

Properties of polypropylene fibers using the green chemical orotic acid as nucleating agent

Roland Vogel*, Harald Brünig and Liane Häussler

Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Hohe Straße 6, Germany

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Abstract. It has been reported in the technical literature that orotic acid can be used in order to induce improved crystallization of biodegradable and biocompatible polymers like poly(L-lactic acid), polyhydroxybutyrate and poly(hydroxybutyrate-co-hydroxyhexanoate). The expected advantage of the changed crystalline structure is a reinforcing effect of the polymers. A lot of papers reported about the application of inorganic and organic agents for acceleration of heterogeneous nucleation. This study reports on an attempt to use orotic acid as appropriate non-toxic nucleating agent for improving mechanical properties of isotactic polypropylene. Special attention is given to demonstrate the effect of nucleation in a typical melt spinning process in order to improve the mechanical properties. The effects were demonstrated using rheology, thermal analysis and tensile testing.

Keywords: polypropylene; orotic acid; nucleation; fiber; mechanical properties

1. Introduction

Polypropylene (iPP) fibers belong to an established generation of chemical fibers, having the fourth largest volume in production after polyesters, polyamides and acrylics (Jamrich and Hodul 1999, Karacan 1999). Due to the low density, high crystallinity, high stiffness and excellent chemical and bacterial resistance, isotactic PP is widely used in many industrial applications. Only isotactic polypropylene is useful for fiber applications. iPP fibers are manufactured using conventional melt spinning (Gregor-Svetec 2009). Subsequent multistage drawing imparts tensile strength and enhances mechanical properties required for industrial applications. However, there is still a need to improve the mechanical properties of iPP fibers that leads to an additional improvement of products quality (Barczewski *et al.* 2013). One of the most common modification methods is a heterogeneous nucleation which causes changes in a polymer structure but requires the addition of nucleating agents (Sterzyński 2000, Jakubowska *et al.* 2008, Gahleitner *et al.* 2011, Varga 2002, Di Lorenzo 1999). These are additives which provide additional nuclei that accelerate crystallization process and promote nucleation for crystal growth (Karacan 1999). As a result, a larger amount of smaller spherulites is generated. It has been reported in the technical literature that also orotic acid (OA) can be used as nucleation agent in order to induce improved crystallization of biodegradable and biocompatible polymers (Jacquel *et al.* 2009, Jacquel *et al.*

*Corresponding author, Ph.D., E-mail: vogel@ipfdd.de

2010, Qiu 2011). Orotic acid is a heterocyclic compound and an acid; it is also known as pyrimidinecarboxylic acid. 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.* used OA as nucleation agent for polyhydroxybutyrate and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) copolymers (Jacquel *et al.* 2009, Jacquel *et al.* 2010). They found an outstanding nucleation effect on these polymers. Qiu and Li (2011) 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. This paper reports on an attempt to use the green chemical orotic acid as appropriate nucleation agent for improving mechanical properties of polypropylene fibers.

2. 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.

3. 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 was selected. The melt 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, respectively were measured as a function of the shear frequency. The complex melt viscosities were calculated.

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

Thermal 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 +230°C with a heating rate of 10 K·min⁻¹ under nitrogen flow. The melting (T_m), and crystallization temperatures (T_c), and the melting and crystallization enthalpies were determined.

The spinning conditions were set at
Piston temperature: 230°C

Die geometry: $\varnothing = 0.3 \text{ mm}$, $l/d = 2$

Winder velocity: 250 m/min

Volume flow rate: $0.775 \text{ cm}^3/\text{min}$.

