Crystallization kinetics of new low viscosity polyamides 66 for thermoplastic composites processing

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ABSTRACT

In this paper, we present the isothermal crystallization kinetics study of a new generation of polyamides 66 (PA 66) over a large temperature range [100–234 °C] using differential scanning calorimetry (DSC) to reach low crystallization temperature at very high cooling rates. This PA 66 with a low viscosity is of high industrial interest since it is dedicated to composite part manufacturing at low pressure ($\leq$0.15 MPa) using new thermoplastic for Resin Transfer Molding (RTM) process with high fiber volume fraction ($\approx$50 vol%). The low viscosity ($\approx$15 Pa s), is one of the major difference between the new generation of PA 66 and the others. A crystallization model based on Avrami's theory is proposed for further simulation of this industrial process in commercial softwares. However, industrial process conditions require to know the crystallization kinetics over a large temperature domain. For this purpose, isothermal crystallization is quantified from Flash DSC 1 experiments using two methodologies. The measurements were compared to standard DSC data to validate the results. Then, the effects of the molar mass, additive and the sample size of the Flash DSC 1 on the crystallization kinetics were studied. As a result, crystallization of PA 66 without additive exhibits a bimodal temperature dependence. The molar mass has only an effect on the crystallization kinetics in the high temperature range, suggesting a change in the nucleation mechanism. However, the presence of additives suppresses this bimodal behavior. Finally, the effect of the sample mass on the Avrami parameters was also discussed. The results obtained in this study can be used to accurately compute heat transfer coupled to solidification during the manufacturing of PA 66 parts including processes with high cooling rates.

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1. Introduction

Nowadays, the levels of performances achievable with continuous reinforcement composites are well demonstrated. Among these composites, it is recognized that the use of thermoplastic matrix is a major advantage because of their low environmental impact (no Volatile Organic Compounds (VOC) nor solvent, easy recyclability) and good mechanical resistance (intrinsic ductility...etc.). Indeed, because of their potential to reduce the cycle time and their welding capacity, these composites can strongly compete with thermosetting ones. However, the use of these materials to produce parts with complex geometry is strongly limited for applications involving medium and large production

series (e.g. automotive industry) due to high costs and production demands. Among the interesting composite processes compatible with all requirements, Liquid Composite Molding (LCM) [1–3] appears to be of great interest. However, one difficulty is the high viscosity of melted polymers, making the impregnation of continuous reinforcements (performs) at low pressure (lower than 0.15 MPa) extremely difficult and especially when the fiber content is high ($\geq$50 vol%), as required for structure parts applications.

PA 66 is among the oldest polymers largely used in the world [4]. It is considered as an engineering thermoplastic polymer with excellent mechanical and chemical properties. Polyamides are often molded with fibers by an injection process and are also widely used for automotive applications. The recent development of new thermoplastic polymers with low viscosity ($\eta \approx$15 Pa s) in the melted state opens the possibility to use the LCM process. The chemical structure of PA 66 macromolecule consists of amide groups separated by methylene sequences. The polymorphic

structures of polyamides result from differential spatial arrangement in the hydrogen bonding between the oxygen in the carbonyl group of one polyamide molecular chain. The crystals structures observed in polyamide mainly fall into two categories: α crystalline phase and γ crystalline phase. The α phase of PA 66 is more stable than γ phase at room temperature [5,6] and also evolves during heating (Brill transition ≈220–240 °C).

A high production capacity and part quality imply LCM process with a high filling rate, a good impregnation of the reinforcement but also a significant decrease of heating and cooling times. For this reason, the chemical structure of the new generation of PA 66 was modified by Solvay Company for decreasing the viscosity. Consequently, it allows to reduce the filling time (during the injection) and also to improve the impregnation of the preform at low pressure. However, the part quality and production rate are strongly linked to the thermal history during the molding. Therefore, an accurate description of the heat transfer is key to succeed in the simulation and optimization of the process. In addition, residual stresses due to the crystallization must be low to prevent micro cracks of parts. Therefore, the crystallization kinetics must be known which allows coupling the heat transfer, crystallization and the residual stresses computation during the simulation of the forming process.

