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

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## Abstract

The addition of nucleating agents to semicrystalline polymers is largely used in the processing industry of plastic materials to improve some properties of polymers as well as for economical and technological reasons. In this work, the influence of talc concentration on the nucleation efficiency of poly(propylene) (PP), as well as on the non-isothermal kinetics of the crystallization of that system were determined by differential scanning calorimetry (DSC). The nucleating efficiency was determined by Fillon's method, and the dynamic nucleation by Ozawa's method at cooing rates of 2, 5 and 10°C $\text{min}^{-1}$. The results show that both the degree of crystallinity and the crystallization temperature increase with the filler content and decrease at higher cooling rates and that Ozawa's ($n$') exponent and the nucleation efficiency increase with temperature and filler content. It was also shown that the nucleating efficiency of talc in poly(propylene) is comparable to the best heterogeneous nucleating agents available.

**Keywords:** DSC, dynamic crystallization, nucleation, poly(propylene)

## Introduction

When semicrystalline polymers are cooled from the melt, they may crystallize forming partially ordered structures. Polymer crystallization, which normally occurs in two stages (nucleation and growth of the spherulites), causes a contraction which may reduce the volume of the system up to 30%. Cooling conditions may strongly affect the degree of crystallinity, crystalline perfection and volumetric shrinkage, causing changes in mechanical, thermal, physical properties as well as on polymer morphology [1, 2].

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Talc is one of the mineral fillers which is extensively used with polymers, particularly with poly(propylene) to modify polymer characteristics. Studies have shown that talc addition affects the degree of crystallinity, the orientation and morphology of the crystalline phases of poly(propylene) [3–5] and that these characteristics are also dependent on particle size and concentration [6]. Some studies have also shown that the material used for the DSC pan (gold, platinum or aluminum) also affect the $T_c$ and the nucleation of PP [7]. According to Trotignon *et al.* [8] talc was a better nucleating agent for PP than mica or wollastonite, which was attributed to better filler dispersion and the smaller particle size of the talc employed. Morales and White [9] compared the nucleating effect of talc and sepiolite as heterogeneous nucleating agents for poly(propylene). Their results show that sepiolite nucleated PP crystallized in much shorter time than talc nucleated samples and concluded that sepiolite was a better nucleating agent for PP than talc. Some authors have shown that surface treatment of mineral fillers can further enhance [10–13] or hinder [9] the nucleating ability of these fillers. The nucleating ability of a given substance depends on factors such as its physical and chemical nature, agent/polymer interaction and its dispersion in the polymer matrix. Organic nucleating agents are more extensively used in polyolefins because they are more compatible with these systems than inorganic agents [13]. In part, this higher effectiveness has been attributed to better dispersion [10].

One of the present tendencies in polymer processing is the reduction of injection cycles which is achieved by faster cooling rates and the addition of nucleating agents. Nucleating agents increase moulding productivity by raising the crystallization temperature, which allows demolding at higher temperatures (i. e., decrease moulding cycles) and reducing shrinkage during crystallization. Their use also generates a higher number of small spherulites, and therefore yields products with good, more isotropic mechanical and optical properties in comparison to polymers without nucleating agents [14].

A better understanding about the relationship among processing, structure and properties of semicrystalline polymers may be obtained if the kinetics of non-isothermal crystallization is studied under dynamical conditions. Quantitative studies on polymer crystallization have been based in experiments made under isothermal conditions, almost universally described by the Avrami equation $\alpha(T)=\exp(-kt^n)$.

Polymer processing, however, takes place under dynamic conditions. Although many modifications have been proposed on the Avrami theory over the years to fit non-isothermal crystallization, Ozawa's model is considered to be the simpliest and the most accurate one that actually reflects the real process. Therefore, Ozawa's method was used in the present study. In this work the influence of talc concentration on the nucleation efficiency of poly(propylene) (PP), as well as the kinetics of non-isothermal crystallization of that system were determined by differential scanning calorimetry (DSC). The nucleating efficiency was determined by Fillon's method [15] and the dynamic nucleation by Ozawa's method at cooling rates of 2, 5 and 10°C $\text{min}^{-1}$.

# Experimental

## *Chemicals*

A commercial grade of isotactic poly(propylene) (KM6100 ($MFI$=3.5 g (10 min)$^{-1}$) and Steamic Talc 00S (98% lamellae particles) both supplied by Polibrasil S/A (Brazil) were used.

