPE component in the iPP matrix. Due to the presence of nano size filler, additional heterogeneous nucleation of the iPP nuclei occurs through the enhancement of the interface area.

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1. Introduction

The extent of crystallization and the morphology formed during polymer processing are critical for the determination of the resulting physical properties of the polymer products, thus influence their end-use values. Almost all the crystallized polymers are partly crystalline and partly amorphous. This specific semi-crystalline structure allows the adjustment of polymer products physical properties according to the application requirements. Formation of ordered solid phase, such as crystals, typically starts with nucleation, in which a seed, or a tiny embryo of the new phase, is formed. Nucleation occurs during a first order phase transition, in which a new phase is generated from an old phase that has higher free energy. Crystal growth, the overlapping process accompanying nucleation, is the successive deposition of polymer chains on the nucleus of the aligned polymer chains (Mandelkern 2004).

Understanding the mechanism of nucleation and crystal growth is critical for manufacturing process and determination of the final product properties, such as crystal size distribution, thermal stability and mechanical properties. Blending two thermodynamically immiscible polymers to create a material with desirable properties is an attractive alternative to synthesizing new polymers. A common example is rubber toughening. A small amount of rubbery polymer is dispersed into a glassy polymer in the

melt state and the resulting material is often much tougher and has a higher impact strength, when compared to the bulk glassy polymer (J. Yang, B.J. McCoy and G. Madras 2005). The microstructure of the blend often determines its physical properties. It is well-known that the impact resistance of thermoplastics can be improved by blending it with filler and elastomers (Bucknall, 1977; Galli et al., 1984; Kolarik et al., 1986a; Al Robaidi, 2001). For polypropylene, a variety of rubbers are suitable for this purpose, but it turns out that a second thermoplastic, polyethylene also increases the impact resistance of polypropylene at low temperatures (Al Robaidi, 2001; Kolarik et al., 1986b; Yang et al., 1984; Flaris and Stachurski, 1992). Unfortunately, this desirable mechanical behavior is often accompanied by a decrease in other properties, such as elastic modulus and stiffness. A way to overcome this disadvantage is to melt-blend the polymers with a compatibilizer and fillers. Compatibilizers act at the interface between the two components (Barensten and Heikens, 1973) and it is expected that the modification of the interface influence both the nucleation and the crystallization kinetics. It is the aim of this study to demonstrate that the interface of a compatibilized thermoplastic blend alters the nucleation of the matrix and consequently alters its morphology.

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2. Experimental Procedures

2.1. Materials and Sample Preparation

The starting materials were isotactic polypropylene (iPP, $\rho=0.905 \text{ g/cm}^3$). Linear Low Density Polyethylene (LLDPE, $\rho = 0.919 \text{ g/cm}^3$) and a kaolin as a nano filler. All these polymers are standard commercial grade materials with a typical additives present. The kaolin particles applied were prepared on a nano mill in the range averaging 50-80nm in diameter. To improve the dispersion and the compatibility of the filler in the matrix the particles were coated with 2.5% weight silane.

The materials were melt-blended in a brabender plastograph. Six samples were investigated: pure iPP and five blends as listed in table 1.

Table 1. Polymer characterization data

Material	Concentration
iPP	100 reference
iPP + LLDPE	80%/20%
iPP + LLDPE + coated Kaolin	70%/20%/10
iPP + coated kaolin	90%/10%
iPP + coated kaolin	80%/20%
iPP + coated Kaolin	70%/30%

The Polypropylene and LLDPE starting materials were characterized using gel permeation chromatography (GPC) and differential scanning calorimeter (DSC) to determine the melting points, molecular number, weights and distribution respectively. These results are summarized in Table 2. Samples thereof for Charpy impact tests were prepared by injection molding. The tests were carried out on a Ceast Impact Tester at a temperature of 20°C.

Table 2. Polymer characterization data

Material	Tm[°C]	Mn	Mn/M
iPP	161.4	64.300	4.2
LLDPE	123.5	37.300	3.7

2.2. Nucleation Kinetics Measurements

For the observations in the optical microscope (Leitz Metallux II), the samples were pressed to a thickness of approximately 100 μm , placed between glass slides, and put in the hot-stage microscope. Here, they were heated to 200°C for five minutes and then cooled to the isothermal crystallization temperature. Crossed polarizers were used and the crystallization was monitored on a video screen and recorded. From the recording, the growth of the spherulites as well as the number of nuclei as a function of time was determined. Isothermal crystallization temperatures were chosen between 130°C and 139°C.

