Thermal and Mechanical Characterization of Drawn Polypropylene Fibres

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Abstract. The main objective of this work was to investigate the effect of different cellulose (CEL) content and the draw ratio on the thermal and mechanical properties of drawn polypropylene (PP) fibres. The modification of PP fibres during their production can help to prepare PP fibres with improved properties, guarantees new opportunities for the expansion of an assortment of PP fibres in the clothing and domestic textile industries. The modified PP/CEL fibres were prepared from PP pellets and PP/cellulose masterbatch via the melt spinning technique at 260 °C followed by drawing for various draw ratios in the company Chemosvit, Fibrochem a.s. (Svit, Slovakia). Differential scanning calorimetry (DSC) was used to evaluate the thermal properties of PP fibres. The mechanical properties (tenacity and elongation at break and modulus of elasticity) and low cycle loading of modified PP fibres were also studied. The obtained experimental results of drawn PP/CEL fibres were compared with neat PP fibre prepared under the same technological conditions. Cellulose had a minimal effect on the melting temperatures of fibres and increased of the PP crystallization temperatures in comparison with the neat drawn PP fibre. The limited decrease of mechanical properties of prepared fibres were observed, but the decreases do not influence on the fibres commercial use.

1. Introduction

Polypropylene (PP) is an important commercial polymer with wide range of applications in packaging, furniture products, consumer goods, automotive products, industrial products, textile fibres, filaments and fabrics [1]. Its wide use exhibits stems from an attractive combination of low cost, low weight, easy processability, as well as desirable end-use properties [2]. The fibres of polypropylene were introduced to the textile market in the 1970s [3]. PP fibres belong to the newest generation of large-scale, manufactured chemical fibres, having the fourth largest volume in production after polyesters, polyamides and acrylics [4, 5]. PP is one of the most successful commodity fibres, reaching a world production capacity of four million tons a year [6]. However, due to the dominance of Asian production of standard man-made fibres in the world, a necessity for the sophistication of European fibres and textile arises [7].

One of the most perspective way to ensure sophisticated properties of textiles is modification of their mass by additives. Additives such as CaCO₃, TiO₂ [8, 9] or pigments such as quinacridone [10] are commonly used in large quantities in the processing of PP for various applications. One of the natural additives applied in polymer composites is cellulose. Cellulose is the most abundant biodegradable polymer derived from renewable resources, which makes it very attractive from an economic point of view. It is generally synthesized by plants, but it is also produced by some bacteria [11]. Combination of polypropylene and cellulose can offer new utility properties of final textile product. In this paper, the investigation of thermal and mechanical properties of the PP fibres modified with cellulose is presented.
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 (LDPE) homopolymer wax (Honeywell A-C® 6A) in a powder form used as dispersant was produced by Honeywell, Morris Plains, NJ, United States. Ethylene-acrylic acid zinc ionomer (Aclyn® 295A) in a powder form used as dispersant was produced by Honeywell, Morris Plains, NJ, United States. Ultra-fine cellulose in powder form with particles size ~ 8 µm as modifier was supplied by J.RETTENMAIER & SÖHNE GMBH + CO.KG, Rosenberg, Germany. Spinning oil (Stantex S 6898) was produced by Pulcra Chemicals, Gerestried, Germany.

2.2. Polypropylene/cellulose fibre preparation

The series of drawn PP fibres with various content of cellulose (0.15, 0.45, 1.25, wt. %) as well as a sample of reference PP fibre were prepared from mixture of PP granulated polymer and PP masterbatch of cellulose using the classical discontinuous process of melt spinning and drawing [12] in Chemosvit, Fibrochem a. s., Svit, Slovakia through two steps:

1) Preparation of PP masterbatch contained 15 wt. % of cellulose: PP masterbatch of cellulose were prepared using 15 wt. % of ethylene wax-based dispersant (Honeywell A-C® 6A), 0.3 wt. % of ethylene-acrylic acid zinc ionomer (Aclyn® 295A), 69.7 wt. % of PP (Moplen HF 501N) and 15 wt. % of ultra-fine cellulose. The mixtures were then homogenized with subsequent pelletization using a ZSK-25 twin screw extruder with L/D ratio 44 (Coperion GmbH, Stuttgart, Germany) and pelletizer Scheer (C.F. Scheer & Cie GmbH & Co. KG, Stuttgart, Germany).

