Evaluation of the Crystallization of Polypropylene at Melt Spinning Conditions Using the Green Chemical Orotic Acid as Nucleating Agent

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Abstract

The melt spinning process makes extremely high demands on the melted polymer. It must be able to deform continuously by highest deformation rates. The rheological properties of the melt were also significantly increased during the rapid cooling in the spin-line. The cooling rate of the fiber increases above 1000 K.s-1in dependence on the applied melt spinning conditions. Additionally, for semi crystalline polymers crystallization during the spinning process occurs at typical temperatures. The mechanical properties step up in order of magnitudes immediately. Crystallization is strongly dependent on the cooling rate. Therefore, Flash DSC was used in order to realize real cooling rates for evaluation of crystallization in the spin-line. However, there is still a need to improve or modify the mechanical properties of polypropylene fibers. A common modification is an improvement of the heterogeneous nucleation using a nucleating agent. For example, the green chemical orotic acid was used as appropriate nucleating agent. The nucleating effect was also evaluated at real cooling conditions.

Keywords: Flash DSC; Polypropylene; Orotic acid; Nucleation; Fiber

Introduction

Melt spinning or melt blowing are the most convenient and economic methods for polymer fiber manufacturing at industrial scales. In this processing technique a short time load of the melt occurs with rapid increase of the extensional strain and simultaneous extreme cooling of the polymer between spinneret and winding point [1,2]. A drastic decrease of the melt stream diameter from the die to the filament diameter at the crystallization temperature in connection with the distinct increase of the formation velocity up to around 4000 m-min^{-1} is caused. Under these conditions, the cooling rates increase up to 1000 K-s^{-1}. In the standard setup, however, the thermo mechanical history is often hard to control along the spin line, resulting in poor controllability of the processing and the fiber structure.

Usually, indirect information about the crystalline structure of melt-spun fibers can be obtained by means of conventional DSC methods [3]. The melting process is observed during the sample is heated at a typical rate (10 – 20 K-min^{-1}). The curve shows exothermic peaks for secondary crystallization and endothermic peaks for the melting of crystallites. The amount of crystallinity is proportional to the melting enthalpy. But the crystalline structure changes during the measurement. In cause of reorganization, smaller crystals grow during heating. It means that the melting behavior measured in a conventional DSC is not related to the pristine crystalline structure anymore. Therefore, the standard DSC curve implies higher melting temperatures and larger melting peaks. Reorganization of polymer chains is a very fast process. Endothermic and exothermic processes occur simultaneously. For this reason, they cannot be directly detected in a conventional DSC. Therefore, the measured heating scan often does not represent the original structure. Wunderlich [4] recommended to measure at high heating rates in order to prevent the reorganization. In verification of this need fast calorimetry based on chip technology was developed. This method was realized and made universally applicable by launching of the Flash DSC. The measuring cell of the Flash DSC is realized using a chip. The thermal capacity is very low. Therefore, it can provide heating and cooling rates of several 1000 K-s^{-1} [5]. Reorganization of polymer morphology can be avoided or controlled and technical processes can be simulated by means of such an instrument [6-9]. The measurement of the crystallization during cooling is a very important method to analyze crystallization behavior, because the non-isothermal crystallization at high cooling rates corresponds to processing conditions. As a result of the high cooling rates, the crystallization occurs at high supercooling.

Isotactic Polypropylene (PP) was chosen as the polymer for this study. Due to the low density, high crystallinity, high stiffness and excellent chemical and bacterial resistance, PP is widely used in many industrial applications. Only PP is useful for fiber applications. PP fibers are manufactured using conventional melt spinning [10] or melt blowing. Subsequent multistage drawing imparts tensile strength and enhances mechanical properties required for industrial applications. Several studies about the evaluation of the crystallization behavior using Flash DSC were reported in technical literature [11-12]. Changes in phase structures like mesophase, rigid amorphous phase, mobile amorphous phase and crystalline phase in dependence on the cooling rate were discussed.

