Structure and properties of nucleated polypropylene fibres

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Abstract. This work is focused on the evaluation of the structure and properties of the nucleated polypropylene (PP) fibres prepared by melt spinning technique at lower take-up velocities as pre-oriented fibres (POY) containing 0.3–1.5 wt. % of additives - nucleating agents like 1,3:2,4-dibenzylidene sorbitol (DBS), quinacridone (QA) and calcium carbonate (CC). The thermal properties of nucleated PP fibres were determined by using differential scanning calorimetry (DSC). Used additives promote nucleation activity, DBS and QA better than CC, as they increased the crystallization temperature to higher extent than CC. Effect of CC seems to be negligible, due to very little impact on melting point and crystallization temperature. Morphological characteristic of the PP fibres were observed by means of scanning electron microscopy. The morphology of nucleated PP is different significantly from that of reference non-nucleated PP fibre. The measured values of the above mentioned properties were compared with parameters of non-nucleated PP fibre prepared under same technological conditions.

1. Introduction

Polypropylene (PP) is a versatile polymer with a wide range of applications. Commercial quantities of isotactic polypropylene began to be available in 1957 and although it was not primarily used as a raw material for fibre production [1], PP fibres are one of the most important applications of PP [2]. PP fibre production and use currently accounts for around 6 % of worldwide fibre production, which is 4.3 million tonnes per year [3]. Thanks to low production costs, ease of processing and excellent properties, PP fibres find a wide range of applications in different sectors [1]. Since polypropylene is a semi-crystalline polymer, its properties depend on its crystalline characteristics. These can be further improved and modified according to the end use of the product. Increased production of synthetic fibres also requires simplification of processing technology. This can also be achieved by adding additives to the polypropylene prior to spinning.

Additives affect both, the processability and the resulting properties. Therefore, the production of fibres with the desired properties requires careful selection not only of the processing parameters (e.g. take-up speed, length of the spinning line, cooling conditions, extrusion temperature, etc.), but also the additives. Changing any of them can have a huge impact on the fibre structure and thus on their resulting properties [4].

The most common procedure for modifying of PP fibres is to add inorganic or organic additives, which are added to the polymer during fibre production [5]. These chemical compounds are generally divided into two groups: physical property modifiers and additives to protect against aging and degradation. Often the added component has more than one function, e.g. they can act as heterogeneous nucleating agents [6]. Additives added to the PP melt during fibre formation affect the fibre structure.
The interactions between additives and PP melt are based on two different mechanisms. The first mechanism – for additives that lack PP nucleating ability – is based on a change in fibre structure resulting from a change in melt viscosity caused by the addition of additives. A second mechanism occurs with additives that exhibit the ability to nucleate crystallization of PP. The effect of these substances is reflected in the fibre structure at low spinning speeds. Nucleation is the process by which a new crystalline phase is initiated at sites called nuclei. Heterogeneous nucleation is characterized by variable rate and relatively low supercooling due to the presence of foreign bodies in the polymer melt, which increase the crystallization rate and act as heterogeneous nuclei [7]. These additives are called nucleating agents (NA) and allow the polymer to crystallize at a higher temperature, create a larger number of smaller spherulites and improve some properties, crystal size and crystal structure. This in turn, will induce a higher crystallization temperature, which eventually will result in shorter moulding cycles and consequently, in the reduction of manufacturing costs [8]. The nucleation capacity of NA in the polymer is a function of various factors: free surface energy, crystalline surface morphology, size of nucleation particles and degree of agglomeration of these particles in the polymer melt. Their melting point should be higher than the melting point of the polymer and should have a good dispersion in the polymer [6].

The nucleating ability of additives is of great importance in the proper choice of formation parameters of PP fibres. This study presents the nucleating efficiency of three different nucleating agents. 1,3:2,4-Dibenzylidene sorbitol (DBS) is a commercially available nucleating and clarifying agent offered under various trade names, such as SW-ZC-3988, Millad 3988, OMNISTAB® 3940 or Argunuc® [8]. Calcium carbonate (CC) is used as a filler for thermoplastics and as rheology modifier, which also impacts the number and size of spherulites presented in final product [9, 10]. Quinacridone (QA) is primarily used as pigment, but it is also known as very good nucleating agent for polypropylene. It was observed that after crystallization of PP in the presence of QA a high amount of β-modification was achieved. Pigments in PP fibres as nucleating agents provide a foreign surface and reduce the free energy of formation of a new polymeric nucleus [11–13].

In this paper, the impact of these various nucleating agents on the thermal properties and surface morphology of the pre-oriented (POY) polypropylene fibres is presented.

