NUCLEATING ABILITY OF CORK IN POLYPROPYLENE-BASED COMPOSITES

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Abstract

The nucleating activity (Φ) of cork-polymer composites (CPC) in a polypropylene (PP) matrix was analyzed by Dobreva and Gutzow method. CPC with 15 %wt of cork powder was used in this study. The non-isothermal crystallization behaviour was studied using differential scanning calorimetry (DSC) at four different cooling rates (5, 10, 15 and 20°C/min). Results show that cork acted as an active surface by revealing Φ value lower than 1. This suggests that cork can act as a nucleating agent during non-isothermal crystallization.

1. Introduction

The demand for new materials derived from renewable resources has been increasing, mostly due to environmental concerns and waste accumulation, driven by the restrictive measures imposed by the European Commission. Nowadays, there is a need for more innovative, sustainable and recyclable materials, combined with an increase market demand for products with lower ecological footprint.

Lignocellulosic materials' incorporation in synthetic polymers has become an effective approach to develop new sustainable materials [1]. Cork is a well-recognized Portuguese raw material and product. Cork is the outer bark of oak tree *Quercus suber L.*, which regenerates in every 9-10 years. The main chemically component is suberin (33-50%), followed by lignin (20-25%); the carbohydrate fraction is composed by cellulose and hemicelluloses (12-20%); extractives represent nearly 14-18% and ≈1% are ashes [2]. Cork possesses an unique combination of properties, more specifically, low density, elasticity and compressibility (without lateral expansion), high recovery capacity after impact, impermeability to liquids and gases, excellent thermal and acoustic insulation and, microbial and fire resistance [2]. Stoppers are the major cork product and its production generates ≈ 30% wt of industrial residues. These residues are usually burned (thermal energy recovery) representing a low value disposal solution. The development of new polymeric materials based in these cork by-products is a promising strategy to upcycle these residues. Low density, hardness and cost, good relation between strength/weight, good insulation properties and high levels of filling are some of the advantages of applying natural materials as fillers in thermoplastic matrices. Natural materials are also renewable, readily available and non-toxic [3].

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The present study is part of a larger project that focuses on the research of cork-polymer composites (CPC) for injection molding applications. Studies on CPC thermal behavior are essential in fields like injection molding, in order to improve thermal resistance, mechanical properties and material processing. During injection molding process, plastic matrix composites experience non-isothermal crystallization rather than isothermal crystallization. A previous work [4] regarding the CPC non-isothermal crystallization study showed that the presence of cork particles can influence the crystallization process, mostly by revealing nucleating activity. Moreover, composites mechanical properties can be partially dependent on how cork influences the crystallization behavior.
In this particular study, the evaluation of cork nucleating activity was assessed by Dobreva and Gutzow method [5, 6]. Nucleating activity is defined as a factor in which three-dimensional (3D) nucleation decreases with the addition of a foreign substrate. If the foreign substrate is active Φ approaches to 0, while for inert substrates Φ approaches to 1.

2. Experimental Procedure

2.1. Materials

The polymeric matrix used is a homopolymer PP (PPH 10060) from Total Petrochemicals, having a Melt Flow Index (MFI) of 35g/10min (230°C, 2.16 Kg) and a melting temperature (T_m) of 165°C. Cork powder was supplied by a Portuguese cork producer. It was fractionated through sieving (Retsch, Germany) and the relative amount of particles according to its size was determined (Table 1). The average particle size, d_p, was calculated using (Eq. 1), where w_i is the weight fraction of the *i*th particle size and d_i is the diameter of the *i*th particle.

$$d_p = \frac{\sum w_i d_i^4}{\sum w_i d_i^3} \tag{1}$$

Table 1. Cork particles: physical characteristics.

Granulometry (µm)	Cork powder (%)	Average particle size (µm)
1000	2.3±0.1	596
800	45.8±0.1	
400	51.4±0.1	
200	0.6±0.1	

2.2. CPC formulation

Prior to compounding, cork particles were dried at 70°C for 24h in a vacuum oven (Carbolite AX60 model) to stabilize moisture content. It is known that cork structure and composition do not suffer significant changes up to 250°C [7]. CPC were compounded in a Brabender type internal mixer with a mixing volume chamber of 355 cm^3. Firstly, PP pellets were charged and melted during 2 minutes at 180°C and 40 rotations per minute (rpm). Then, cork particles (15 %wt) were added and materials were mixed for additional 8 minutes.