Furthermore, a nucleation agent was used for better demonstration of the crystallization effects by means of Flash DSC. A nucleation agent is an additive which provides additional nuclei

that accelerate crystallization process and promote nucleation for crystal growth [13]. As a result, a larger amount of smaller spherulites is generated. It has been reported in the technical literature that also the green chemical Orotic Acid (OA) can be used as nucleation agent in order to induce improved crystallization of biodegradable and biocompatible polymers [14-16]. Orotic acidis a heterocyclic compound and an acid; it is also known aspyrimidine carboxylic acid [CAS: 65-86-1]. Historically it was believed to be part of the vitamin B complex and was called vitamin B13, but it is now known that it is not a vitamin. It can be synthesized by human. Jacquel et al. [14,15] used OA as nucleation agent for poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) copolymers. They found an outstanding nucleation effect on these polymers. Qiu and Li [16] reported on an attempt to use OA for the improvement of the crystallization kinetics of poly(L-lactide). They found that small OA contents are well suited to enhance the overall melt crystallization.

The aim of this study is to investigate the crystallization behavioral the real cooling rates of a typical melt spinning process. A nucleation agent was used in order to determine the influences of nucleation. For this purpose, the capabilities of Flash DSC should be used.

Materials

The isotactic polypropylene HG455FB® from BOREALIS was used as the basic material. It is a polypropylene homopolymer with anti-gas fading stabilisation intended for fiber applications. It has a narrow molecular weight distribution and a MFI of 27 g/10 min (230 °C, 2.16 kg) (data provided by the manufacturer).

The used orotic acid [CAS 65-86-1] was obtained from the Carl Roth GmbH + Co. KG, Germany. The commercial chemical was used as received without further purification.

Experimental

The polymer samples were processed in one step using a co-rotating twin-screw-extruder ZSK 30 (Werner & Pfleiderer, Germany) with pelletizer. A mass flow rate of 5 kg-h^{-1} was selected. The mass temperature in the six heating zones was kept at about 200 °C. Samples without (PP) and with 0.5 (PP 0.5 % OA) and 1 wt.-%OA (PP 1 % OA) were prepared.

The basic rheological measurements in the melt state were carried out by means of an ARES G2 rotational rheometer (TA Instruments, USA) using small amplitude oscillatory frequency sweeps and temperature ramps. The selected geometry for frequency sweeps and heating/cooling sweeps in the molten state was the parallel plate geometry (gap of about 2 mm, and diameter of 25 mm). All rheological measurements were carried out using nitrogen as the heating gas. Each test was started 4 minutes after insertion of the specimen into the rheometer. This allowed for the attainment of thermal equilibrium. Both storage and loss modulus, were measured as a function of the shear frequency respectively. The complex melt viscosities were calculated.

Standard DSC analysis was carried out by using a Differential Scanning Calorimeter DSC Q1000 equipped with an auto-sampler (TA Instruments, USA). Heating and cooling scans for the polymers were performed in a temperature range of -80 to +220 °C with a heating rate of 10 K-min^{-1} under nitrogen flow. Data for a cycle of
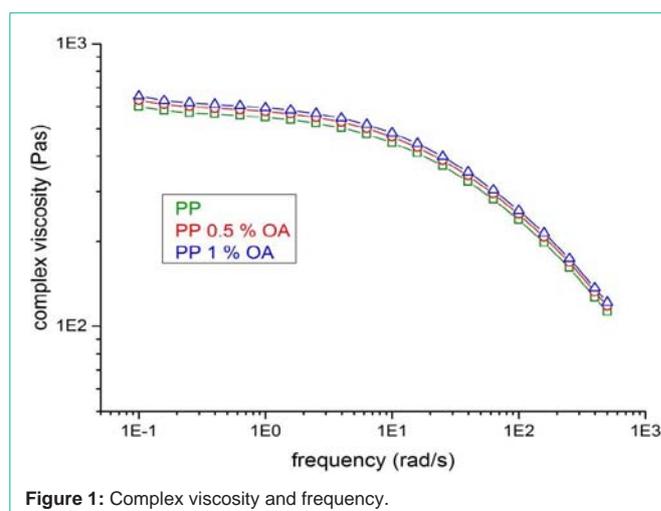

Figure 1: Complex viscosity and frequency.

first heating, cooling and second heating were collected. The Glass Transition (Tg), Melting (Tm), and crystallization Temperatures (Tc), and the melting and crystallization enthalpies were determined.

