

NUCLEATING EFFECT AND DYNAMIC CRYSTALLIZATION OF A POLY(PROPYLENE)/ATTAPULGITE SYSTEM

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Abstract

In this work, the influence of attapulgite concentration on the nucleating efficiency of isotactic polypropylene (iPP) and on the kinetics of non-isothermal crystallization were ascertained. The study was conducted by DSC. The nucleating efficiency was determined according to the procedure described by Fillon and the kinetics of non-isothermal crystallization was determined using Ozawa's method using cooling rates of 2, 5 and 10°C min⁻¹. Our results indicate that both the relative crystallinity and the crystallization temperature increase with filler content and that a maximum occurs at 2% mass/mass filler content. Both parameters decrease with increasing cooling rates. The Ozawa's exponent tended to increase with temperature and filler content.

Keywords: DSC, dynamic crystallization, mineral filler, nucleation, polypropylene

Introduction

There is a growing interest in the use of nucleating agents in injection moulded parts. Nucleating agents are able to increase crystallization rates and mould removal temperature, thus reducing moulding cycles and increasing productivity [1–4].

One can better understand the processing-structure-property relations of semi-crystalline polymers if one was to follow their crystallization characteristics under dynamical conditions [1]. Most quantitative studies on the kinetics of crystallization are done under isothermal conditions and are almost essentially described by Avrami's equation [5]. Practical processes, however, occur under dynamical conditions, i.e. under non-isothermal conditions and many models have been proposed to explain polymer crystallization under these conditions. Among these models, the one proposed by Ozawa is one which closely resembles real processes and the most simple to be used, and this is the reason why it was employed in the present investigation [6].

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In this work the thermal properties and the dynamic crystallization of iPP samples nucleated by attapulgite were investigated by DSC. The nucleating efficiency as function of filler content, for concentrations ranging from 1–5% in mass and cooling rates ranging from 2–10°C min⁻¹, was determined by the method described by Fillon *et al.* [5]. Dynamic crystallization studies of these systems were performed applying Ozawa's method [1, 7, 8] to the DSC curve data.

Experimental

Chemicals

Two commercial grades of isotactic polypropylenes were provided by Polibrasil S.A., Bahia, namely KM6100 (*MFI*=3.5 g 10 min⁻¹) and TM 6100 (*MFI*=16 g 10 min⁻¹). Attapulgite was provided by União Brasileira de Mineração, UBM S.A, Paraíba, Brazil.

Thermal measurements

Dynamic crystallization was carried out in a DP Instruments Thermal Analyst 2000 operating with a DSC-10 cell. The samples were heated at 10°C min⁻¹ up to 210°C; kept for 5 min at this temperature to reset the thermal history and then cooled at different rates (ranging from 2–10°C min⁻¹). The nucleating effect of the filler was determined by the method described by Fillon and non-isothermal kinetics was determined by the DSC curves using Ozawa's method [1, 7, 8].

Nucleating efficiency – Fillon method

The effect of filler content on the nucleation efficiency (*NE*) was performed according to Fillon method. This method compares the crystallization temperatures of nucleated and self-nucleated samples, defines the upper and the lower crystallization temperatures of a pure polymer and introduces an efficiency scale for the nucleating agents in non-isothermal experiments [5].

According to that method [5], the nucleating efficiency is calculated as:

$$NE (\%) = [(T_c - T_{c_1}) / (T_{c_{2,max}} - T_{c_1})] 100$$

where T_c – the crystallization temperature of the sample being analyzed ; T_{c_1} – the lowest crystallization temperature of the polymer (iPP) and $T_{c_{2,max}}$ – the highest crystallization temperature for the auto-nucleated polymer.