2) Preparation of PP/CEL fibres: In the next step, resulting pellets of PP/CEL masterbatches were mechanically mixed with PP granulate (Tatren HT 2511) 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 discontinuous laboratory-scale spinning line with single spinneret with 50 orifices with diameter 0.35 mm (Research Institute for Man-Made Fibres, a.s., Svit, Slovakia). The speed of the spinning line metering pump was calibrated using pure PP to achieve final fineness of 140 dtex. The winding speed, spinning temperature, temperature and flow of cooling air, and flow of spin finish were kept constant and the melt pressure in the spinneret was monitored. The spinning temperature was 260 °C, metering pump speed 7.80 rpm, take-up speed 1000 m/min and drawing speed was 1040 m/min. The resultant pre-oriented polypropylene/cellulose fibres were subsequently drawn using drawing equipment at drawing temperature 125 °C and final drawing speed 698 m/min. The draw ratios were $\lambda = 1.4$ and 1.7. The linear density of the drawn fibres was 84 dtex.

2.3. Methods used

Differential scanning calorimetric (DSC) measurement

The non-isothermal crystallization and melting behaviour of drawn PP fibres under investigation were studied using a TGA/DSC 2 HT/1100 STARE System (Mettler Toledo, Schwerzenbach, Switzerland). The test fibre samples were prepared by cutting to very small stripes of approximately 20±2 mg weight and pressed into aluminium crucibles. Subsequently, they were heated from 50 to 250 °C at a heating rate of 10 °C/min in nitrogen atmosphere under flow rate 20 ml/min. The melting endotherms of samples with melting temperature ($T_m$) and melting enthalpy ($\Delta H_m$) were obtained. The samples were then held at 250 °C for 5 min to remove the thermal history of the fibre preparation. After that, the samples were cooled to temperature 50 °C at a cooling rate of 10 °C/min and the crystallization exotherms 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 ($X_c$) (%) using the following equation:

$$ X_c = \frac{\Delta H_m^*}{\Delta H_m} \times 100 \quad (1) $$
where $\Delta H_m^\ast = 198.11 \text{ J/g}$ is the extrapolated value of enthalpy corresponding to 100 % crystalline PP [13].

**Mechanical properties of PP/CEL fibres**

The mechanical properties (tenacity and elongation at break and modulus of elasticity) of the studied PP/CEL fibres were determined according to standard ISO 2062:2009 [14] and measured using Autograph AG-X plus 5kN Shimadzu Japanese universal testing device with an initial gauge length between clamps of a test machine of 50 mm, pre-load speed of 10 mm/min, pre-load force of 0.01 N and loading speed of 250 mm/min at temperature of $20 \pm 2 ^\circ\text{C}$ and relative humidity of $65 \pm 2 \%$. The average of at least 9 individual static tensile measurements was used for each type of PP/CEL fibre.

**Low cycle loading tests of textile fibres**

The method for low-cycle loading tests of selected textile fibre on universal testing device was designed with an initial gauge length of 50 mm, pre-load speed of 10 mm/min, pre-load force of 0.01 N and loading speed of 250 mm/min at temperature of $20 \pm 2 ^\circ\text{C}$ and relative humidity of $65 \pm 2 \%$. The five cycles are used. Every cycle is defined as loading to 30 % of elongation between clamps of test machine and unloading to 15 % of elongation between clamps of testing device. The fifth cycles can be considered as stable cycle (the stress-elongation characteristics is stabilized) based on standard DIN 53835-13 [15]. After the fifth cycle, the loading was continued to failure of the test specimens. The designed method is in Figure 1.

**Figure 1.** Design of methods for PP/CEL fibre in Trapezium X software.

### 3 Results and Discussion

Drawn PP/CEL fibres with various content of cellulose (0.15, 0.45, 1.25, wt. %) as well as a sample of reference – neat PP fibre were prepared. The influence of cellulose and draw ratio on the thermal and mechanical properties of PP fibres was investigated.

#### 3.1. Thermal properties of drawn PP/CEL fibres

DSC was used for non-isothermal measurement of thermal properties of drawn PP/CEL fibres and neat PP fibres.

The results of thermal properties of studied drawn PP fibres such as melting temperature ($T_m$) and crystallization temperature ($T_c$), enthalpy melting ($\Delta H_m$) and enthalpy crystallization ($\Delta H_c$) are presented in Figures 1, 2 and Table 1. The DSC measurements were preceded by heating and cooling run. The results obtained from the heating reflects the thermal history of fibre preparation and indicates PP crystallization during melt spinning and drawing of the PP fibres in the presence of cellulose.