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

4. Results and discussion

4.1 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 . Fig. 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 a filler. But the increase of the viscosity is relative low, 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 to the temperature of 140°C . Oscillatory shear

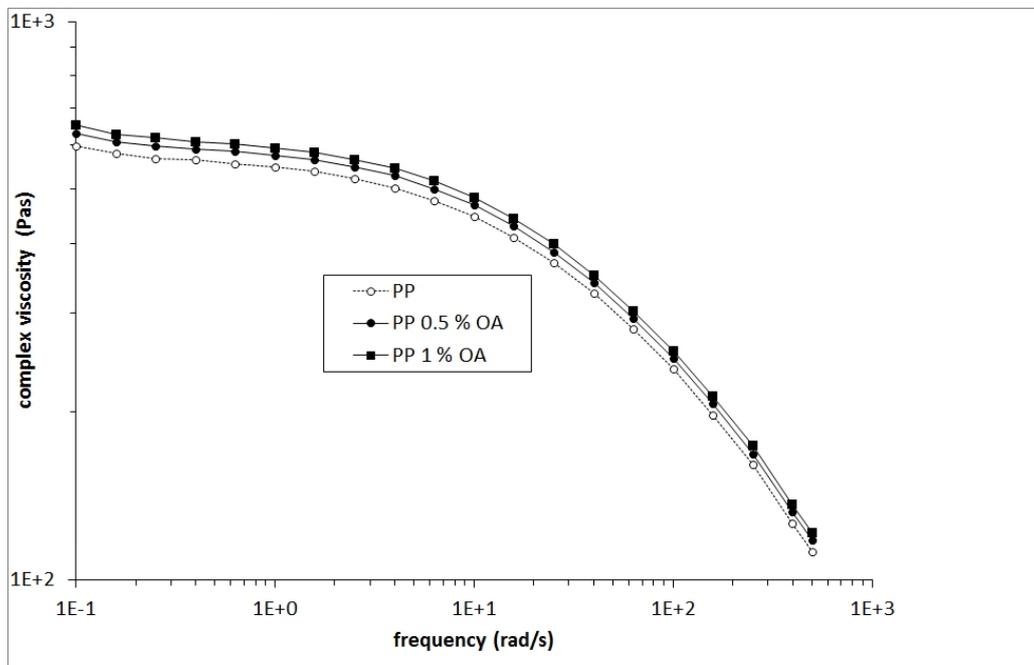


Fig. 1 The complex melt viscosities at 210°C

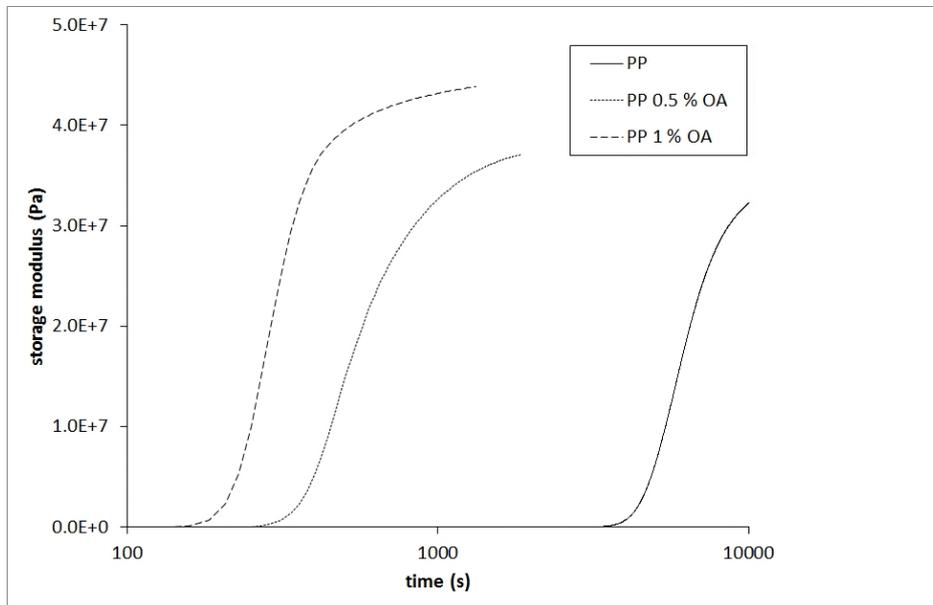


Fig. 2 The storage modulus during isothermal crystallization at 140°C

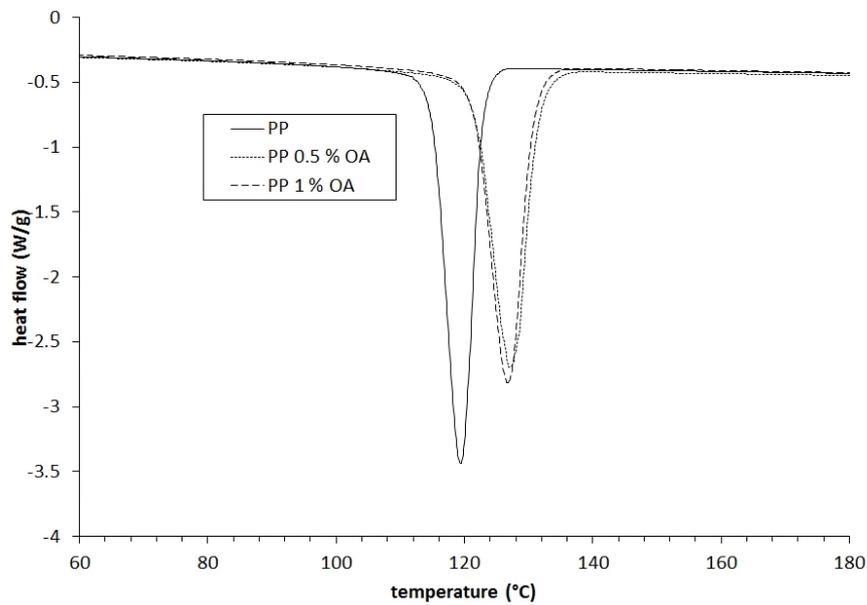


Fig. 3 Cooling scans of the granulates of pristine PP and PP containing orotic acid

