The Activity of Inorganic Substrates in the Catalysed Nucleation of Different Polymer Melts

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SUMMARY: The activity of inorganic substrates in the catalysed nucleation of polymer melts was studied using a nonisothermal differential scanning calorimetry technique (DSC). The analysis of the results was made by using the method developed by Dobreva-Veleva et al.[1)]. In this method the kinetics of nonisothermal overall crystallisation of polymers was analysed in terms of the general non steady state nucleation theory at small undercooloings. Two examples of the applicability of this method are presented.

Introduction

The activity of substrates in the catalysed nucleation of polymer melts is an important parameter that, as previous results have shown, can be correlated with the modification of the physical properties of different filled polymers[2,3)]. In this sense a number of methods for determining the kinetic of constant overall crystallisation from nonisothermal experiments have been suggested in the literature[4,5)]. Recently, Dobreva-Veleva et al. developed a formalism[1)] to calculate the activity of substrates in the catalysed nucleation of polymer melts using data from cooling DSC runs. In the present work the previous method is applied to two different kinds of materials.

Theoretical Background

Dobreva et al. developed a method for determining the nucleating activity of substrates by analysing nonisothermal kinetics of overall crystallisation at small undercoolings[1)]. According to this approach, the cooling rate, q, and the undercooling, ΔT_p, at which the crystallisation curve reaches its maximum, are connected as follows:

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$$\log q = const - \frac{B}{2.3\Delta T_p^2} \quad (1) \quad \text{where} \quad B = \frac{16\pi\sigma^2\sigma_e V_m^2}{3k\Delta S_m^2 T_m n} \quad (2)$$

In the above equations, $\Delta T_p = T_m - T_p$, T_m and T_p being the melting temperature and the temperature corresponding to the peak of crystallisation curve, respectively; k is the Boltzmann constant; V_m, the molar volume of the crystallising substance; ΔS_m, the entropy of melting; σ the lateral surface energy; σ_e the end surface energy; and n the corresponding Kolmogorov – Avrami exponent.

In the heterogeneous case, equation 1 takes the form

$$\log q = const - \frac{B^*}{2.3\Delta T_p^2} \quad (3)$$

where

$$B^* = B\Phi \quad (4)$$

The function Φ can be used as a measure for the nucleating activity of a foreign substrate. For absolutely inert particles Φ is unity, and for very active substrates Φ is practically zero. Moreover, Dobreva and Guztow[1)] derived a simple expression, which describes the dependence of the activity Φ on the melting temperature of the substrate, T_{ms}.

$$\Phi = a_0 - a_1\left(\frac{T_{ms}}{T_m}\right)^{1/2} + a_2\left(\frac{T_{ms}}{T_m}\right) \quad (5)$$

Here, the parameter a_2 accounts for the influence of misfit effects, while the parameter a_1 reflects the interaction energy across the substrate/overgrowing crystal-phase boundary. The constant a_0 depends both on the cohesive forces as well as on the natural misfit. Equation 5 allows one to assess the relative significance of the structural mismatch to the bonding energy.

Materials and Experimental

Two kinds of materials can be distinguished:

Samples of pure polyethylenterephtalate (PET) and high-density polyethylene (HDPE) and samples with 0.3% content in volume of NaCl, KCl, KI for PET and NaCl, KCl, KI

and LiF for HDPE were studied. The samples with substrates were prepared through simultaneous extrusion of polymer and substrates. Previous results of the nucleating activity of AgBr, AgI, PbF_2, Ag_2S, LiF and CaF_2 were also considered[6]. Injection moulded discs (78 mm diameter) of polypropylene (PP), talc-filled PP composites (denoted as PPN), and silane-treated talc-filled PP composites (denoted as PPF), with a 20% in weight of talc were also prepared[3].

DSC measurements were performed using a Mettler DSC-30 thermal analysis system. Samples weighing about 5 mg were used. The measurements were conducted with several cooling rates: 1, 2, 5, 8, 10, 20 and 50 K/min. All runs were carried out in a stream of dried nitrogen. The dynamic temperature program was preceded by an isothermal period of 5 minutes at a temperature approximately 30 K above the end melting point of the respective polymer in order to erase any previous thermal history. Dynamic mechanical properties (storage modulus and loss tangent) of samples cut from the injection moulded discs were recorded in a Perkin-Elmer DMA7 in a three-point bending measurement system. These properties were measured at 1Hz, in the temperature range between –20°C and 50°C with a heating rate of 5°C/min.

Results

The results obtained for the cooling rate dependence of the crystallisation temperatures for plain and for nucleated PET are shown in Fig. 1. The activity Φ, according to equation 1, would be obtained from the ratio of the slopes of the log q vs. $1/\Delta T_p^2$ function for the homogenous and heterogeneous case. In order to obtain precise results only slow rates, up to 10K/min, were used to determine the straight line fit. It is clear that significant deviation from linearity occurs for rates above 10 K/min. Therefore, in order to apply this method only the data at low cooling rates have to be considered. The values of the nucleating activity for the different substrates are collected in tables 1 and 2.

Table 1: Nucleating Activity of Substrates in PET.

Substrate	KCl	NaCl	KI	AgBr	AgI	PbF_2	Ag_2S	LiF	CaF_2
Φ	0.70	0.55	0.56	0.43	0.45	0.49	0.47	0.45	0.50

Table 2: Nucleating Activity of Substrates in HDPE.