Measurements with high cooling rates were realized by means of a Flash DSC (Flash DSC 1, Mettler-Toledo AG, Schwerzenbach, Switzerland). The samples were heated from -80 until 220 or rather 230 °C with a heating rate of 1000 K-s^{-1}. Subsequently, the samples were annealed at this temperature for 0.1s corresponding to [8] in order to reach the thermal equilibrium condition. A longer annealing time causes no further effect. Then, the cooling scans were measured using cooling rates from 2 to 2000 K-s^{-1}.

The melt spinning experiments were carried out using a self-constructed device, which consists of plunger and piston.

The spinning conditions were set at:

Piston temperature: 230 °C

Die geometry: ∅ = 0.3 mm, l/d =2

Winder velocity: 250 m-min^{-1}

Volume flow rate: 0.775 cm^3-min^{-1}.

Under these conditions, the mean cooling rate of the fiber amounts ~ 400 K.s-1.

Mechanical properties were measured on a UPM zwicki 2,5 (Zwick GmbH und Co, Ulm, Germany) testing machine according to DINEN ISO 5079. The average values of the tensile tests result from 10 specimens of each run. The test conditions were set at a length between clamps 25 mm and a test velocity 25 mm-min^{-1}.

Experimental Results and Discussion

Small amplitude oscillatory tests

Small amplitude oscillatory frequency sweeps were carried out for all samples using the rotational rheometer. The samples were tested at 210 °C. Figure 1 summarizes the results of the complex viscosities.

It can be seen that the samples containing OA show an increase of the complex viscosity. The OA is solid at measurement temperature and can act as filler. But the increase of the viscosity is relative low,
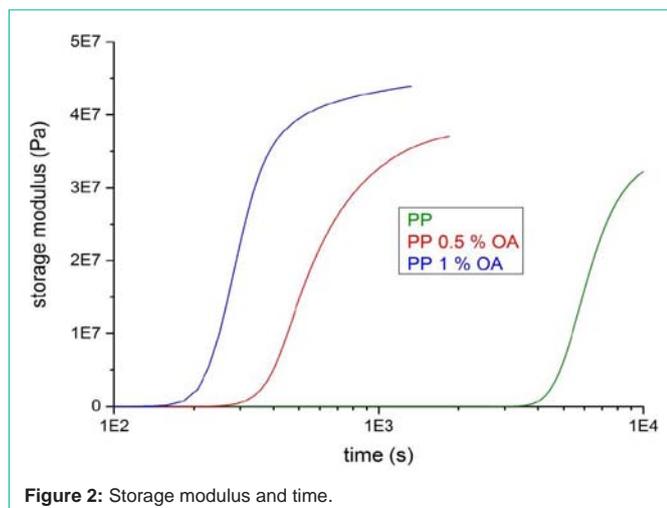
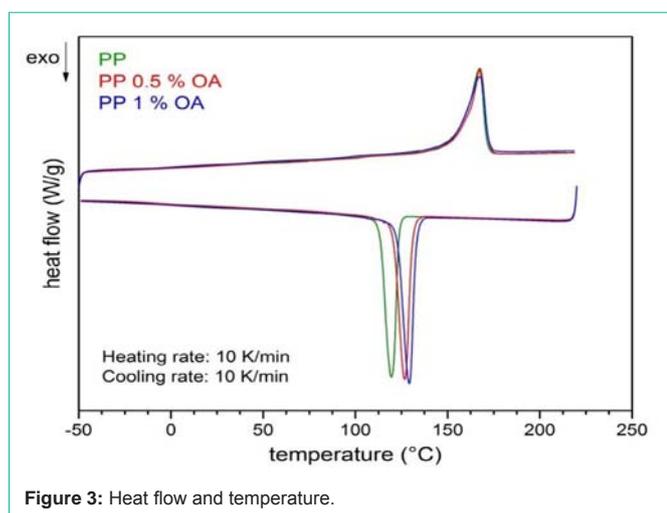**Figure 2:** Storage modulus and time.