2.3. DSC analyses

Crystallization behavior analysis was carried out in a Shimadzu DSC-60 apparatus. The equipment was calibrated using indium as reference material. Samples weights varying between 5.0 and 6.0 mg were encapsulated in aluminum pans. Each sample was heated from 20°C to 200°C at a scan rate of 200°C/min and held for 2 minutes at this temperature to eliminate thermal history and prevent self-seeding of PP [8]. Then, they were cooled until -80°C and heated again up to 200°C. Four different

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heating/cooling rates (φ) – 5, 10, 15 and 20 °C/min – were used. Only the second run was considered to analyze the crystallization behavior process: crystallization temperature (T_c) and melting temperature (T_m).

3. Results and Discussion

3.1. Non-isothermal behavior

Thermal parameters of PP and CPC are listed in (Table 2). Melting temperatures of PP and CPC at different cooling rates did not vary significantly. On the other hand, T_c shifted to lower values as the cooling rates increase. This indicates a cooling rate effect on the crystallization kinetics. Polymer chains, at higher cooling rates, are less movable and have shorter time to diffuse into the crystalline phase, which results in a decrease of T_c. Contrarily, lower cooling rates promotes better conditions for the development of polymer crystals due to a kinetic process. The length and branches of the polymer chains also influence the crystallization process [9].

Table 2. Non-isothermal crystallization parameters obtained by DSC.

Samples	φ (°C/min)	T_m (°C)	T_c (°C)
PP	5	164.51	114.81
	10	164.39	106.13
	15	164.01	103.61
	20	164.97	99.22
CPC	5	160.13	118.32
	10	162.99	114.55
	15	162.46	111.60
	20	161.68	108.77

From (Table 2), it is also visible that, for a specific cooling rate, T_c values were higher for CPC when compared to PP. The crystallization process is governed by two major events, namely nucleation and crystal growth. In a neat polymer matrix, like PP, polymer chains have to overcome the free energy of primary nucleation and create a new surface for crystal growth [10]. While in the case of CPC, the incorporation of a foreign substrate (cork) can reduce the free energy needed for nucleation, leading to a faster crystallization process. Consequently, more crystals are formed and a higher T_c value is obtained.

3.2. Nucleating activity

Dobreva and Gutzow developed a simple method [5, 6] to estimate the nucleating activity of a foreign substrate in a polymer melt. The nucleating activity is defined as a factor in which three-dimensional (3D) nucleation decreases with the addition of a foreign substrate. It is determined as the ratio of β parameters (Eq. 2) in heterogeneous (β*) and homogeneous (β) medium.

$$\Phi = \frac{\beta^*}{\beta} \tag{2}$$

For homogeneous nucleation, β parameter can be calculated from (Eq. 3):

$$\ln(\varphi) = const - \frac{\beta}{\Delta T_P^2} \tag{3}$$

, where β is related to the 3D nucleation and ΔT_P^2 is the degree of supercooling (Eq. 4).

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$$\Delta T_P^2 = T_m - T_c \tag{4}$$

For heterogeneous nucleation, β* parameter can be calculated from (Eq. 5):

$$\ln(\varphi) = const - \frac{\beta^*}{\Delta T_P^2} \tag{5}$$

Both β and β* for PP and CPC can be obtained from plotting ln (φ) against the reciprocal of ΔT_P^2. These plots are presented in (Figure 1) and nucleating activity values for samples are listed in (Table 3).

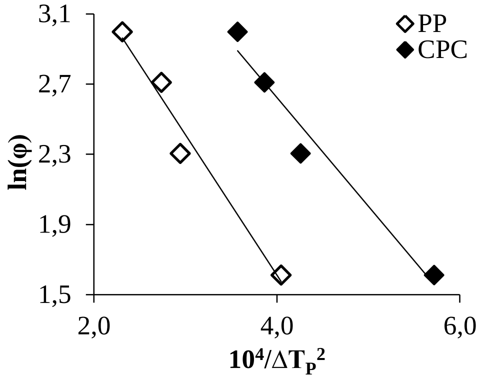

Figure 1. Plots of ln(φ) against reciprocal ΔT_P^2 for PP and CPC.

As referred above, for active substrates the Φ value approaches to 0, while for absolutely inert substrates Φ is 1. The obtained Φ value for CPC was lower than 1 suggesting that cork acted as an effective nucleating agent in PP matrix, creating an active surface.

Table 3. Nucleating activity.

Samples	β	β*	Φ	R^2
PP	0.80	-	-	0.97
CPC	-	0.62	0.78	0.96

4. Conclusions

The presented work focuses on the study of cork nucleating activity on a PP matrix through non-isothermal crystallization analyses. Dobreva and Gutzow method was used and it was possible to estimate the nucleating activity value. It was found that Φ was lower than 1 (equal to 0.78), which indicates that cork acted as an active surface promoting the crystallization process.

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