These values (T_{c_1} and $T_{c_{2,max}}$), were obtained by the following procedure: a) the polymer (iPP) (without a nucleating agent) was heated from 50 to 210°C at 10°C min⁻¹ and kept at that temperature for 10 min, b) the sample was cooled at the same rate to 50°C and its crystallization temperature (T_{c_1}) was determined, c) the sample was again heated until partially melted (T_s) to a temperature close to its melting temperature (T_m) and d) the sample was cooled and its T_{c_2} ($T_{c_2} \geq T_{c_1}$) was determined. The reference data employed in the calculations were: $T_{c_1} = 110.4^\circ\text{C}$ and $T_{c_{2,max}} = 138.1^\circ\text{C}$ obtained at a T_s of 166°C.

Ozawa's method

The dynamic crystallization was ascertained by Ozawa's method [1, 7, 8] which is applied to non-isothermal crystallization and which allows the determination of an 'n' coefficient which is related to the crystalline morphology of the material under investigation. The sample crystallinity is estimated at different temperature intervals during its cooling. The relative crystallinity, i.e., the crystallinity of the sample at a given time interval, was determined from crystallization peak as:

$$\alpha(T)=[A(T)/A(\text{total})]$$

where $\alpha(T)$ – the relative crystallinity at a given temperature (T); $A(T)$ – the partial area of the peak at that temperature and $A(\text{total})$ – the total peak area.

The Ozawa's equation was employed under the form:

$$\ln\{-\ln[1-\alpha(T)]\}=\ln X(T)-n'\ln\beta$$

where β is the cooling rate.

Degree of crystallinity

The degree of crystallinity X_c , i.e., the sample mass fraction which is crystalline, was determined from the DSC curves. The enthalpy of fusion of the polypropylene sample ($\Delta_{cr}^1 H$) was determined and divided by the enthalpy of a completely crystalline (100%) ($\Delta_{cr}^0 H$) sample. A value of 207.0 J g^{-1} [9] was used for the 100% crystalline iPP.

Results and discussion

Table 1 shows the crystallization temperature (T_c), degree of crystallinity (X_c) and nucleation efficiency (NE) of a PP(KM6100)/attapulgitite system as a function of attapulgitite content. Heating and cooling rates of $10^\circ\text{C min}^{-1}$ were employed.

Table 1 Crystallization temperature, nucleating efficiency and degree of crystallinity of attapulgitite according to Fillon (samples were cooled at $10^\circ\text{C min}^{-1}$)

Attapulgitite/mass%	iPP	$T_c/^\circ\text{C}$	$NE/\%$	$X_c/\%$
0	KM6100	110.47	0.0	42.94
1	KM6100	113.01	9.19	40.72
2	KM6100	127.47	61.28	45.57
5	KM6100	124.30	49.87	53.20

The data indicates that attapulgitite acts as a good nucleating agent for PP and that a maximum nucleating efficiency of 61.28% was obtained at 2% mass/mass filler content. The reason for the decrease in T_c and NE at the higher filler content is attributed to a tendency for particle agglomeration at higher loads, decreasing the effective number of nuclei available to promote crystallization [1, 5].

The degree of crystallinity, on the other hand, increases with filler content for the concentration range under investigation. This is attributed to the fact that the degree of crystallinity is a measure of the amount of sample which is crystalline and is not affected by crystallite size and perfection. At higher filler contents, there is probably a larger number of imperfect crystals and the overall effect was an increase on the amount of sample which was crystallized. It would be expected that a further increase in filler mass fraction would lead to a decrease in the degree of crystallinity due to crystallite imperfections [7].

Table 2 shows the effect of cooling rate on the T_c of PP/attapulgitic systems as a function of filler content and of the polypropylene sample employed, i.e., KM6100 ($MFI=3.5 \text{ g } 10 \text{ min}^{-1}$) and TM6100 ($MFI=16 \text{ g } 10 \text{ min}^{-1}$). The results show that both systems behave in a similar fashion, i.e., the crystallization temperature (T_c) tends to increase with filler content and decrease with increasing cooling rates. The increase in T_c with filler content is taken as an indication that attapulgitic acts as a nucleating agent for isotactic polypropylene.

