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Isothermal crystallization of polypropylene/titanium dioxide nanocomposites by flash scanning calorimetry

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Abstract

A wide range of crystallization temperatures of polypropylene (PP) nanocomposites was obtained by using a combination of conventional differential scanning calorimetry (DSC) and flash DSC. This covered the conditions related to polymer processing. The kinetics of crystallization were explained by the Lauritzen-Hoffman equation. The results verify that the equation is still valid even at low temperatures. The decrease in the nucleation parameter (K_g) and surface free energy (σ_e) values in the presence of titanium dioxide (TiO_2) proves that TiO_2 can be a useful nucleating agent leading to a faster crystallization. The finding gives new insights into crystallization behaviors under low temperature conditions that can be used in the industrial process for the crystallization of PP. It can be concluded that the addition of TiO_2 might enable shorter cycle times, resulting in lower processing costs in part manufacturing.

Keywords: Nanocomposites, Isothermal crystallization, Flash DSC, Polypropylene, Titanium dioxide

1. Introduction

Recently, polymer nanocomposites have gained much attention because of their extraordinary performance developments in comparison to traditional polymers [1]. Polypropylene (PP), as a well-known commodity plastic, is the fastest growing class of thermoplastic polymers and the most widely used in various industries. It is not only low cost but also has an ease of processability. The balance between its physical and mechanical properties, along with its chemical resistance, make it appropriate for a variety of applications. However, PP has some trivial shortcomings, such as relatively low strength and stiffness when compared to engineering plastics [2]. Several nanoparticles, such as $CaCO_3$ [3], SiO_2 [4], and TiO_2, etc. [5], have been integrated with PP based nanocomposites to enhance the performance of PP. In general, nanoparticles change the final mechanical properties of the polymer matrix by either acting as a reinforcing agent or nucleating agent for the polymer matrix. Therefore, nanoparticles can affect the crystallization as well as the morphological properties of polymer matrices such as the size of the spherulites, the thickness of the lamellae, and the degree of crystallinity.

It is well-known that the ultimate properties of polymers rely upon the final morphology of the products, especially in semi-crystalline polymers. Generally, the crystallization process during production governs the morphological structure of such products. In general, an investigation of polymer crystallization is performed by using conventional differential scanning calorimetry (DSC) where the usual conditions of the instrument are far from the extreme conditions found in industrial production [6]. Actually, the simulations presented in [7] show that cooling rates of up to 3000 $^{\circ}$C/s are achieved with injection-molded components in areas near the mold wall. This allows crystallization to occur at temperatures below 100 $^{\circ}$C and therefore, far below the isothermal crystallization temperatures which can be realized in a standard DSC. Using a so-called flash DSC there is,

however, a new approach to investigate the crystallization behavior at high cooling rates similar to the conditions during industrial processing. This flash DSC gives new insights into the crystallization behaviors under rapid cooling of miscellaneous semi-crystalline polymers such as polyamide 6 (PA 6) [8], poly(lactic acid) (PLA) [9], and isotactic polypropylene (iPP) [10].

The kinetics of quiescent crystallization are commonly analyzed under isothermal or non-isothermal circumstances. This study can help to clarify the crystallization mechanism, which is crucial for optimizing the polymer processing and understanding the process-structure-property relation. The kinetic of isothermal crystallization is generally investigated using data received from exothermic peaks in the DSC thermogram. This kinetics is based on the hypothesis that the heat derived during the evolution of crystallization directly corresponds to the progress of crystallinity [11]. The Avrami and the Lauritzen-Hoffman theories are commonly applied to study the mechanism of crystallization in polymers [12,13]. Due to the Avrami assumption being only suitable for the crystallization of the primary stage [12], the Lauritzen-Hoffmann theory [13] suggests that the nucleation and transport of the macromolecules govern the crystallization of the polymer. This assumption describes the radial growth rate (G) to the secondary nucleation rate and the lateral growth rate. The Lauritzen-Hoffmann theory can be applied to interpret the dependence on temperature of the overall crystallization rate [14]. In our previous work, we were able to show that the non-isothermal crystallization kinetics of PP incorporating titanium dioxide (TiO_2) nanoparticles can be well described by the Lauritzen-Hoffmann theory [15]. However, to illuminate the crystallization kinetics of polymers, an examination of the kinetics of isothermal crystallization of PP/TiO_2 nanocomposites was performed using a typical DSC and a flash DSC. The use of the different DSCs enables the investigation of the behavior in an expanded range of temperature, which is comparable to the temperatures along with the wall thickness of an injection-molded component.

