Structure and properties of PP/organoclay composite fibres

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Abstract. In this paper, the effect of uniaxial deformation of PP/organoclay composite fibers in spinning and drawing on their supermolecular structure, thermal and mechanical properties is presented. The commercial organoclays Cloisite C15A and Cloisite C30B, both based on montmorillonite (MMT) were used in experimental work as inorganic fillers. The supermolecular structure of fibers was investigated by DSC analysis and X-ray diffraction (WAXS). The DSC measurements were carried out using conventional method (CM) and constant length method (CLM) in which the fibers with constant length during measurement were assured. Intercalation of polypropylene in the interlayer galleries of organoclay was evaluated by SAXS method. Tensile strength and Young’s modulus of composite fibers are discussed in the paper with regard to their thermal properties and supermolecular structure as well as intercalation and exfoliation of (nano)filler in polymer matrix.

1. Introduction
The incorporation of the organoclay into the semicrystalline polymers affects their crystalline properties such as crystallization kinetics, crystal structures and total crystallinity [1, 2]. The layered silicates in the polypropylene (PP) matrix behave as effective heterogeneous nucleating agents. They enhance the crystallization rate [2], and at the same time decrease the spherulite size, perfection of the crystals and shift the cooling crystallization temperature to higher values [3]. Besides, the silicate nanoplatelets affect the shear flow induced crystallization and retardancy of the crystallisation kinetic of matrix at the quiescent crystallization of the PP/montmorillonite (MMT) composites [4]. The preferential orientation of PP lamellae perpendicular to the surface of the organoclay layers was found for PP/talc composite by TEM observation. The lamellar orientation on the clay layers was ascribed to nucleation and crystallization at the surface of the silicate platelets. Moreover, the asymmetric morphology of crystals was observed in PP/organoclay nanocomposites at higher temperature and at shear induced formation of the oriented threadlike crystallites [1].

Simultaneously with the development of highly oriented polymers the suitable methods for investigation of the oriented polymer structure were developed or modified. The special method of DSC analysis of fibers, known as “constrain method” or method of “constant length of fibers” (DSC-CLM), has been described in several papers. This DSC method is particularly suitable for evaluation of oriented structure elements of composite fibers [5].

In our previous papers the effect of organoclay on mechanical properties of PP fibers was studied [6, 7]. The positive effect of organoclay on mechanical properties of fibers was found for very low concentration of solid particles, only. In this case, the effect of nanoparticles as hard segments on
Mechanical properties is negligible. Thus, enhancement of the mechanical properties of composite fibers is affected indirectly by suitable changes in the structure of fibers. Some convenient methods were used for characterization of structure and morphology of PP composite fibers in our experimental work to explain their mechanical properties. The results are presented in this paper.

2. Experimental

2.1. Materials used

Polymers: Commercially available types of PP were used in the experimental work: polypropylene HPF (PP HP) with melt flow index (MFI) 8.0 g/10 min, in powder form and fiber-grade polypropylene TG 920 (PP) with MFI 10.5 g/10 min. Both polypropylenes were produced by Slovnaft a. s., Bratislava, Slovak Republic.

Fillers: Two kinds of organoclays (OC) used in this work were Cloisite 15A (C15A) and Cloisite 30B (C30B), both produced by Southern Clay Product, Inc, Gonzales, TX 78629, USA.

Compatibilisers: Two non-reactive compatibilisers-dispersants were used for the preparation of concentrated dispersion of organoclay in the PP HP. Commercially available Slovacid 44P (S44P) based on the ester of stearic acid and polypropylene glycol, produced by Sasol GmbH, Brunsbuettel, Germany and Tegopren 6875 (TEG) based on poly (alkylsiloxane) produced by Degussa Co., Düsseldorf, Germany.

2.2. Preparation of PP/MWCNT composite fibres

1. The PP HP, organoclay and compatibiliser were mixed in a high rpm mixer for a defined time. Powder mixture was melted and kneaded using twin screw corotating extruder \( \phi \) 28 mm. The temperature of the extruded melt was 229°C. The concentration of organoclay in PP HP was 10.0 wt.%. Content of compatibiliser was 4.0 wt. %.

2. The chips of organoclay concentrate dispersion and PP were mixed and spun using a single screw extruder \( \phi \) 30 mm and a spinneret with 40 orifices. The spinning temperature was 280°C, metering of melt 30 g/min, spinning speed 360 m/min and the fineness of spun fibers (drawn ratio 1:1, \( \lambda_1 \)) was 840 dtex. Fibers were drawn using laboratory drawing machine for draw ratio 1:3 (\( \lambda_3 \)) and for maximum drawn ratio (\( \lambda_{\text{max}} \)) at drawing temperature 120°C.