The nucleating efficiency was evaluated during the non-isothermal crystallization of isotactic polypropylene.

2. Experimental part

2.1. Materials used
Isotactic polypropylene (Tatren HT 2511) with melt flow index 25 g/10 min in pellets form was produced by Slovnaft a.s., Bratislava, Slovak Republic. Polypropylene (Moplen HF 501N) with melt flow index 10 g/10 min in powder form was obtained from Lyondellbasell, Tarragona, Spain. Low density polyethylene homopolymer wax (Honeywell A-C® 6A) in a powder form used as dispersant was produced by Honeywell, Morris Plains, New Jersey, United States. 1,3:2,4-Dibenzylidene sorbitol was a product of Argus Additive Plastics GmbH, Büren, Germany. Quinacridone (Pigment Violet 19) in powder form was supplied by Clariant, Basel, Switzerland. CaCO₃ was produced by Imerys Minerals, Cornwall, United Kingdom; particle size was ~ 1.3 μm and specific surface area 4.8 g m⁻².

Spinning oil (Stantex S 6898) from Pulcra Chemicals, Gerestried, Germany.

2.2. Fibres production
The series of POY PP fibres with different content of nucleating agents: DBS (0.3 and 0.7 wt. %), QA (0.5 and 1.5 wt. %), CC (0.3 and 0.5 wt. %) and a sample of non-nucleated pure PP fibre were prepared via the melt spinning technique through two steps as intermediate products for further drawing and texturing operations (Chemosvit, Fibrochem a. s., Svit, Slovakia). First, PP masterbatch of QA pigment and CC were prepared using 78 wt. % of PP (Moplen HF 501N) as carrier, 12 % of polyethylene wax-
based dispergator (Honeywell A-C® 6A) and 10 wt. % of agent CC or QA. DBS was already supplied as a polypropylene based masterbatch. The mixtures were then homogenized with subsequent pelletization using a ZSK-25 twin extruder with \( L/d = 44 \) and peletizer (Coperion GmbH, Stuttgart, Germany). In the next step, PP granulate (Tatren HT 2511) were mixed with such amount of masterbatch to achieve desired concentration of NA in fibres and melt compounded using a laboratory scale twin screw extruder and pelletizer (Research Institute for Man-Made Fibres, a.s., Svit, Slovakia). The resulting mixtures were spun using a laboratory scale spinning line with single spinneret with 50 orifices with diameter 0.35 mm (Research Institute for Man-Made Fibers, a.s., Svit, Slovakia). The speed of the spinning line metering pump was calibrated using pure PP to achieve final fineness of 140 dtex. Parameters of the above technological process were as follows: spinneret temperature 260 °C; take-up speed 1 000 m min\(^{-1}\); drawing speed 1 040 m min\(^{-1}\); metering pump speed 7.80 rpm; cooling air temperature 18 °C; cooling air velocity 0.4 m s\(^{-1}\).

2.3. Methods used

The DSC measurements were carried out using a TGA/DSC 2 HT/1100 STARe System (Mettler Toledo, Schwerzenbach, Switzerland). The test POY PP fibre samples were prepared by cutting to very small stripes of approximately 20 ± 2 mg weight and pressed into aluminum crucibles of volume 70 μl. Subsequently, they were heated from 50 to 250 °C at a heating rate of 10 °C min\(^{-1}\) in nitrogen atmosphere under the flow rate of 20 ml min\(^{-1}\). Thus, a melting endotherm of sample with melting temperature \( T_m \) and melting enthalpy \( \Delta H_m \) were obtained. Then the sample was held at 250 °C for 5 min to remove the thermal history of the fibre preparation. The sample was then cooled to temperature 50 °C at a cooling rate of 10 °C min\(^{-1}\) and the crystallization exotherm with the crystallization temperature \( T_c \) and crystallization enthalpy \( \Delta H_c \) were obtained.

The melting enthalpy \( \Delta H_m \) was also used for the calculation of degree of crystallinity \( X_c \) (% of the samples according following equation [14][14]:

\[
X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100
\]

where \( \Delta H_m^0 = 198.11 \) J g\(^{-1}\) is the extrapolated value of enthalpy corresponding to 100% crystalline PP [14].

Subsequently, two samples – reference pure POY PP and PP/QA/1.5 were exposed to a second heating under the same conditions as the first one. Same parameters were obtained, but different values, telling us only about chemical nature of fibres and impact of pigment on structural characteristic of PP, compared to the first heating, which is the sum of the thermal history of the fibre due to the processing and chemical nature of the fibre.