3. Results And Discussion

For an isothermal experiment, the observed number of nuclei in a given volume as a function of time is:

$$N_{(t)} = M[1 - \exp(-vt)] \quad (1)$$

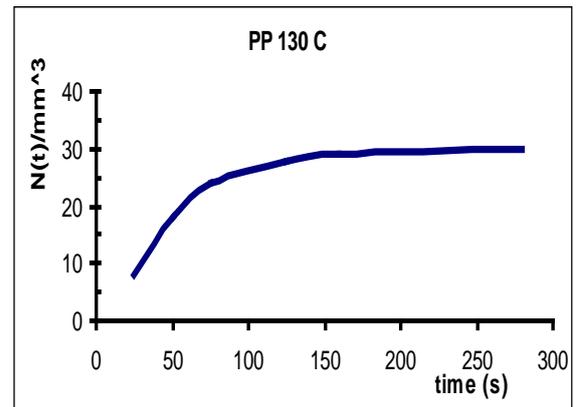
Where

v = the probability of nuclei development per unit time

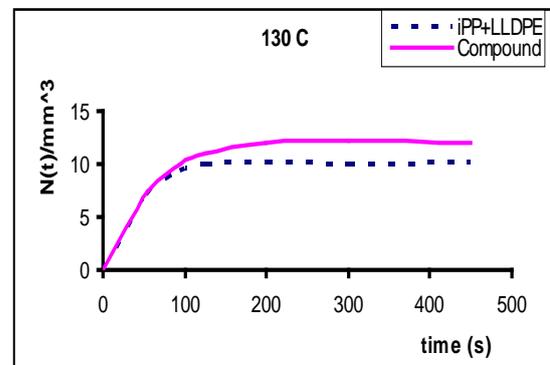
M = the nucleation density (Mandelkern, 2004; Aggarwal *et al.*, 1966; Icenogle, 1985)

$N(t)$ = a characteristic function for the nucleation behavior of the sample investigated

Representative data, $N(t)$ for the tested samples, iPP, iPP+LLDPE and the iPP+ 20% kaolin composite samples are shown in Figure 1.



a



b

Figure 1. Development of the number of nuclei as a function of time for (a) iPP and (b) the blend 80% iPP/20% LLDPE.

Differentiation of equation (1) yields the nucleation frequency per unit of untransformed volume at time t :

$$N_{(t)} = vM \exp(-vt) \quad (2)$$

The temperature-dependence of the nucleation density can be described by a cumulative Gauss-function ($\text{erf}(T)$):

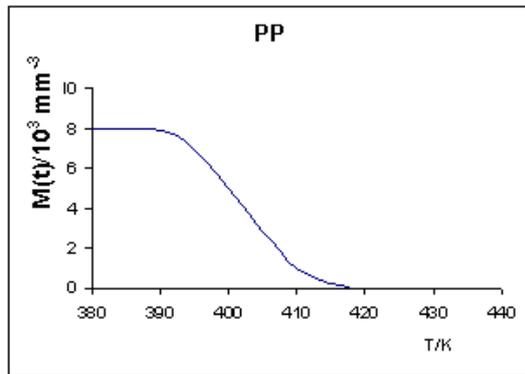
$$M(T) = M_a \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{T_c} \exp\left(-\frac{(T-\bar{T})^2}{2\sigma^2}\right) dT \quad (3)$$

Where M_a is the total nucleation density and σ is the variance. \bar{T} is the temperature of the distribution maximum. Figure 2 shows $M(T)$ for the two selected samples PP and iPP+LLDPE. The values for the nucleation density are listed in

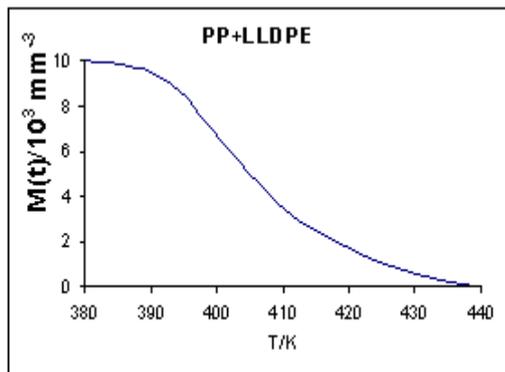
Table 3. Results from nucleation and crystallization kinetics for sample listed in table 1

Sample	Nucleation density M/mm^3	C_3 $10^5/k^2$	G_0 $10^6/mm/s$	G_{max} mm/s	T_{max} $^{\circ}K$	$\sigma\sigma_e$ $10^2 erg^2/cm^4$	Avrami number m
iPP	375	4.51	56.4	.33	341	12.7	2.3
iPP + LLDPE	542	3.83	90.3	.49	346	14.9	2.2
iPP+LLDPE+Kaolin	1005	4.01	12	.60	344	12.2	1.6
iPP + kaolin	517	4.39	121	.64	342	12.4	1.5
iPP + 20% Kaolin	657	3.95	118.5	.67	341	12.8	1.43
iPP + 30% Kaolin	1215	4.43	127	.72	343	14.1	1.37