Table 2 Dependence of T_c as a function of the iPP matrix, cooling rate and attapulgitic content

Attapulgitic/mass%	iPP	Cooling rate/ $^{\circ}\text{C min}^{-1}$				
		2	3	4	5	10
0	TM6100	124.36	122.23	121.12	118.34	110.05
0	KM6100	123.66	121.49	120.67	118.10	110.47
1	TM6100	125.32	123.04	122.36	120.89	117.42
1	KM6100	124.12	121.56	120.82	116.78	123.01
2	TM6100	125.00	123.00	122.15	121.32	118.52
2	KM6100	134.92	132.85	131.93	130.32	127.47
5	TM6100	126.04	124.22	123.13	122.40	119.98
5	KM6100	130.34	128.96	127.97	125.06	124.30

Despite their differences in melt flow index, which is an indirect measure of molecular mass, the T_c values obtained for both systems were very similar, which indicate that the crystalline structure of PP was equivalent for both systems. The only difference in the behavior of the two systems seems to lie on the fact that, for KM6100, a maximum on T_c was obtained at 2% filler content while for TM6100, T_c increased with filler content for all the studied concentrations.

The decrease in T_c with increasing cooling rates is to be expected. The higher is the cooling rate, the faster is the increase in viscosity and the loss of mobility of the polymer chains, resulting in less perfect crystallization. Slower cooling leads to the maintenance of chain mobility for longer times and allows a better accommodation of the crystalline arrangement [8].

Figure 1 illustrates the non-isothermal crystallization behavior of the PP/attapulgitic systems as a function of filler content (1, 2 and 5 mass%) and cooling rate (2, 5

and $10^{\circ}\text{C min}^{-1}$). The plots were constructed from the data obtained from the DSC curves, according to the method described by Ozawa.

The data shows that the relative crystallinity ($\alpha(T)$), i.e., the percent crystallinity at a given temperature, increases with decreasing cooling rates and tends to increase with filler content up to 2 mass%, decreasing at higher concentrations. This behavior may be attributed to a greater crystallite interference during crystal growth at higher filler concentrations which leads to a decrease in the relative crystallinity of the composite.

The Ozawa exponent (n') was calculated from data obtained from DSC curves. Plots such as the ones presented in Fig. 1, of the relative crystallinity vs. T at different cooling rates, were constructed and the value of $\alpha(T)$ at a given temperature was measured as a function of the cooling rate (β) for each sample studied. A plot of $\log\{-\ln[1-\alpha(T)]\}$ vs. $\log(\beta)$ at a given temperature was constructed, yielding straight

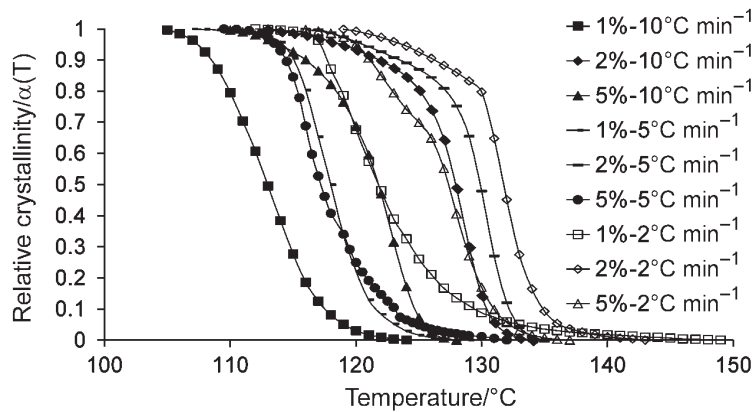


Fig. 1 Relative crystallinity as a function of cooling rate and attapulgite content for the PP(KM6100)/attapulgite system