The fibres surface morphology and dispergation of NA in fibres volume were investigated using termo emission scanning electron microscope Vega 3 TESCAN with EDX analyser x-act (Oxford Instruments). Samples were observed in the secondary electron (SE) mode to assess surface micromorphology and the backscattered electron (BSE) mode to assess material contrast. For evaluation of fibres surface was chosen magnification in the range from 2500 to 5000×. The samples were subjected to ultrasonic cleaning in an isopropyl alcohol environment prior to analysis and thus free of surface loose particles, moisture and traces of fats. Then the samples were fixed on an aluminum stub holder with a carbon conductive double-sided adhesive tape. A conductive surface of fibres was created by device the Quorum Sputter Coater. A surface conductive layer consisting of Au and Pd chemical elements was formed on the samples thus prepared.

3. Results and discussion

Parameters obtained from first DSC measurement are presented in table 1. Additionally, figure 1 shows DSC melting curves of pure POY polypropylene (pure PP) fibre, POY PP fibres containing calcium carbonate (PP/CC), quinacridone pigment (PP/QA) and 1,3,2,4-Dibenzylidene sorbitol (PP/DBS). Also figure 2 present DSC crystallization curves of these samples.
Table 1. Parameters of Melting and Crystallizations of PP fibre samples containing different content of NA.

| Sample/Content of NA (wt. %) | $T_{onset}$ ($^\circ$C) | $T_m$ ($^\circ$C) | $\Delta H_m$ (J g$^{-1}$) | $T_{onset}$ ($^\circ$C) | $T_c$ ($^\circ$C) | $\Delta H_c$ (J g$^{-1}$) | $\chi_c$ (%) |
|-----------------------------|------------------------|-------------------|--------------------------|------------------------|-------------------|--------------------------|--------------|
| PP/DBS/0.3                  | 153.32                 | 167.26            | 63.77                    | 120.05                 | 116.18            | 76.87                    | 32.19        |
| PP/DBS/0.7                  | 153.78                 | 167.61            | 66.02                    | 132.13                 | 127.02            | 79.38                    | 33.32        |
| PP/QA/0.5                   | 149.64                 | 168.26            | 71.65                    | 128.11                 | 117.68            | 81.70                    | 36.17        |
| PP/QA/1.5                   | 150.12                 | 167.62            | 68.00                    | 130.25                 | 127.00            | 82.54                    | 34.32        |
| PP/CC/0.5                   | 151.09                 | 167.19            | 65.29                    | 120.61                 | 116.48            | 81.70                    | 32.96        |
| PP/CC/1.5                   | 150.28                 | 167.16            | 72.83                    | 120.76                 | 116.85            | 81.01                    | 36.76        |
| PP/0                        | 152.03                 | 170.48            | 80.27                    | 120.43                 | 116.78            | 80.21                    | 40.52        |

Melting point of PP is strongly depended on the tacticity and thermal history [15]. From figure 1 we can see that every sample shows a broad endotherm, which can arise from melting crystals of different polymorphic form (in iPP – α$_{1,2}$, β, γ) [15, 16]. However, β-form has a lower melting temperature and γ-form is made only under special conditions [4, 17], broad endotherms correspond to the melting of α-crystals of different size and perfection. The different content of nucleating agents in POY PP fibres had a minimal effect on $T_m$.

Figure 1. DSC melting curves of nucleated and pure POY PP fibres.

Figure 2. DSC crystallization curves of nucleated and pure POY PP fibres.

Melting curves of POY PP/CC and PP/QA are very similar, they have maximum of peaks – melting temperature – in range 167–169 °C, which is less than that for pure POY PP – 170.48 °C. It is known [18] that the structure of PP in POY PP/NA fibres at the selected drawing speed (1040 m min$^{-1}$) may not be primarily influenced by the content of nucleating agents but also by the orientation of macromolecular chains due to processing. So, the same production parameters of given samples caused a similar fibre structure. Samples of POY PP/DBS have quite different melting curves, although also
broad, but maximum have on the other side than previous ones and around 167 °C, which is also less than in pure PP. We can assume that crystals in these POY PP/NA samples have more defects.