The crystallization of polymers is commonly restricted to the temperature range between the equilibrium melting temperature of crystals and the glass transition temperature of the amorphous phase [7]. At cooling rates lower than 100 K/min the isothermal crystallization of nylon can be measured in a temperature ranges of 220–240 °C [8–12]. Therefore, the choice of isothermal crystallization temperature depends strongly on the cooling rate. For that reason, the study of the isothermal crystallization over large temperature range requires high cooling rates (>2000 K/s) (to prevent that the crystallization occurs during the cooling phase and before the isothermal step). The cooling capacity of standard differential scanning calorimetry DSC (100–500 °C/min) is far to be representative of heat transfer existing in processes such as injection (>1000 K/s). Therefore, the Flash DSC [13,14] has been employed to study the isothermal crystallization kinetics of PA 66, where the cooling rate could reach 10^4 K/s. Relatively few studies exist on polyamides, but the group of R. Androsch has recently studied the behavior of PA 66 by using Flash DSC 1 [6]. They determined the half-time of crystallization for a PA 66 dedicated to injection molding. Our study is complementary since it is new PA 66 formulated for the recent process thermoplastic RTM. It also provides a description of the crystallization kinetics which can be implemented in process simulation software.

For several polymers, the plot of the crystallization half time associated to isothermal crystallization versus the temperature exhibits a bimodal curve [15,19]. In the case of isotactic polypropylene (i-PP) the low temperature peak was observed at 60 °C [15] and at 130 °C in the case of PA 66 [6]. This phenomenon is discussed in the literature in terms of change of nucleation mechanism (from heterogeneous to homogeneous nucleation) and/or the formation of another crystal phase/mesophase. In case of PA 6, a specific study [17] demonstrates that the mesophase domains do not have a lamellar structure and are not spatially ordered.

In this paper, the isothermal crystallization kinetics of low viscosity PA 66 and at high cooling rates is considered within the framework of Avrami's theory [20–22] as shown in the next sections. The influence of molar mass, and of additives on the crystallization kinetics are investigated and quantified. These results are of primary importance since they can be directly used in a heat transfer model to compute temperature and crystallization degree fields during the manufacturing of thermoplastic composites. A discussion of the effect of the mass of the sample used in Flash DSC 1 experiments is also proposed.

Table 1
Molar mass, additive percentage and the cooling rate applied for reach the crystallization temperature for each studied PA 66.

PA 66	Molar mass [g/mol]	wt% Additives (PF)	Viscosity at 280 °C [Pa s]	Cooling rates [K/s]
PA 66$_A$	20,400	–	400	5000
PA 66$_B$	8,500	–	70	5000
PA 66$_C$	5,800	–	7	7000
PA 66$_D$	8,500	20	15	2000
PA 66$_E$	8,000	4	20	7000
PA 66$_F$	8,000	0	25	7000

2. Kinetics theory

The phase change of semi-crystalline polymers from the molten state (amorphous) to the solid state (semi-crystalline) could be described by overall crystallization kinetics theories [23]. Most of the theories used to describe macroscopically the isothermal and non-isothermal crystallization kinetics in thermoplastic polymers generally assume [20–28] that the semi-crystalline entities, e.g., spherulites (in 3 dimensions), are growing in an infinite volume. According to Avrami's approach, the crystallization kinetics is modeled according to Eq. (1) [20–22] and is especially easy to use for isothermal crystallization and in the specific cases of instantaneous or sporadic nucleation.

$$\alpha(t) = 1 - \exp\left(-K_{Av} \cdot t^n\right) \tag{1}$$

In this equation, K_{Av} is the Avrami's kinetic function and "n" the Avrami's exponent. K_{Av} depends on the temperature and pressure and can be expressed versus nucleation density and the growth rate of the growing entities. The Avrami's exponent "n" depends on the nature of the nucleation process (sporadic or instantaneous nucleation) and the geometry of semi-crystalline entities. The growth and nucleation rates depend only on the temperature at a given pressure. In the case of crystallization at a constant cooling rate, Ozawa [24] proposes another model to extend the theory of Avrami. Finally, the model of Nakamura [27,28] based on isokinetic assumption, generalizes the Avrami's model to any thermal history leading to the well-known differential equation given by Patel et al. [29]. In fact, this latter model is often used for modeling heat transfers coupled to the crystallization kinetics during polymer and composite processing and particularly in injection molding [29,30].

3. Experimental

3.1. Materials

The polyamides 66 used in this study were provided by Solvay Company®. Six kinds of low viscosity PA 66 have been studied (Table 1). These polymers are currently under development for thermoplastic composite processing. An additive (phenol formaldehyde) is added in different proportions for PA 66$_{D,E}$. The molar mass is varying between 20,400 and 8000 g/mol. The main characteristics are presented in Table 1.

In recent years, the phenol formaldehyde has been used to modify the chemical structure of polyamides in order to further improve mechanical performance and/or to achieve new desirable properties such as the increase of glass transition temperature or lower water absorption. The influence of phenol formaldehyde on the structure and the morphology of PA 66 were already studied [23,31]. It was noticed that the phenol formaldehyde could modify by chemical reaction, the crystallization behavior (morphology) of PA 66 [31]. For this reason, this paper studies the influence of additives on the crystallization kinetics.