Figure 3: Heat flow and temperature.

Figure 4: Heat flow and temperature.

Table 1: Quantitative data of the first heating scan of the melt spun fibers.

Sample	$\sum\Delta H_M$ (J/g)	ΔH_{SC} (J/g)	$\sum(\sum\Delta H_M +\Delta H_{SC})$ (J/g)	T_M (°C)
PP	66.6	-13.6	53.0	162.7
PP 0.5 % OA	78.2	-3.0	75.2	163.6
PP 1 % OA	79.1	-2.8	76.3	164.2

Figure 4 depicts the heating scans of the melt-spun fibers obtained from the thermal analysis using standard DSC. Obviously, it can be seen that there are differences in the region of secondary crystallization (80 – 140°C). The effect of secondary crystallization is nearly complete diminished for the samples containing OA. Furthermore, these samples show a higher melting peak having its maximum at a higher temperature (Figure 4).

The quantitative data of the first heating are compiled in (Table 1). The values $\sum\Delta H_M$ represent the melt enthalpies and ΔH_{SC} the enthalpy of the secondary crystallization. The values $\sum(\sum\Delta H_M +\Delta H_{SC})$ represent the crystallinity at room temperature for each sample (Table 1).

A distinct increase of crystallinity was realized by adding 0.5wt.-% OA. The addition of 1wt.-% OA causes no further improvement. From Table 1 it can also be seen that the samples containing OA show only very little effect of secondary crystallization.

Due to reorganization processes during heating, only indirect information about the crystalline structure could be obtained by means of the standard DSC methods.

Flash DSC

The results of the Flash DSC measurements revealed that different cooling rates cause different types of crystallization.

In (Figure 5) can be seen that the peak maximums of the crystallization were shifted from 100 to 50°C and the enthalpies of the peaks decrease with increasing cooling rates. No further crystallization was detected above critical cooling rates of 1500 K-s^{-1} for the pure PP and 2000 K-s^{-1} for the nucleated samples. Only one peak (α-crystals) was seen in the range from 2 until 100 K-s^{-1}. At cooling rates above 200 K/s occur double peaks. The second peak is observed at lower temperatures. This peak of isotactic polypropylene is described as the so-called mesophase. It is a conformationally disordered glass [17] (Figure 5a and 5b).

especially at higher shear frequencies. Therefore, a negative influence on the processing properties will not be expected.

Further rheological measurements were carried out in order to determine the crystallization behavior. At first, the samples were melted at 230°C and annealed for 4 min at this temperature to eliminate the pristine crystalline structure. Then they were cooled with a rate of -15 K-min^{-1} to the temperature of 140°C. Oscillatory shear with a frequency of 1 rad-s^{-1} was appplied during cooling and under the isothermal condition at 140°C. The strain was set to 0.5 % during cooling and for measurement of isothermal crystallization. The results can be observed in (Figure 2).

It can be seen that the samplescontainig 0.5 and 1wt. -% OA show a remarkably earlier begin of crystallization and a faster increase of the storage modulus G' than the reference sample PP.