2. Materials and methods

2.1 Materials

PP homopolymer as a polymer matrix was obtained from Borealis GmbH (HD120 MO, Borealis GmbH, Burghausen) and TiO_2 nanoparticles as a nanofiller were provided from Huntsman (Hombitec RM130 F, Huntsman, Duisburg). These type of TiO_2 nanoparticles exhibits an acicular form and have, according to the supplier a mean diameter of about 15 nm.

2.2 Nanocomposite preparation

A twin-screw extruder (Theysohn, Theysohn Extrusionstechnik GmbH, Korneuburg) was used to produce the PP/TiO_2 compounds. Three loading levels of TiO_2 nanoparticles, 0 vol.% (Neat PP), 1 vol.% (PP-TV1) and 4 vol.% (PP-TV4) were prepared. After extrusion, injection molding (Arburg Allrounder 420C, ARBURG GmbH + Co KG, Loßburg) was used to prepare the testing materials. The whole detailed preparation sequences are described in [4].

2.3 Differential scanning calorimetry (DSC) analysis

The samples were prepared from the middle of the injection-molded part. The DSC analysis was performed on a TA instruments device (TA Q20, TA instruments, Eschborn) in combination with the Refrigerated Cooling Systems (RCS90). For isothermal investigation, the samples were heated up to 220 °C with a heating rate of 20 °C/min and held at 220 °C for 3 min to eliminate the processing experiences. The materials were then cooled to different isothermal crystallization temperatures (T_i) (varied from 128 to 134 °C) with a cooing rate of 40 °C/min and held at the target temperature until the completion of crystallization. The samples were then heated up again to 220 °C at 20 °C/min. The peak of the endothermic thermograms was measured and employed to define the melting temperature (T_m). The equilibrium melting temperature (T_m°) was estimated using Hoffman-Weeks plots [16].

2.4 Flash differential scanning calorimetry (Flash DSC) analysis

Isothermal crystallization analysis was implemented using a flash differential scanning calorimetry (FLASH DSC 1, Mettler Toledo, Gießen) equipped with an Intracooler (Huber TC100). Prior to the actual experiments, the material was heated with a very slow heating rate (0.1 °C/s) to ensure an efficient seal between the material and the sensor chip. After pre-melting, the material was heated to 220 °C with a heating rate of 1000 °C/s and held at 220 °C for 0.1 s. Then, the material was quenched with a quenching rate of 4000 °C/s to the required T_i, varying between 0 to 150 °C, and held until the completion of crystallization.

3. Results and discussion

3.1 Equilibrium melting temperature (T_m°)

The equilibrium melting temperature T_m° is required to compute the degree of supercooling and is applied to determine the nucleation parameters in the polymer crystallization process. Based on the Hoffman-Weeks plot, the linear correlation between the melting temperature (T_m) of the polymer and its isothermal crystallization temperature (T_i) has been widely accepted to predict T_m° [10]. According to the Hoffman-Weeks relationship, T_m° is described as the temperature of melting of an ideal perfect crystal with infinite crystal size. As can be seen in Figure. 1, a line of $T_m = T_i$ refers to a perfect crystal in thermodynamic equilibrium with the melting, the so-called linear Hoffman-Weeks. The intersection values extracted from the plot of T_m refers to the T_m° of each material.