Considering crystallization in all cases a single exotherm corresponding to the crystallization process was observed. An exothermic peak occurs at 116.78 °C for pure PP fibre. Maximum of exothermic peak for PP/CC fibres and PP/DBS/0.3 sample are similar ~ 116 °C. So, we can conclude that CC and DBS (0.3 wt. %) doesn’t show any nucleating effect for crystallization of PP. But for the higher content of DBS the increment in the crystallization temperature occur, comparing to the pure POY PP and PP/DBS/0.3 wt. % the increment is about 10 °C. For samples PP/QA the crystallization peaks occur at higher temperatures of 125.7 and 127 °C. In the case of the quinacridone pigment the increment in T_c compared with that of the pure polypropylene is about 10 °C. For PP/QA the main part of the crystallization proceeds in the temperature above the T_c of pure PP. The addition of pigment causes starting crystallization at lower supercooling and proceeds in the range in which the pure PP still does not crystallize. In the temperature in which the crystallization of the pure POY PP starts the crystallization of PP-containing pigments is practically finished. The same phenomenon is observed in the case of PP/DBS samples. However, the DBS concentration must be sufficiently high. Since it does not show nucleating effect at concentration of 0.3 % wt., at concentration of 0.7 % wt. the shift T_c to a higher value is apparent and the increment is 10 °C. According to the PP/CC crystallization curves, nucleating activity of this NA seems to be negligible. The T_c at both concentrations is similar to pure PP.

Figure 3 presents first and second heating scan of PP/QA/1.5 and pure PP. Parameters from this measurement are presented in table 2. The first heating run eliminates any internal stresses or thermal history. This allows the effect of QA on structure of PP to be observed in the second heating run. Endotherms from first heating are very similar for both samples, exhibiting broad peaks, influenced by processing parameters. Samples contain molecules of different size and perfections. In contrast, the second heating scans exhibit narrow peaks, in the PP/QA sample sharper than that in pure PP. The crystals in these samples are more uniform.

![Figure 3. 1st and 2nd heating scan of pure POY PP and PP/QA/1.5 fibres.](image)

Degree of crystallinity are higher when calculated from second heating, it is caused by slower cooling rate than that during processing. Samples had enough time to create more crystals and more uniform crystals.

Table 2. Parameters of 1st and 2nd Melting of POY PP/QA/1.5 and PP samples.

| Sample/Content of NA (wt. %) | 1st Melting | 2nd Melting |
|------------------------------|-------------|-------------|
|                              | T_{onset} (°C) | T_m (°C) | ΔH_m (J g⁻¹) | X_c (%) | T_{onset} (°C) | T_m (°C) | ΔH_m (J g⁻¹) | X_c (%) |
| PP/QA/1.5                    | 151.05      | 170.24     | 71.83        | 36.26    | 151.05      | 166.34     | 86.21        | 43.52    |
| PP/0                         | 149.93      | 168.44     | 76.21        | 38.47    | 153.01      | 163.72     | 79.67        | 40.21    |
Figures 4–10 represent images from SEM microscopy of tested PP fibres on the left side of each image from SE mode and on the right side from BSE mode. The fibre surface of pure POY PP samples is smooth, without any breaking or cracks. Samples with QA and DBS have similar surface, with only very small structural inequalities that can be caused by the production process.

**Figure 4.** SEM images of pure PP fibres (magnification 2500×).

**Figure 5.** SEM images of PP/QA 0.5 % wt. (magnification 5000×).

**Figure 6.** SEM images of PP/QA 1.5 % wt. (magnification 5000×).

**Figure 7.** SEM images of PP/DBS 0.3 % wt. (magnification 5000×).

**Figure 8.** SEM images of PP/DBS 0.7 % wt. (magnification 5000×).

**Figure 9.** SEM images of PP/CC 1.5 % wt. (magnification 2500×).

**Figure 10.** SEM images of PP/CC 1.5 % wt. (magnification 5000×).
Due to the CaCO₃ in the PP/CC fibres, it is obvious how is the additive dispersed in the fibre and how agglomerates it forms. Figures 9 and 10 present images of fibre containing 1.5 % of CC, which create small agglomerates gently protruding from the fibre, forming a bumpy surface, which may be reflected in the surface structure of the fabric made from these fibres.

4. Conclusion
Nucleated POY polypropylene fibres with three different nucleated agents were prepared and studied under dynamic thermal conditions. Their morphological characteristics were observed too. The impact of different content of these nucleated agents was evaluated and compared to pure POY PP fibre properties. Based on the obtained results only DBS and QA promote nucleating activity toward crystallization of PP as they increased the crystallization temperature about 10 °C, so the crystallization will run faster. However, DBS needs higher concentration. Effect of CC seems to be negligible, due to very little impact on melting point and crystallization temperature. Degree of crystallinity was found to be in the range of 32–41 %. In the planned research, the wide X-ray scattering (WAXS) method will be used to provide more information about polymorphic structure of PP fibres.

5. References
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