The results of thermal properties (melting temperature and crystallinity) of PP/CEL fibres show that the various content of CEL in the PP/CEL fibres only moderately affected these properties.

The crystallinity of neat PP fibre with $\lambda = 1.4$ (1.7) was 52.45 (53.01) %. The increasing content of CEL in PP fibres resulted in the reduction of crystallinity.
Melting temperature increase with higher draw ratio of PP fibres. From Figures 2a and 3a we can see that every sample shows a broad endotherm, corresponds with melting temperatures of crystal modifications, which were created under normal strain at the spinning and drawing processes of drawn PP fibres [8]. Broad melting peaks may be associated with melting crystals of different size and perfection.

The melting temperatures \( T_m = 160.20 - 167.19 \) °C) obtained at heating of fibres correspond with melting temperature of \( \alpha \)-modification of PP.

Figures 2b and 3b show the DSC crystallization curves of drawn neat PP and PP containing the various content of CEL. However, as seen on DSC crystallization curves, the exothermic peaks of PP/CEL fibres are shifted to higher temperature in contrast of reference PP fibres.

**Figure 2.** DSC melting curves (a) and crystallization curves (b) of drawn PP/CEL fibres with \( \lambda = 1.4 \).

**Figure 3.** DSC melting curves (a) and crystallization curves (b) of drawn PP/CEL fibres with \( \lambda = 1.7 \).
Table 1. Thermal properties of drawn PP/CEL fibres (melting (Tm) and crystallization (Tc) temperatures, melting (ΔHm) and crystallization (ΔHc) enthalpies and crystallinity (Xc)).

| No. | Content of CEL (wt. %) | λ | Melting | Crystallization |
|-----|------------------------|---|---------|----------------|
|     |                        |   | Tm (°C) | ΔHm (J/g) | Tc (°C) | -ΔHc (J/g) | Xc (%) |
| 1   | 0                      | 1.4 | 163.68  | 103.90    | 115.44  | 95.14     | 52.45  |
| 2   | 0                      | 1.7 | 164.62  | 105.02    | 115.18  | 92.56     | 53.01  |
| 3   | 0.15                   | 1.7 | 164.81  | 94.00     | 115.44  | 92.23     | 50.53  |
| 4   | 0.45                   | 1.4 | 165.69  | 100.10    | 117.66  | 91.35     | 50.53  |
| 5   | 0.45                   | 1.7 | 167.19  | 102.63    | 115.44  | 94.73     | 51.81  |
| 6*  | 0.45+TiO₂°             | 1.4 | 161.26  | 102.28    | 118.20  | 95.21     | 51.63  |
| 7*  | 0.45+TiO₂°             | 1.7 | 160.40  | 97.68     | 117.78  | 90.73     | 49.31  |
| 8   | 1.25                   | 1.4 | 160.20  | 102.28    | 116.32  | 96.31     | 51.63  |
| 9   | 1.25                   | 1.7 | 165.30  | 104.92    | 118.43  | 97.59     | 52.96  |

*70 dtex, °0.23 wt. %, λ - draw ratio

3.2. Mechanical properties of drawn PP/CEL fibres

The basic mechanical properties of the PP/CEL fibres, in dependence on cellulose content and draw ratio in drawing process are presented in Table 2. The data show that the mechanical properties of PP/CEL fibres are lower than for neat PP fibres. Cellulose similar as different additives e.g. nCaCO₃, Cloisite 30B [8] decreases tenacity and elongation at break of PP fibres.

Dependences between stress on elongation at break of drawn PP/CEL fibres and reference PP fibres are presented at Figure 4.

Table 2. Mechanical properties of drawn PP/CEL fibres with fineness 84 dtex.

| No. | Content of CEL (wt. %) | λ | Tenacity (cN/dtex) | Ductility (%) | Modulus of elasticity at 5 % elongation (LASE 5) (cN/dtex) |
|-----|------------------------|---|-------------------|---------------|--------------------------------------------------|
| 1   | 0                      | 1.4 | 3.507 ± 0.124     | 132.805 ± 9.647 | 20.380 ± 0.585 |
| 2   | 0                      | 1.7 | 3.568 ± 0.074     | 90.424 ± 9.711  | 22.364 ± 0.413  |
| 3   | 0.15                   | 1.7 | 3.401 ± 0.106     | 89.367 ± 4.888  | 17.648 ± 0.804  |
| 4   | 0.45                   | 1.4 | 2.510 ± 0.073     | 85.513 ± 9.869  | 19.854 ± 0.270  |
| 5   | 0.45                   | 1.7 | 2.971 ± 0.103     | 77.210 ± 8.488  | 19.960 ± 0.827  |
| 6*  | 0.45+TiO₂°             | 1.4 | 2.609 ± 0.074     | 31.138 ± 1.543  | 19.311 ± 0.502  |
| 7*  | 0.45+TiO₂°             | 1.7 | 3.069 ± 0.131     | 30.583 ± 2.535  | 20.924 ± 0.760  |
| 8   | 1.25                   | 1.4 | 2.689 ± 0.083     | 129.575 ± 9.454 | 17.784 ± 0.772  |
| 9   | 1.25                   | 1.7 | 2.804 ± 0.068     | 74.333 ± 7.717  | 19.582 ± 0.886  |