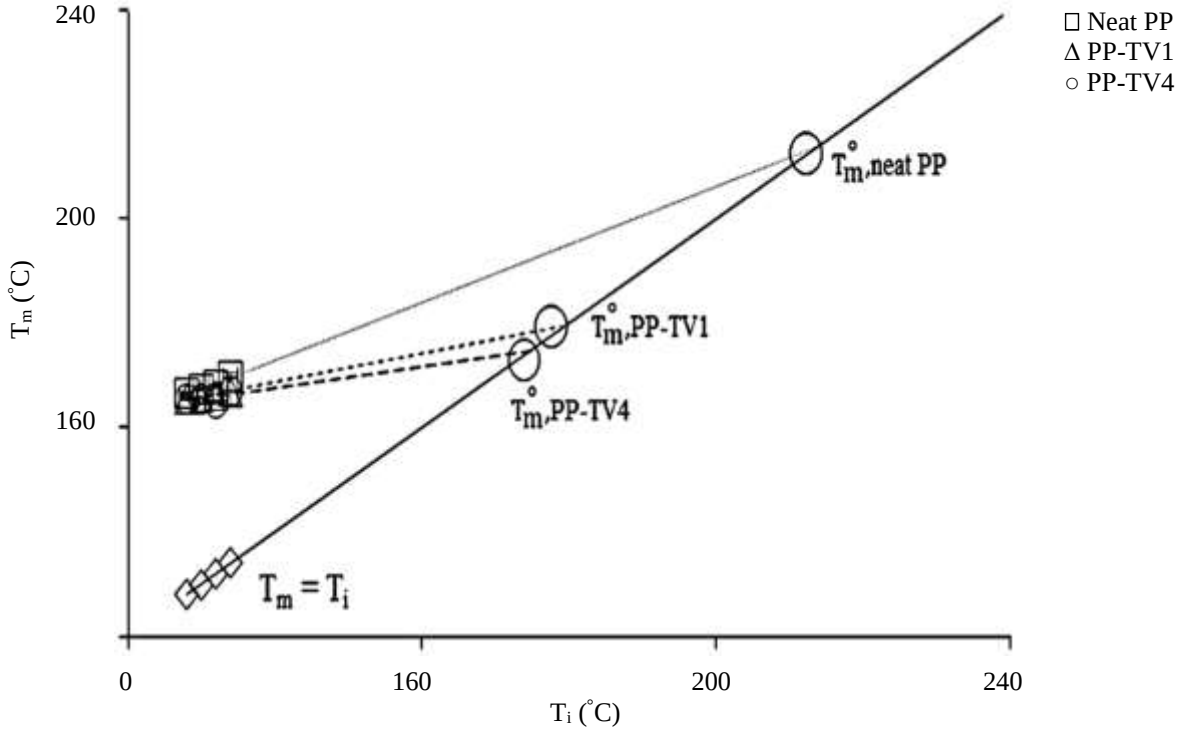

Figure 1 Hoffman-Weeks plots for neat and TiO_2-filled PPs.

Figure 1 shows the plots of the Hoffman-Weeks relationship for neat and TiO_2-filled PPs, and the results are listed in Table 1. In this work, the T_m° of neat PP is observed around 213.6 °C. This result is in good agreement with previous reports (212–215 °C) [2,17]. It is apparent that the inclusion of TiO_2 reduces the T_m° of PP, suggesting that the crystals in PP filled with TiO_2 nanoparticles are less perfect compared to neat PP. Several studies have reported similar results where the addition of fillers gave rise to a decrease of T_m° [2,18,19]. However, these values must be considered with some restrictions. Based on the theory of the linear Hoffman-Weeks relationship, the coefficient of lamellae thickening is the lamellar thickness ratio at the melting time and the critical nucleus at T_i (independent of T_i and time). This assumption has been proved to overestimate the thickening coefficient and underestimate the T_m° [18].

Table 1 Values of T_m°, K_g, and σ_e for neat and TiO_2-filled PPs.