## *Preparations*

Talc was sieved through a No 325 standard sieve (1 mesh size=44 μm), dried in an oven at 110°C for 45 min and manually mixed to PP in concentrations ranging from 1 to 5 mass% and processed in an internal mixer attached to a Haake–Buchler System 90 torque rheometer operating at 180°C and 50 rpm for 10 min. The mixture was ground in a mill and pressed in an uniaxial press operating at 180°C and 4.0 kgf mm$^{-2}$ for 5 min in order to obtain films with an average thickness of 0.346 mm. These films were immediately cooled to 5°C and samples for DSC analysis were cut from them.

## *Thermal measurements*

Dynamic crystallization was carried out in a 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 2, 5 and 10°C min$^{-1}$.

## *Nucleating efficiency – Fillon method*

The effect of filler content on the nucleation efficiency 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 [15].

According to Fillon *et al.* [15], in order to control the self-nucleation of poly(propylene), the following four steps are needed: a) PP is heated from 50 to 210°C at 10°C min$^{-1}$ and kept at that temperature for 10 min to guarantee its complete fusion; b) it is cooled at a given rate (usually 10°C min$^{-1}$) and then $T_{c1}$ (the lower limit of the crystallization range) is determined; c) self-nucleation is carried out by partially melting the polymer, i.e. by heating it to selected temperatures $T_s$ which are lower but close to melting temperature. In this stage there is an increase in the concentration of the remaining crystal fragments as $T_s$ decreases, reaching saturation for $T_s$=$T_{s2}$; d) the sample is cooled at a given rate and $T_{c2}$ ($T_{c2}$≥$T_{c1}$) is measured. $T_{c2max}$ is the highest possible crystallization temperature obtained for a self-nucleated sample [4].

Thus, the nucleation efficiency is given by Eq. (1):

$$NE = 100\frac{T_c - T_{c1}}{T_{c2max} - T_{c1}} \tag{1}$$

where $T_c$ is the crystallization temperature of the pure or nucleated polymer; $T_{c1}$ is the lower crystallization temperature of the pure polymer and $T_{c2max}$ is the upper crystallization temperature of the self-nucleated polymer.

### *Ozawa method*

The dynamic crystallization was ascertained by Ozawa method.

The relative crystallinity was determined by Eq. (2):

$$\alpha(T)=\frac{A_{(T)}}{A_{(Total)}} \tag{2}$$

where $\alpha(T)$ – relative crystallinity; $T$ – temperature; $A_{(T)}$ – area at the temperature interval $\Delta T$; $A_{(Total)}$ – total area of the crystallization peak.

### *Degree of crystallinity*

The degree of crystallinity $X_c$ was determined from DSC curves. The enthalpy of fusion of the poly(propylene) sample ($\Delta H_f$) was determined and divided by the enthalpy of a completely crystalline (100%) ($\Delta H_{f^0}$) sample. A value of 207.0 J g$^{-1}$ [20] was used for the 100% crystalline iPP.

$$X_c(\%)=100\left(\frac{\Delta H_f}{\Delta H_f^0}\right) \tag{3}$$

## Results and discussion

### *Nucleation efficiency (NE)*

The nucleation efficiency of the PP/talc system was determined according to Fillon's method. The values obtained for the virgin polymer are: $T_{c1}$=110.47°C; $T_{c2max}$=138.12°C and $T_s$=166°C, as shown in Table 1. These results are nearly identical to those obtained by Fillon *et al.* [15] for a similar iPP/talc(1%) system. In our case, for a PP/talc(1%) system, $T_{c2max}$ was 138.1°C; $T_c$ was 119.7°C and *NE* was 33.6%, whereas Fillon's results were $T_{c2max}$ 137.4°C; $T_c$ was 121.4°C and *NE* was 32%. This was taken as an indication that our experiments were properly conducted and that for the polymers under investigation, neither the molecular mass nor the polydispersity play an important role in their $T_{c2max}$, $T_c$ and nucleating efficiency.

The results show that talc acts as a good nucleating agent to the iPP. Both the nucleating efficiency (*NE*) and the degree of crystallinity ($X_c$) increase with filler content, although in the first case a maximum was obtained at 5% filler content and, in the other, at 1%. The reason for this discrepancy is that although talc acts as a nucleating agent, at higher filler content there is a lot of interference to crystal growth. Therefore, a large number of small and less perfect crystals are generated and the result may be a decrease in the overall degree of crystallinity.