Thermal analysis using conventional DSC

Heating and cooling scans are carried out for granulates of extruded PP and PP samples containing OA in order to demonstrate the nucleation effect. The results are plotted in (Figure 3). It can be seen that the addition of OA shifts the initiation of crystallization towards higher temperatures.
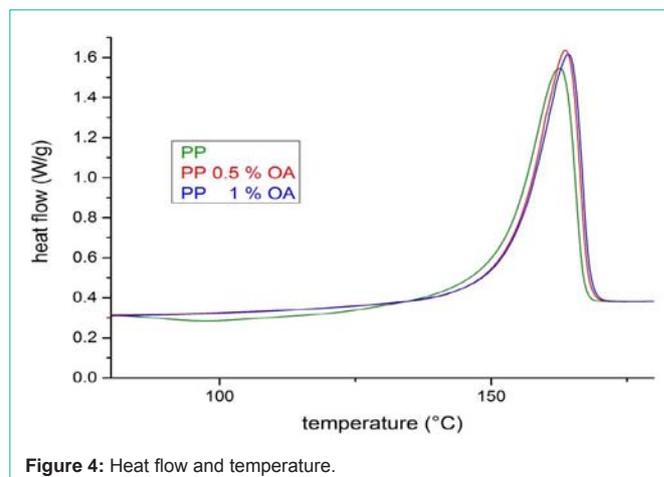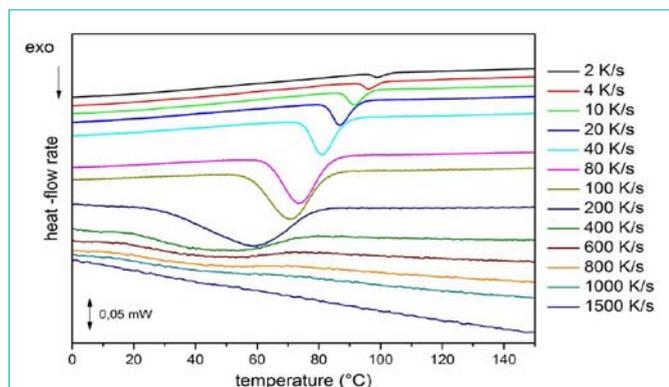
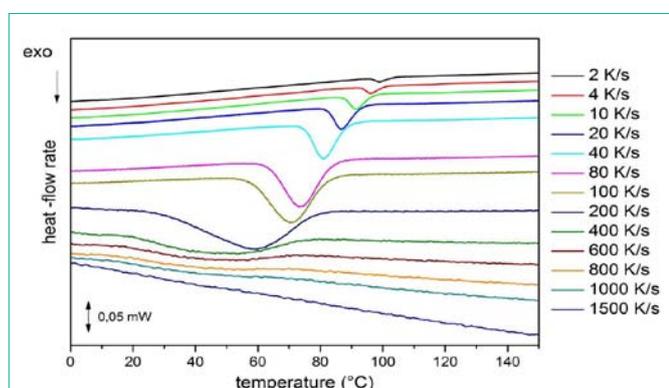**Figure 5: A)** Heat flow rate and temperature.

Figure 5: B) Heat flow rate and temperature.

This glass is a super cooled disordered crystal which is restricted to change into a completely ordered crystalline structure by cooling below its glass transition during its formation. The results are in accordance with reports in the technical literature [10-17]. Typical parameters of the cooling scans are compiled in (Table 2). The cooling scans with the start temperature of 220 °C reveal a sharp increase of the crystallization peaks of the samples containing OA. Therefore, a clear-cut nucleation effect of the used OA is verifiable. An influence of the nucleating agent on the temperatures of the peak onsets and the peak maxima cannot be seen. But only a weak increase of the enthalpies is observed using the start temperature of 230°C for the cooling scans. The influence of the nucleating agent deteriorates at this start temperature. A possible explanation of this effect is originated in the well-known effect of thermal degradation of isotactic polypropylene in the melt state [18,19]. The preferred degradation mechanism of isotactic polypropylene is the chain scission. Qian et al. [19] have shown that an increasing content of lower molecular
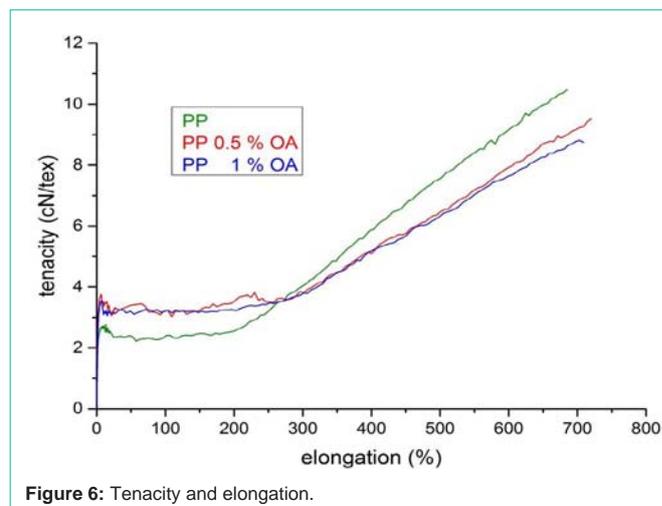