Materials	T_m° (°C)	K_g x 10^{-5} (mJ/m^2)	σ_e (mJ/m^2)
Neat PP	213.6	12.2	23.3
PP-TV1	179.4	4.3	8.8
PP-TV4	174.6	4.0	8.2

3.2 Kinetics of isothermal crystallization by crystallization half-time ($t_{1/2}$)

The crystallization half-time ($t_{1/2}$), described as the time taken to attain 50% of the ultimate crystallization process, can indicate the kinetics of crystallization and is shown in Figure 2. A greater value of $t_{1/2}$ implies a slower crystallization rate, and vice versa. As expected, a reduction in $t_{1/2}$ is recognized with a lowering T_i in all materials. This reveals that a lower T_i contributes to a quicker crystallization rate due to an increment in supercooling when T_i is lowered. The crystallization driving force defined as the free energy of melting, is proportional to the supercooling. The driving force for crystallization increases with decreasing T_i, causing a higher number of nuclei and/or rate of spherulite growth and as a consequence, a rise in the overall rate of crystallization [20].

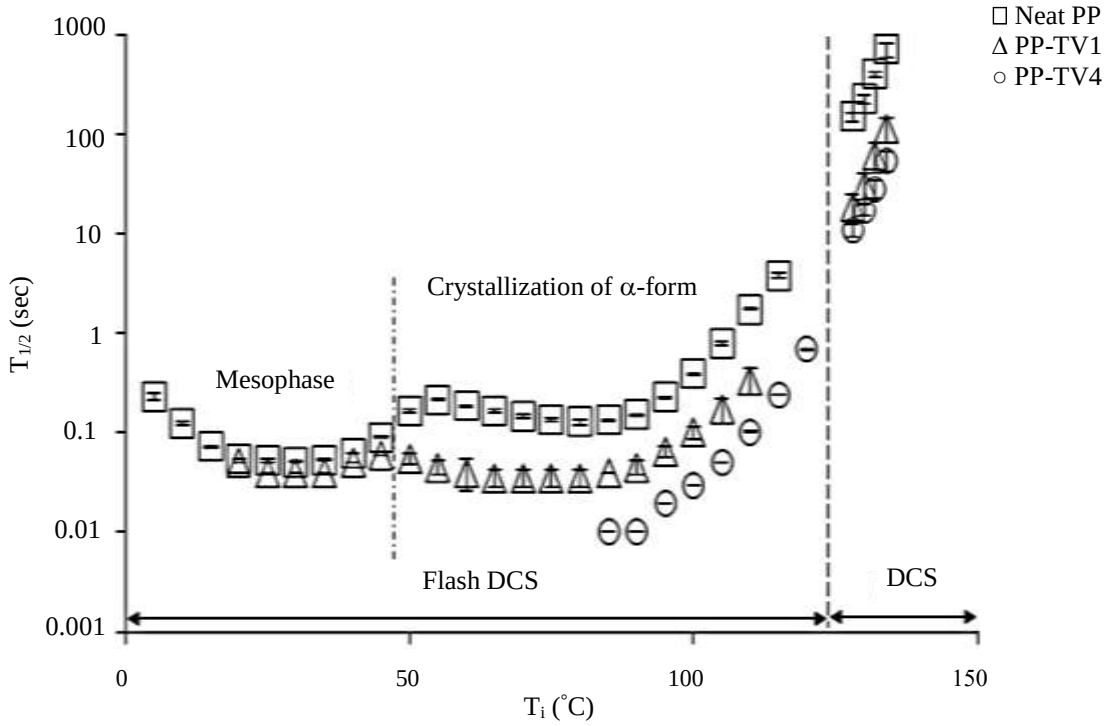

Figure 2 The relation of $t_{1/2}$ versus T_i obtained from DSC and flash DSC.