**Table 1** Nucleating efficiency and degree of crystallinity to a PP depending on filler content; DSC sample cooled at 10°C min$^{-1}$ according to Fillon method

| Talc content/% | $T_c$/°C | $NE$/% | $X_c$/% |
|---|---|---|---|
| 0 | 110.47 | 0.0 | 46.9 |
| 1 | 119.75 | 33.6 | 57.9 |
| 2 | 123.84 | 41.1 | 54.5 |
| 5 | 122.07 | 42.0 | 54.2 |

### *Influence of filler concentration and cooling rate in crystallization temperature of iPP*

The data of Table 2 show the crystallization temperature as a function of cooling rate and filler contents to isotactic poly(propylene) (iPP). A DSC curve showing a crystallization peak is presented in Fig. 1.

**Table 2** Influence of the filler content and cooling rate in crystallization temperature to iPP

| Talc content/% | Crystallization temperature/°C | | |
|---|---|---|---|
| | Cooling rate/°C min$^{-1}$ | | |
| | 2 | 5 | 10 |
| 0 | 124.12 | 118.10 | 110.05 |
| 1 | 128.26 | 123.88 | 119.75 |
| 2 | 129.18 | 124.31 | 121.84 |
| 5 | 130.15 | 126.29 | 122.07 |

From the obtained data, it can be inferred that crystallization temperature increases with filler content and decreases with greater cooling rates. This behavior is due to the fact that, at high cooling rates, there is an abrupt decrease in polymer melt viscosity and, therefore, in polymer chains mobility, impeding a perfect crystallization to happen. Slower cooling rates allow that the polymer molecules maintain their

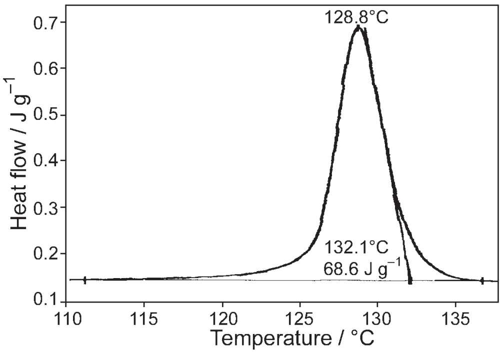

**Fig. 1** DSC curve showing a crystallization peak of the iPP/2% talc heated at 10°C min$^{-1}$ and cooled at 2°C min$^{-1}$

mobility for a longer period and consequently allow a better accommodation in crystalline arrangement [16]. The increasing tendency of $T_c$ with the filler content is attributed to heterogeneous nucleation caused by fillers. The data show that, to the used filler content and under the adopted experimental conditions, talc acts as a good nucleating agent in poly(propylene).

### *Kinetics of non-isothermal crystallization*

Kinetics of non-isothermal crystallization of isotactic poly(propylene) filled by talc and Ozawa exponent (*n*'), which describes crystal morphology, was analyzed according to Ozawa method.

Data demonstrate that relative crystallinity $\alpha(T)$ increases according to the decrease of cooling rate and it also grows with the filler content – to the limit of 2% in this experiment, decreasing at higher contents. This behavior is attributed to an interference in crystal growth at higher filler content, reducing relative crystallinity of the composite as a consequence. As expected, crystallization temperature is higher when the melt is cooled more slowly due to its longer period at lower viscosity temperatures, when polymer chains have greater mobility, easily arranging themselves to form more perfect crystallites, as Fig. 2 shows.

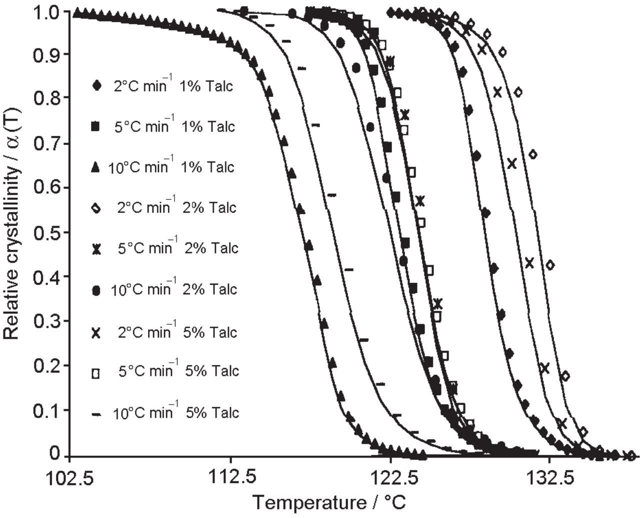

**Fig. 2** Variation of relative crystallinity according to the filler content and cooling rate

The Ozawa exponent (*n*') was calculated from the presented data in Fig. 3, with different cooling rates. The values of relative crystallinity $\alpha(T)$, at a given temperature, was measured for each investigated sample, as a function of the cooling rate ($\beta$), as listed in Table 3.