with a frequency of 1 rad/s was applied 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 Fig. 2.

It can be seen that the samples containing 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.

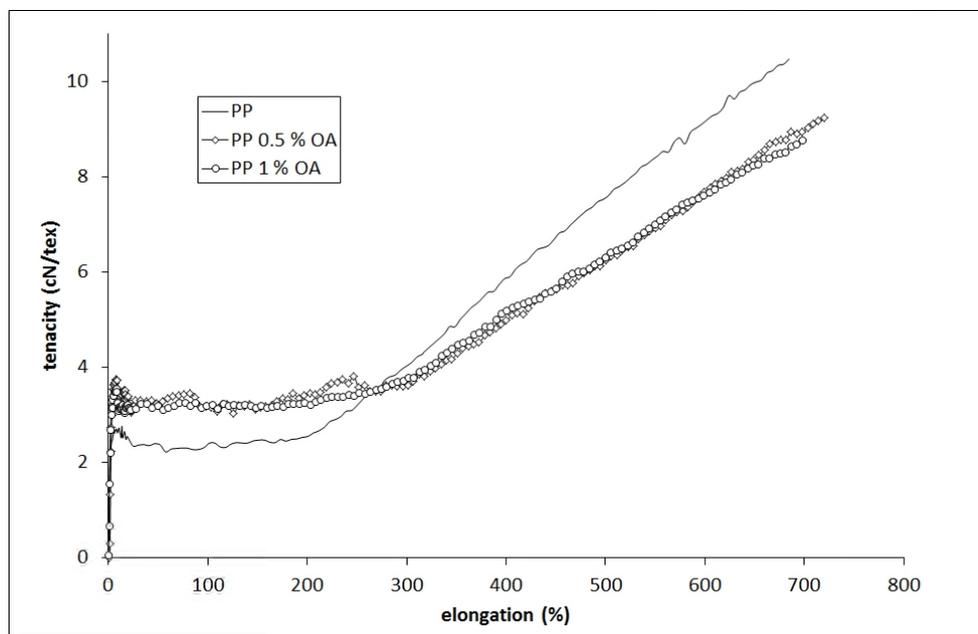


Fig. 4 First heating scans of the melt-spun fibers

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

Sample	$\Sigma\Delta H_M$ (J/g)	ΔH_{SC} (J/g)	$\Sigma(\Sigma\Delta H_M + \Delta H_{SC})$ (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

4.2 Thermal analysis

Cooling scans are carried out for granulates of pristine PP and PP containing OA in order to demonstrate the nucleation effect. The results are plotted in Fig. 3. It can be seen that the addition of OA shifts the initiation of crystallization towards higher temperatures.