Figure 6: Tenacity and elongation.

weight components and oligomers can be detected with increasing degradation time and temperature. They found that a second peak occurs in the molecular weight distribution at degradation times at 190°C. The second peak appears at a weight average molecular weight of around 5000 g-mol^{-1}. It can be assumed that these low molecular weight components also cause a nucleation effect. Vogel et al. reported a similar effect for the nucleation of bacterial poly(3-hydroxybutyrate) [20]. They used 2 wt.-% of poly(3-hydroxybutyrate) with a weight average molecular weight of 5250g-mol^{-1} and added it to the pristine poly(3-hydroxybutyrate) a weight average molecular weight of 394 000 g-mol^{-1} and found a sharply increased crystallinity after a typical melt spinning process.

Mechanical testing of the fibers

The melt spinning was realized without any difficulties for all formulations. The results of the tensile tests are shown in (Figure 6 and Table 2).

The calculated parameters of the tensile tests are:

F_H - maximum tensile force,

R_H - tenacity (maximum tensile force in relation to fiber fineness),

ϵ_H - elongation at maximum force,

R_Y - yield stress

T - Titer (fiber fineness in g/1000 m))

E_t - Young modulus at 1% elongation.

The values in (Table 2) represent the average from ten single tests.

Table 2: Thermal parameters of the cooling scans at higher cooling rates using different start temperatures.

Sample	Cooling rate (K/s)	Peak onset (°C)		Peak Maximum (°C)		Enthalpy (J/g)		Glass Transition (°C)	
		220°C	**230°C**	**220°C**	**230°C**	**220°C**	**230°C**	**220°C**	**230°C**
PP	600	74	90	43	68	-4	-8	-17	-1
	800	71	90	44	59	-2	-4	-18	-3
	1000	70	94	42	58	-1	-3	-20	-5
PP 0.5% OA	600	72	90	46	63	-20	-9	-16	-2
	800	71	94	44	57	-9	-6	-17	-5
	1000	69	85	41	51	-5	-2	-18	-3
PP 1% OA	600	75	90	51	60	-26	-7	-18	-3
	800	74	90	47	56	-11	-4	-17	-2
	1000	73	86	47	62	-6	-2	-18	-3

Table 3: Mechanical parameters of the melt spun fibers.

Sample	F_H (cN)	R_H (cN/tex)	ϵ_H (%)	R_{YS} (cN/tex)	T (tex)	E_t (GPa)
PP	23.8	10.3	690	2.57	2.3	1.19
PP 0.5% OA	19.6	8.5	720	3.46	2.3	1.58
PP 1% OA	19.7	8.6	710	3.24	2.3	1.59

Maximum mechanical properties were found for the formulations with OA. Both the Young modulus at 1% elongation Et and the yield stress RYS are significantly higher than values of the reference sample PP.

Conclusions

The processing properties of the used formulations were not deteriorated during the melt spinning process by the addition of OA.

Maximum mechanical properties of the melt-spun fibers were found for the formulation containing 0.5 wt.-% OA. Both the Young modulus at 1% elongation and the yield stress are significantly higher than the values of the pristine sample (Table 3).

The thermal analysis by means of conventional DSC also has shown that the addition of 0.5 wt.-% OA acid yields to a distinct higher level of crystallinity.

The nucleation effect was also seen by means of the cooling scans using Flash DSC. The crystalline structures and the enthalpies of the crystallization peaks strongly depend on the selected cooling rate. The evaluation of the crystallization behavior with and without nucleating agent could be considered at real cooling rates of the melt spinning process.

In consideration of the short residence time of the polymer in the spin-line and the assumption of a mean cooling rate of 400 K-s⁻¹ during the melt spinning process, must be assumed that only a partially crystallization immediately occurs in the spin-line.

An additional influence of the start temperature on the crystallization was found using higher cooling rates and different start temperatures.

It can be summarized that Flash DSC is a very useful tool for studying the thermal behavior of polymers under relevant thermal conditions of melt spinning.

Acknowledgement

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