*70 dtex, °0.23 wt. %, λ - draw ratio

The results in the Figures 5–7 give the more information regarding the effect of cellulose content and drawn ratio on the basic mechanical properties (tenacity, ductility – elongation at break and modulus LASE 5) of drawn PP/CEL fibres. The dependences on the Figure 5 show that tenacity of drawn PP/CEL fibres decreases with increased CEL content in the fibre mass. However, PP/CEL fibres with draw ratio 1.7 are characterized by higher values of tenacity compared to PP fibres drawn with draw ratio 1.4. Ductility of PP/CEL fibres with increasing cellulose content as well as the draw ratio decreased except for the sample PP/CEL-8. The values of ductility of fibres 6 and 7 were significantly lower compared to other fibres due to different composition and production conditions.
Figure 4. The dependences between stress on elongation of drawn PP/CEL fibres.

Figure 5. The dependences of tenacity of drawn PP/CEL fibres with different draw ratios on the content of CEL.

The modulus LASE 5 of PP/CEL fibres was found slight decrease in dependence of cellulose content and increase in dependence of draw ratio (Figure 7). Another part of the research work was devoted to low-cyclic tensile tests extended by PP/CEL-9 sample. The load control was performed by percentage elongation. The methodology of the low-cyclic test consists of 5 cycles. It was verified that the fifth cycle can be considered as stable cycle for selected materials, as the difference between the fifth and the
fourth cycles was less than 1% of the nominal load of the fourth cycle. The dependence of the force on the elongation for the sample PP/CEL-9 is shown in Figure 8. The individual cycles are color-coded.

**Figure 6.** The dependences of ductility (elongation at break) of drawn PP/CEL fibres with different draw ratios on the content of CEL.

**Figure 7.** The dependences of modulus LASE 5 of drawn PP/CEL fibres with different draw ratios on the content of CEL.
Figure 8. The dependence of force on percental elongation of PP/CEL-9 fibre.

4. Conclusions
This work was focused on the preparation of new types of PP fibres, which due to their properties and ecological production process could be a potential replacement of natural fibres. The main aim of the experimental part was to observe and evaluate the effect of different content of cellulose and draw ratio on the thermal and mechanical properties of PP/CEL fibres and compared to neat PP fibres. Based on the obtained data, the results can be formulated into the following conclusions:

- Neat PP fibres and series of drawn PP/CEL fibres with different content of cellulose (0.15, 0.45, 1.25, wt. %) and fineness of 84 dtex were prepared via the melt spinning technique at 260 °C and drawn to draw ratios 1.4 and 1.7 at drawing temperature 125 °C. The process of spinning and drawing if the PP fibres was without any problems.
- The various content of cellulose in PP fibres had a minimal effect on the melting temperatures of PP/CEL fibres.
- The addition of cellulose to PP fibre influenced the increase of the PP crystallization temperatures in comparison with the neat drawn PP fibre.
- The use of cellulose in the PP fibres produced some decrease of mechanical properties of the prepared drawn PP/CEL fibres in comparison with neat PP fibres. However, these decreases do not exclude the possibility for their practical use.
- In the planned research, the wide X-ray scattering (WAXS) method will be used to provide more information about polymorphic structure of drawn PP/CEL fibres.

Acknowledgements
This research work was supported by the Cultural and Educational Grant Agency of the Slovak Republic (KEGA), project No. KEGA 002TnUAD-4/2019 “The influence of temperature and other parameters on the tensile properties of polymer composites and polymers under the uniaxial and biaxial cyclic loading” and the project Advancement and support of R&D for “Centre for diagnostics and quality testing of materials” in the domains of the RIS3 SK specialization, ITMS2014: 313011W442.
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