All materials exhibited a bimodal crystallization behavior, except PP-TV4, indicating that there are two different crystallization processes, and therefore two different crystal morphologies. The lower temperature process (below 55 ˚C), is interpreted as the mesophase formation. The crystallization above 55 ˚C corresponds to the crystallization of the α-phase [10,21]. There are two minima, one at 30 ˚C, and one at about 80-85 ˚C, corresponding to the maximum rates of the mesophase formation and the α-phase crystallization, respectively. In addition, the transition from the mesophase formation to the α-phase crystallization is at around 50-55 ˚C. This result is in agreement with the literature from Schawe [10].

It is important to note that the temperature dependence of both the mesophase formation and the α-phase crystallization is controlled by two processes in which the kinetics display opposite temperature coefficients. The $t_{1/2}$ decreases with increasing supercooling/decreasing temperature. This is explained by an increment of the thermodynamic driving force of the crystallization. When it reaches a minimum point, the $t_{1/2}$ then rises up due to the increasing viscosity of the melt, and consequently, the decreasing mobility of chain segments [8].

The crystallization rate of the α-phase increases in the presence of TiO_2 nanoparticles. This is due to the nucleation effect of nanoparticles as the heterogeneous nuclei, leading to a rise in the rate of overall crystallization. On the contrary, the rate of mesophase formation is not affected by the inclusion of the nanoparticles. Consequently, the development of the α-modification is based on heterogeneous nucleation, whereas the mesophase is formed on homogeneous nuclei.

3.3 Fold surface free energy based on the Lauritzen-Hoffman theory

According to the theory of Lauritzen-Hoffman, the crystallization is governed by two different processes, which are the nucleation and the macromolecular transport in the melt. In principle, the driving force for the polymer crystallization is generally from the internal energy of the excessive thermodynamic free energy in the

system. This free energy is generated from two phenomena; molecular transportation from the amorphous phase to the crystalline phase, and molecular rotation and rearrangement of the molecules of the crystalline phase [22]. By the assumption of Lauritzen-Hoffman [13], Chan and Iayev [23] took the crystallization rate ($\frac{1}{t_{1/2}}$) and pre-exponential factor ($\frac{1}{t_{1/2}}$)$_0$ to replace the growth rate (G) and a pre-exponential factor (G_0), respectively, to explain the overall crystallization rate with temperature dependence, as described in the following:

$$\frac{1}{t_{1/2}} = \left(\frac{1}{t_{1/2}}\right)_0 exp\left[-\frac{U^*}{R(T_i - T_\infty)}\right] exp\left[-\frac{K_g}{T_i(\Delta T) f}\right] \quad (1)$$

where U^* is the activation energy, R is the gas constant. f is the correction factor and $T_\infty = T_g - 30$ K is the hypothetical temperature below which all motion related with viscous flow ceases. The nucleation parameter, K_g is defined as:

$$K_g = \frac{(4b_0\sigma\sigma_e T_m^\circ)}{k_B(\Delta h_f)} \quad (2)$$

where σ is the layer surface free energy, σ_e is the fold surface free energy, b_0 is the nucleus thickness, and k_B is Boltzmann's constant [24]. All the parameter values are reported in [15].

For the isothermal crystallization analysis of the samples, the Lauritzen-Hoffman plots in accordance with equation (1) are displayed in Figure. 3. As can be seen, a straight line fitting between the empirical data and the Lauritzen-Hoffman relationship is achieved for all nanocomposites. In addition, the slopes of the fitting line, labelled K_g, can be used to estimate the σ_e of the samples in accordance with equation (2). The values from the calculation from equation 2 are listed in Table 1. Both K_g and σ_e depict the free energy essential to create a nucleus. The K_g and σ_e decrease significantly with the incorporation of TiO_2 nanoparticles. In general, the crystal growth process requires the proper nucleus size to start growing. The existence of an external surface commonly reduces the required nucleus size. The explanation is that the potential of the crystal formation between the external surface and polymer is higher than that for the corresponding free polymer crystal. A foreign or external pre-existing surface for a heterogeneous nucleation lowers the free energy opposing the nucleation [25]. Accordingly, the reduction in the σ_e value results in an improvement of the crystallization induction time. The decrease in both K_g and σ_e values indicates that the inclusion of the TiO_2 lessens the free energy needed to form a new fold surface thus enhancing the crystallization rates [24]. Using filler particles on the sub-micron scale enables an increase in the specific area of the filler and shows better nucleating effects compared to conventional fillers. Makhlouf et al. proved that the crystallization behaviour of PP depends on both the processing parameters such as the cooling rate and the filler characteristics such as the content and size [26].