Fig. 4 depicts the 1. heating scans of the melt-spun fibers obtained from the thermal analysis using 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. The quantitative data of the first heating are compiled in Table 1. The values $\Sigma\Delta H_M$ represent the melt enthalpies and ΔH_{SC} the enthalpy of the secondary crystallization. The values $\Sigma(\Sigma\Delta H_M + \Delta H_{SC})$ represent the crystallinity at room temperature for each sample. A distinct increase of crystallinity was realized by adding 0.5 wt% OA. The addition of 1 wt% 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.

Table 2 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

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.

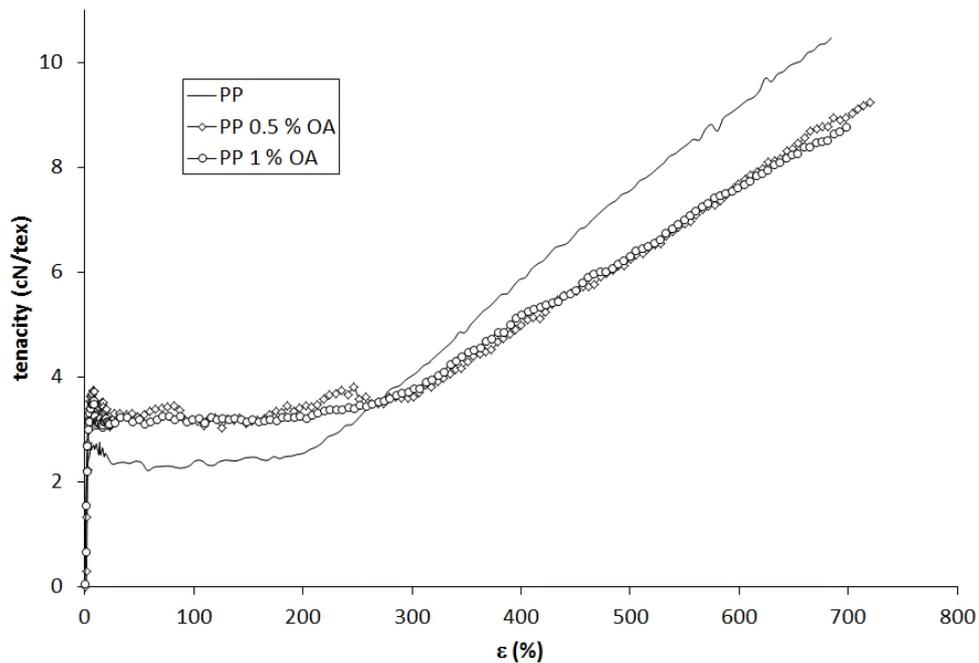


Fig. 5 Specific stress vs. elongation of the melt-spun fibers

4.3 Mechanical testing of the fibers

The melt spinning was realized without any difficulties for all formulations. The results of the tensile tests of the melt-spun fibers are shown in Table 2 and Fig. 5.

The values in Fig. 5 represent the average from ten single tests. Maximum mechanical properties were found for the formulations containing OA. Both the Young modulus at 1 % elongation E_t and the yield stress R_{YS} are significantly higher than values of the reference sample PP.

5. Conclusions

Orotic acid as new nucleating agent for improving mechanical properties of polypropylene fibers was tested. The rheological measurements have shown that the addition of orotic acid causes only small effects on the flow behavior of the melts. The measurements of the isothermal crystallization during oscillatory shear and the cooling scans using thermal analysis have presented that the samples containing orotic acid show an earlier begin of the crystallization than the reference sample PP. The processing properties of the used formulations were not deteriorated by the orotic acid during the melt spinning process. Maximum mechanical properties of the melt-spun fibers were found for the formulation containing 0.5 wt% orotic acid. Both the Young modulus at 1 % elongation and the yield stress are significantly higher than the values of the reference sample. The thermal analysis has shown that the addition of 0.5 wt% orotic acid yields to a distinct higher melt enthalpy at room temperature.

From the results of this study, it can be concluded that the nontoxic orotic acid can be used as suitable nucleating agent for improving mechanical properties of polypropylene fibers.

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