We see that for the iPP+LLDPE, M is higher than for neat polypropylene. This is probably due to the interface of the second component, which causes the nucleation rate to increase by additional heterogeneous nucleation at the surfaces of the LLDPE occlusions. The area of this interface would then govern the amount of the heterogeneous part of the nucleation; a higher dispersion of the LLDPE and the kaolin should yield more heterogeneous nucleation. This assumption, however, cannot be verified by discussing the nucleation density alone.



a



b

Figure 2. Nucleation density as a function of temperature for (a) iPP and (b) the blend 80iPP/20LLDPE.

A good indication of the type of nucleation is the Avrami exponent, which is discussed later. The radial spherulite growth rates of neat iPP and iPP +nano kaolin compound were measured over time. Figure 3 shows the representative data concerning the change in spherulite

radius as a function of time at 130 °C. In all samples, the spherulite diameters increased linearly with time at all crystallization temperatures, indicating that growth rate was independent of the size of the spherulites. If non crystallizable species are excluded from growing spherulites, they will build up on the crystallization growth front and consequently hinder the transport of crystallizable species from the melt to the growing edge. This phenomenon will give rise to a deviation from linear spherulite growth after the spherulite reaches a certain diameter. Since no such deviation from linearity in spherulite growth was observed in the nano composites (Figure 3), it can be concluded that the kaolin particles are not excluded during spherulite growth.

Again, we assume that this behavior is connected with the change in the type of nucleation.

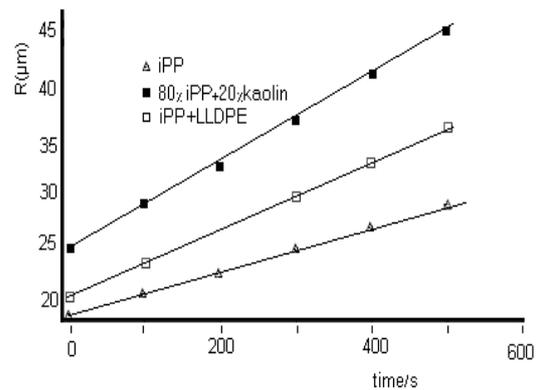


Figure 3. Spherulitic radius as a function of time for (a) iPP; iPP+LLDPE and nano kaolin filled compound.

Within the temperature range investigated, the radius of growing spherulite is expressed as a linear function of time as listed in equation (4) below:

$$r(t) = r_0 + Gt \tag{4}$$

Where r_0 is the radius of the spherulite at the beginning of the experiment and G is the growing rate. The temperature dependency of the growth rate is calculated from¹²⁻¹⁴.

$$G(T_c) = G_0 \exp(-C_1 C_2 / (C_2 + T_c - T_g)) \exp(-C_3 / T_c (T_m - T_c)) \tag{5}$$

Where T_g is the glass transition temperature, T_m is the melting temperature and G_0 , C_1 , C_2 and C_3 are constants. G_0 and C_3 are determined by plotting

In $G + C_1 C_2 / (C_2 + T_c - T_g)$ versus $1 / T_c (T_m - T_c)$. The values obtained from such a plot are listed in Table 3. From equation (5) the maximum growth rate G_{max} can be determined. The calculated values for G_{max} are also listed in Table 3.

We see that G_{max} increases for the sample containing 20% LLDPE from 0.33 mm/s to 0.49 mm/s. This is obviously the influence of the interface, where the nuclei generated by a thermal nucleation that find conditions suitable for undisturbed growth. We expect that G_{max} increase further for the samples containing kaolin. This is indeed the case. G_{max} increases to 0.60 mm/s for the sample containing 10% kaolin up to .72 to samples containing 30% kaolin. Consequently, a different spherulitic distribution is built up which affects the mechanical properties. Figure 4 represent the Charpy impact values for the different formulation investigated. In fact, the sample containing kaolin nano fillers yields the highest impact result; which increases from 0.8 kJ/m² for iPP to 1.2 kJ/m² for the iPP/LLDPE blend, increased further to 1.3 kJ/m² for the sample containing 10% kaolin up to 1.9 kJ/m² for the sample contain 20% kaolin. The kaolin molecules in the domains are crosslinked to the matrix by the silanol end groups; thus improving the toughness and impact energy.