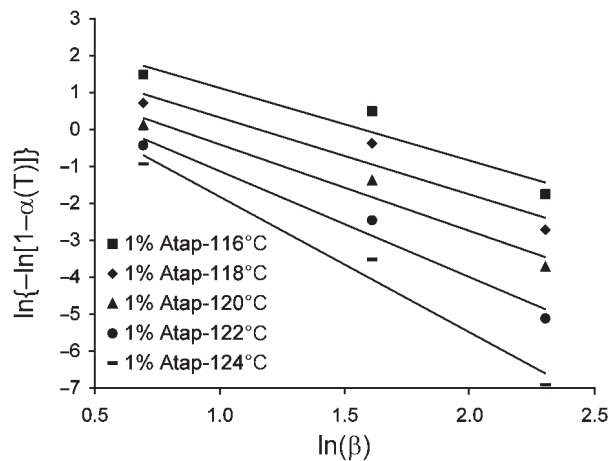


Fig. 2 Linear regression according to Ozawa's for PP(KM6100)/attapulgite system

lines whose slope was (n'), the Ozawa exponent, as illustrated in Fig. 2, for KM6100 with 1% of attapulgite. The results obtained are shown in Table 3.

Table 3 Ozawa's exponent for the different PP/attapulgite systems

Attapulgite content/%	Temperature/ $^{\circ}\text{C}$	Ozawa's exponent PP TM6100/ n'	Correlation factor (R^2) (TM6100)	Ozawa's exponent PP KM6100/ n'	Correlation factor (R^2) (KM6100)
1	116.0	2.0	0.9878	2.0	0.9144
	118.0	2.0	0.9903	2.1	0.9189
	120.0	2.3	0.9916	2.3	0.9587
	122.0	2.9	0.9424	2.9	0.9757
2	127.0	1.3	0.9981	0.4	0.9436
	129.0	1.5	0.9827	1.0	0.9225
	131.0	1.7	0.9653	1.8	0.9704
	133.0	2.3	0.9733	2.3	0.9983
5	122.0	1.0	0.9735	0.7	0.8984
	124.0	1.2	0.9610	1.2	0.8977
	126.0	2.3	0.8860	2.3	0.9551

The Ozawa exponent, just like Avrami's, is related to the shape of the crystal growth during dynamic crystallization of the nucleated polymer [10, 11]. Mineral filler addition can lead to heterogeneous nucleation of polymer systems, i.e., they can start crystallization at temperatures which are lower than those of the pure polymer, or they can inhibit normal crystal growth due to the close proximity of the nuclei and thus affecting the shape and dimensions of the growing crystallites.

The data obtained show that, in the case under study, Ozawa's exponent increases with temperature; decreases with increasing filler content and assumes values which are close to Avrami's for attapulgite nucleated polypropylene i.e., for samples which were crystallized under isothermal conditions. Average values of $n'=1.7-2.0$ were obtained, independent of the polypropylene used as the matrix. This indicates that the morphology of the growing crystals varies from fibrillar ($n'=1$) to disc like ($n'=2$) and is predominantly linear. This behavior is attributed to the acicular structure of the filler (attapulgite) used as a heterogeneous nucleating agent [11].

The variation on the observed values of the Ozawa exponents is attributed to the fact that cooling rates employed generated curves which were too far apart from each other. This leads to difficulties in obtaining the plots as the relative crystallinity tends to vary too much (1-99%) as a function of the cooling rate. In order to obtain more reliable data, one would need to obtain curves by using closer cooling rates such as 2, 3, 4 and $5^{\circ}\text{C min}^{-1}$. Thus data could be obtained in temperature ranges in which the relative crystallinity would vary from 30-70%. This was done and values of n' much closer to 1.7-2.0 were obtained. Variations in n' may also arise from either poor filler

dispersion or from filler agglomeration. Therefore, if much more reliable n' values were to be obtained one should perform the experiments in triplicate and at very similar cooling rates [7].

Conclusions

Our data shows that attapulgite is a good heterogenous nucleating agent for isotactic polypropylene. For PP(KM6100), maximum nucleating efficiency, relative crystallinity and crystallization temperature were attained at 2 mass% filler content. For PP (TM6100), crystallization temperature increased for all attapulgite studied contents. Furthermore, crystallization temperature presented higher values of T_c for KM6100, i.e., the PP with lower *MFI*. The Ozawa's exponent increased with temperature, decreased with filler content and assumed values which were close to Avrami's for attapulgite nucleated polypropylene.

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