Ozawa exponent, like Avrami's, is related to the form of crystal growth during the dynamic crystallization of nucleated polymers [17, 18]. It is supposed that mineral fillers, when incorporated in polymers, may initiate nucleation at temperatures below melting temperature or inhibit the normal crystal growth because of the short distances between nucleation centers, affecting the whole process.

**Table 3** Ozawa exponent ($n$') for PP/talc composites

| Sample | Temperature/°C | Ozawa exponent/$n$' |
|---|---|---|
| 5% talc | 125.0 | 3.0 |
| | 126.0 | 3.3 |
| | 127.0 | 3.5 |
| | 128.0 | 3.5 |
| | 129.0 | 3.4 |
| 2% talc | 126.0 | 2.3 |
| | 127.0 | 2.6 |
| | 128.0 | 3.0 |
| | 129.0 | 3.5 |
| | 130.0 | 3.3 |
| 1% talc | 123.0 | 3.5 |
| | 124.0 | 3.7 |
| | 125.0 | 3.6 |

The obtained data show that the Ozawa exponent ($n$') increases with increasing the temperature but decreases with the increase of the filler content. Its values are similar to Avrami exponent when studied in isothermal crystallization conditions, when the average value is near $n'\cong 3$, indicating, therefore, homogeneous crystal growth prevailing the spherical form [18].

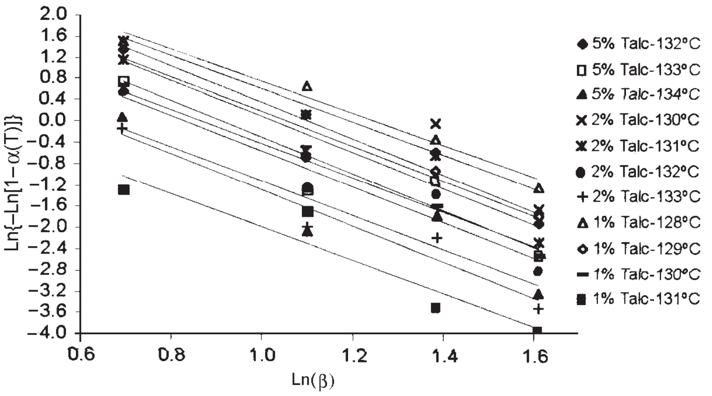

**Fig. 3** Linear regression of the Ozawa method

The notable deviations to $n$' values, according to the filler concentration, determined at different crystallization temperatures are attributed to the fact that cooling rates have generated quite distant curves from each other. Although, the graph construction has to be cautious because the relative crystallinity variation in each sample, cooled at different rates and measured at a pre-set temperature, might be considerable, assuming values ranging from 0.8 to 99%. To obtain more reliable values, it would be necessary for the data to be obtained in a narrow range of relative crystallinity (30 to 70% or 20 to 80%) to a given temperature and filler concentration. Another possible explanation is that, at small concentrations, talc is not well dispersed and, at large concentrations, agglomerations are created in the matrix. Optical micrographs of studied PP/talc films showed that, regardless of the very small agglomeration degree, this problem happened, and it may reduce the reliability of the studied samples [19].

## Conclusions

Analysis of DSC curves shows that, at 5% talc content, a nucleating efficiency of 42% was obtained. It indicates that talc is a good nucleating agent, rating among the best heterogeneous nucleating agents for iPP [15, 19]. According to Fillon *et al*. [15], the best homogeneous nucleating agents for iPP lead to a nucleation efficiency of about 60–65% and the best nucleating agents commonly used in industrial practice are rated around 50% in this efficiency scale.

It was evidenced that, in the used experimental conditions, and to a cooling rate of 10°C $\mathrm{min}^{-1}$, the maximum degree of crystallinity (57.9%) was obtained with 1% talc.

The relative crystallinity $\alpha(T)$ increases with filler content (to the limit of 2% of the matrix mass) and at slower cooling velocities. Ozawa exponent ($n'$) obtained by dynamic conditions are comparable to that of the isothermal crystallization.

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