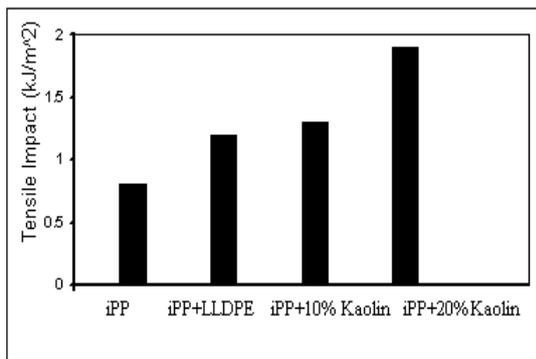


Figure 4. Charpy Impact for sample prepared in table 1

The crystallinity as a function of time in a growing spherulite can be described by the Avrami equation (Avrami, 1941; Mandelkern, 2004):

$$X_c(t) = 1 - \exp(-kt^m) \quad (6)$$

Where $X_c(t)$ is the volume crystallinity at time t , k is a characteristic constant, and m is the Avrami exponent describing the type of crystallization. In our experiment, m has been obtained by determining the volume of the spherulites through the calculation of their cross-sectional areas. Measuring the crystallization half time, $t_{c,1/2}$ can be calculated from can be calculated from (Wenig and Fiedel, 1991):

$$m = \frac{\log\left(\frac{3 \ln 2}{4 \pi G^3 N}\right)}{\log t_{c,1/2}} \quad (7)$$

The Avrami exponents are listed in Table 3. We find that m increases slightly for the samples containing LLDPE. For the blends, containing kaolin we find a sharp drop in the value of m . This indicates that the type of nucleation is indeed changing upon the addition of LLDPE and kaolin to polypropylene. It is in good agreement with

our concept of increasing heterogeneous nucleation, that the sample with the highest maximum growth rate and the highest Charpy impact value exhibits the lowest Avrami exponent.

It is obvious that the addition of kaolin leads to a finer dispersion of the LLDPE occlusions (see figure 5), creating a higher interface area, which in turn increases the secondary nucleation rate.

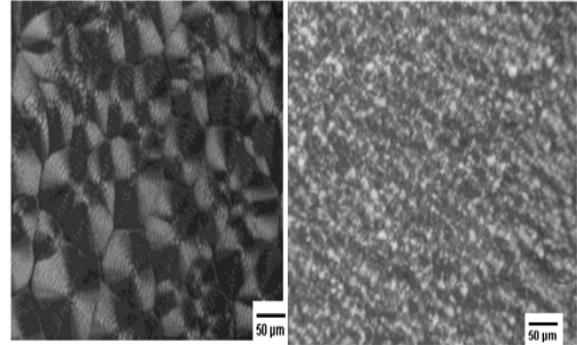


Figure 5. Spherulite structure

The lamellar crystallization itself remains un–changed. This can be demonstrated by calculating the interfacial free energy, σ_e , which can be de–rived from the temperature dependence of the growth rates:

$$\sigma_e = \Delta G \Delta H_m \rho_c \Delta T / 4 b_0 T_m \quad (8)$$

where σ and σ_e are the specific free interfacial energies for the surface and end area of the crystal lamella respectively and b_0 is the thickness of the secondary nucleus (thickness of a monolayer of chains). Values for σ_e are listed in Table 3. Except for the iPP/LLDPE blend, where σ_e is 14.9 erg²/cm⁴, we find the value between 12.1 and 12.7 erg²/cm⁴ for the other blends. As a result of the chang–ing kinetic conditions, the morphology of the iPP matrix should be affected, which is one of the con–ditions to increase the impact resistance. As additional investigations¹⁷ show, this is indeed the case. Calculations of interface distribution func–tions of these blends demonstrate that among other morphological parameters, the lamellar thickness is lowered when a kaolin is added to the iPP blend. It is significant to note that the blend containing kaolin yields the highest impact value and has the smallest lamellar thickness.

4. Conclusion

The crystallization behavior of Iso-tactic polypropylene blended with LLDPE and kaolin particles was investigated. The result obtained and presented in this paper has shown that the crystallization kinetics of miscible polymer blends is influences by filler type and copolymer, used. Adding a second polymer influences the crystallization mainly through thermodynamics and kinetics (equilibrium solubility and deposition mechanism). These effects are incorporated by varying the initial values of ingredients concentration and growth rate coefficient. Because of the chang–ing kinetic conditions, the morphology of the iPP matrix was affected, which is one of the con–ditions to increase the impact resistance. It is significant to note that the impact resistance was increased for the samples containing coated silane kaolin.

A finer dispersion of the filler was achieved, which is responsible for impact increase. The lamellar crystallization itself did not change. This was demonstrated by calculating the interfacial free energy $\sigma\sigma_e$. We find that the avrami exponent m increases slightly for the sample containing LLDPE, but decreasing significantly when kaolin is added, which indicates that the type of nucleation is changing.

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