2.3. Methods used

DSC measurement: The measurements were performed using Perkin Elmer DSC 7 in the temperature range 30-200°C. The standard heating rate was 10°C/min. The measurements were carried out using conventional method (DSC-CM) in which the cut fibers with length 1-2 mm were used, and constant length method (DSC-CLM) in which the constant length of fibers during measurement was assured. The constant length of the fibers was achieved through winding and fixation of fibers on a wire. The melting peak temperature \( T_m \) and melting enthalpy \( \Delta H_m \) were evaluated.

X-ray scattering method: Wide-angle scattering (WAXS) method: The structure of fibers was evaluated by a wide-angle X-ray scattering method. The investigations were carried out using a Seifert X - ray diffractometer. On the basis of the WAXS patterns the parameters characterising the fiber structure were determined. The total crystallinity \( X_c \) and the content of the mesophase \( X_m \) were calculated as a ratio of the area under crystalline or mesophase peaks to the total area [18].

Small-angle scattering (SAXS) method: All SAXS patterns were recorded with an MBraun SWAX camera with the Kratky collimation system equipped with a PSD 50 MBraun linear position sensitive detector.

Mechanical properties: The Instron (3343 model) was used for the measurements of mechanical properties of fibers (according to ISO 2062:1993). They were evaluated from 15 measurements.
3. Results and discussion

3.1. Thermal properties and supermolecular structure of fibers

The DSC-CM method provides simple one-peak thermogram for undrawn fibers and characteristic double-peak thermogram for middle draw ratio of fibers (Figure 1a). The radically different shapes of melting endotherms were observed for PP fibers in dependence on the draw ratio using DSC-CLM method. The endotherm peak is shifted to higher temperature gradually when the draw ratio increases (Figure 1b, 1c). One-peak endotherm becomes wider with the increase of draw ratio.

The melting temperature ($T_m$) for PP fibers and for PP/C15A composite fibers increase proportionally with the draw ratio up to maximum values (Figure 2a). The dependence of melting enthalpy (crystallinity) on organoclay concentration passes through clear maximum at 0.1 wt.% and practically does not change with the presence of compatibiliser-dispersant (Figure 2b).

Generally, DSC-CLM method provides the higher melting enthalpy for PP/organoclay fibers (higher crystallinity) in contrast to DSC-CM method, particularly for lower draw ratio.

Figure 1 DSC-CM (a) and DSC-CLM (b, c) melting thermograms of PP and PP/0.1%C15A composite fibres in dependence on draw ratio

Figure 2 DSC-CLM melting temperature $T_m$ (a) versus draw ratio and melting enthalpy $\Delta H_m$ (b) versus concentration of organoclay in the PP and PP composite fibres
3.2. WAXS and SAXS measurements
The total crystallinity of the oriented PP matrix of fibers consists of the fraction of $\alpha$-form modification $X_\alpha$ and fraction of mesophase $X_m$ (Table 1). On the basis of WAXS measurements the maximum total crystallinity was found for low concentration of organoclays, and at the same time for maximum draw ratio. Results are consistent with these obtained from DSC-CLM method. With higher concentration of C15A organoclay the total crystallinity of the PP matrix gradually decreases mainly due to significant decrease of the mesophase fraction $X_m$. The higher content of $\alpha$-modification was found for drawn fibers and for higher content of C15A organoclay. The sizes of $\alpha$-form crystallites passes through minimum at 0.1% C15A in PP fibers.