Substrate	LiF	NaCl	KI	KCl
Φ	0.88	0.92	0.96	1.0

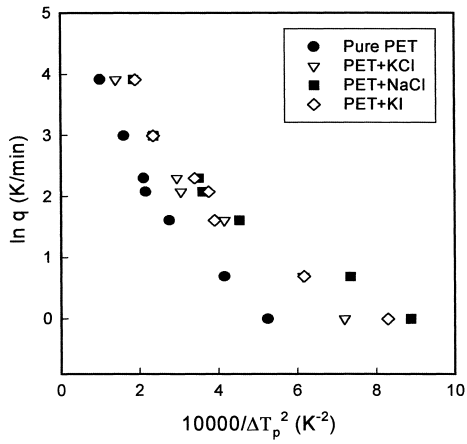

Fig.1: log q vs. $1/\Delta T_p^2$ for the PET samples.

Fig. 2 shows the dependence of Φ on the melting temperature of some of the substrates, T_{ms}[6]. It is qualitatively seen that the nucleating activity of the substrates in PET decreases when T_{ms} increases. This result is an indication of considerable misfit values[6].

High-density polyethylene shows a different behaviour for all the substrates. The slope of the log q vs. $1/\Delta T_p^2$ for the unfilled polymer is similar to those for the filled HDPEs, which means that the activity is close to 1 (table 2).

The values of the activity for samples cut from the PP-talc injection moulded discs are collected in table 3. It is clear that the activity of the filler is higher in the PPF composites, the nucleating effect increases with the presence of silanes. In this sense the treated talc is more active. Consequently, the interaction between the filler and the matrix will be higher, or in other words the filler will influence the matrix structure to a greater extent.

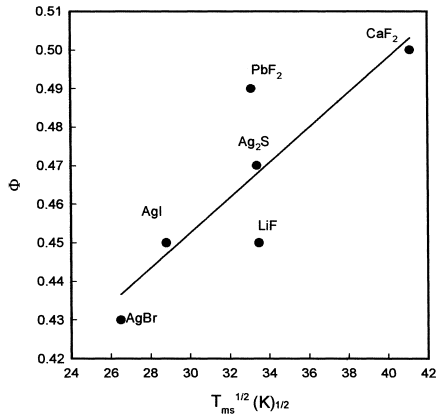

Fig. 2: Dependence of Φ on $T_{ms}^{1/2}$. The line is drawn in a qualitative manner to shown the tendency of decreasing activity.

Table 3: Nucleating Activity of Talc in PP.

Substrate	Talc (PPN)	Silane treated talc (PPF)
Φ	0.48	0.34

Fig. 3 shows the evolution of the storage modulus with temperature for samples cut from the same zone of the different discs. The storage modulus always increases with the adding of the filler. Moreover, the presence of the talc produces a more rigid interface in the PP matrix. If the talc is a treated one, the interface seems to be stiffer, and due to this reason the silane treated composite has the highest storage modulus.

Another important result is obtained if the glass transition (T_g) temperature is measured by dynamic mechanical analysis (as the peak in the loss tangent curve) (figure 3). The following trend is obtained: T_g(PP) (≈14°C) > T_g(PPN) (≈11°C)> T_g(PPF) (≈8°C). Despite previous studies on filled polymers, where the adding of a filler resulted in a higher glass transition temperature, the experimental results show that in the case of PP-talc composites the T_g occurs at lower temperatures. This can be explained with the aid of the activity results: the talc acts as a nucleating agent, and this effect leads to a faster crystallisation of the PP. This speed-up crystallisation causes an amorphous phase with a bigger mobility in the PP-talc composites, which results in a lower T_g value. For

analogous reasons, the PPF composite, in which the talc is more active, has a T_g at lower temperatures than the PPN composite.

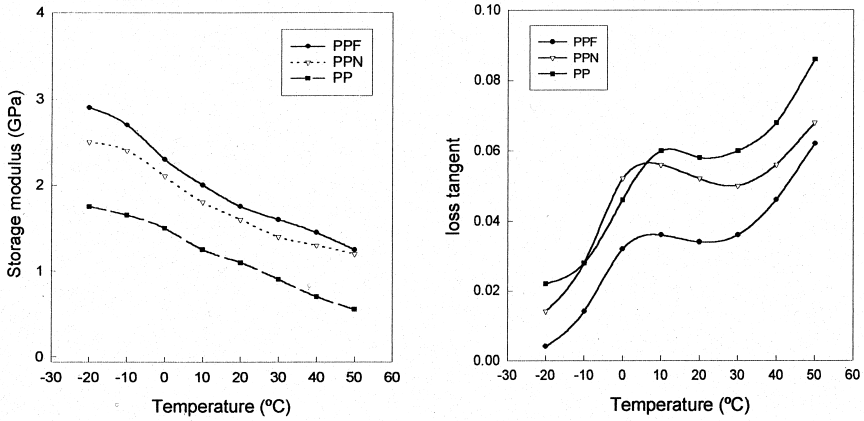

Fig. 3: Storage modulus and loss tangent of samples cut from the injection moulded discs.

Conclusions

The method developed by Dobreva-Veleva[1)] for the determination of the nucleation activity of substrates has been applied to different composites. Some experimental aspects related with this method and the kind of information that can be obtained have been shown. Some of them are: 1. In this method only the data at low cooling rates have to be considered. 2. For PET considerable misfit values have been observed. 3. The parameter activity can be used to quantify the filler-matrix interaction in PP-talc composites. 4. The glass transition of the PP-talc composites is modified by the addition of talc.

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