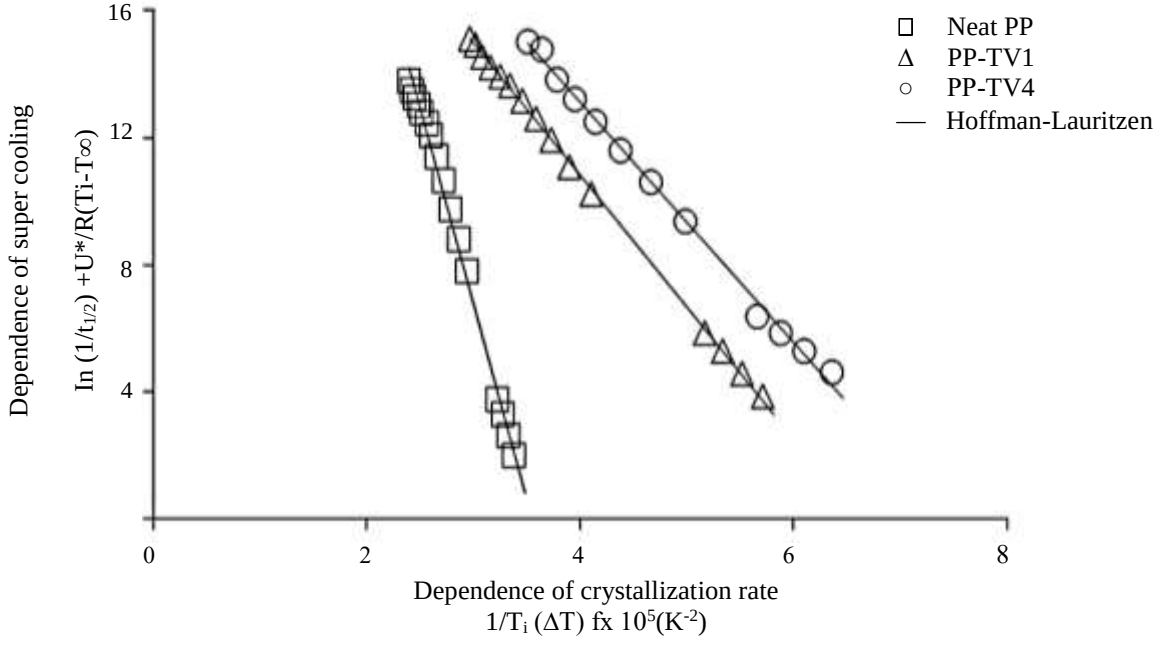

Figure 3 Lauritzen-Hoffman plots for neat PP and TiO_2-filled PP**.**

4. Conclusion

Investigations of the crystallization of PP using a combination of conventional and flash DSCs allows a deeper look into the crystallization behaviors of industrially relevant processes. It was discovered that two different modifications, the α-form and the mesophase, are formed in PP where the α-phase develops at temperatures above 55 ˚C, while the mesophase forms at temperatures lower than about 55 ˚C. The presence of TiO_2 nanoparticles in the PP-based nanocomposites only enhances the α-phase crystallization, while it obstructs the mesophase formation at high TiO_2 nanoparticle loadings.

The evaluation of the data accomplished by both the DSC and flash DSC according to the Lauritzen-Hoffman theory show that the K_g and σ_e constants of PP filled with TiO_2 are smaller in comparison with neat PP. This implies that the TiO_2 also facilitates the PP crystallization at low temperatures (related to high cooling speeds).

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