Table 1 Results of WAXS measurements of PP/organoclay composite fibres

| Sample           | Draw ratio $\lambda$ | Total crystallinity $x_C$ | Fraction of $\alpha$ form $x_\alpha$ | Fraction of mesophase $x_m$ | Sizes of crystallites of $\alpha$ form $D_{(110)}$, nm | Sizes of mesophase crystallites, nm |
|------------------|----------------------|---------------------------|---------------------------------------|----------------------------|------------------------------------------------------|----------------------------------|
| PP               | 3.0                  | 0.621                     | 0.338                                 | 0.283                      | 6.5                                                  | 3.4                              |
| PP               | 4.5                  | 0.625                     | 0.311                                 | 0.314                      | 5.4                                                  | 3.1                              |
| PP/1.0% C15A     | 1.0                  | 0.620                     | 0.272                                 | 0.348                      | 8.4                                                  | 3.3                              |
| PP/1.0% C15A     | 3.0                  | 0.668                     | 0.407                                 | 0.261                      | 7.1                                                  | 3.4                              |
| PP/0.02% C15A    | 5.0                  | 0.714                     | 0.338                                 | 0.376                      | 6.2                                                  | 2.7                              |
| PP/0.1% C15A     | 5.0                  | 0.688                     | 0.347                                 | 0.341                      | 4.6                                                  | 2.8                              |
| PP/1.0% C15A     | 4.5                  | 0.627                     | 0.311                                 | 0.316                      | 7.0                                                  | 3.1                              |
| PP/3.0% C15A     | 3.0                  | 0.571                     | 0.388                                 | 0.183                      | 11.6                                                 | 3.5                              |
| PP/1.0% C30B     | 3.0                  | 0.616                     | 0.409                                 | 0.207                      | 7.7                                                  | 3.7                              |
| PP/1.0% C30B     | 4.5                  | 0.658                     | 0.389                                 | 0.269                      | 6.3                                                  | 3.1                              |
| PP/1.0% C30B/TEG | 3.0                  | 0.636                     | 0.396                                 | 0.240                      | 6.6                                                  | 3.8                              |
| PP/1.0% C30B/TEG | 4.5                  | 0.636                     | 0.435                                 | 0.201                      | 5.2                                                  | 4.0                              |

Figure 3 SAXS curves for evaluation the d-spacing of PP/organoclay composite fibres in dependence on concentration of C15A for $\lambda_{max}$ (a) and draw ratio of PP/C30B 1.0 wt.% fibres (b).

SAXS measurement was used for evaluation of d-spacing between silicate layers in the C15A and C30B organoclays (Figures 3). The peak for C15A in PP fibers is weak and broad. It could not be resolved for high draw ratio and lower concentration (0.02-0.1%), (Figure 3a). The results show that cold drawing of the fibers contributes to intercalation and exfoliation of C15A organoclay in the
matrix of PP fibers. Based on SAXS results the d-spacing of C30B collapsed and layers distance decreased from 1.9 to 1.5 nm. The organic phase partially removes from the layers space in the PP matrix. The SAXS results have shown that d-spacing of C15A organoclay in PP fibers grows during spinning and drawing mainly at low concentration and maximum draw ratio. In contrast, no positive change regarding to intercalation and exfoliation of C30B organoclay was observed.

3.3. Mechanical properties
Both organoclays positively affect the tensile strength and Young’s modulus of PP composite fibers only at a low concentration, up to 1.0 wt% (Tables 2, 3). A lower tensile strength was found for PP fibers containing C30B without compatibiliser and with S44P one.

Table 2 Tensile strength $\sigma$, elongation at break $\varepsilon$ and Young’s modulus E of PP/C15A nanocomposite fibres

| Fibres           | $C_{OC}$ in fibre, % | Draw ratio $\lambda_{max}$ | $\sigma$, cN/tex | $\varepsilon$, % | $E$, N/tex |
|------------------|----------------------|----------------------------|------------------|-----------------|-------------|
|                  |                      |                            |                  |                 |             |
| -                | -                    | 41.6 ± 0.7                 | 33.8 ± 4.1       | 4.73 ± 0.17     |             |
| PP/C15A          | 0.02                 | 54.2 ± 3.5                 | 27.7 ± 4.1       | 4.89 ± 0.25     |             |
|                  | 0.1                  | 55.0 ± 1.9                 | 25.6 ± 2.0       | 4.54 ± 0.42     |             |
|                  | 1.0                  | 41.7 ± 2.4                 | 36.1 ± 5.6       | 4.30 ± 0.28     |             |
|                  | 3.0                  | 24.3 ± 0.8                 | 98.5 ± 7.9       | 2.34 ± 0.08     |             |
| PP/C15A/S44P     | 0.02                 | 51.7 ± 2.9                 | 27.2 ± 4.4       | 4.65 ± 0.30     |             |
|                  | 0.1                  | 53.1 ± 1.0                 | 26.0 ± 1.3       | 4.57 ± 0.26     |             |
|                  | 1.0                  | 43.2 ± 1.8                 | 34.2 ± 9.4       | 4.58 ± 0.24     |             |
|                  | 3.0                  | 38.3 ± 2.0                 | 41.0 ± 12.4      | 3.76 ± 0.16     |             |
| PP/C15A/TEG      | 0.02                 | 52.2 ± 1.9                 | 25.3 ± 2.0       | 4.92 ± 0.16     |             |
|                  | 0.1                  | 51.4 ± 1.3                 | 24.1 ± 1.6       | 4.99 ± 0.11     |             |
|                  | 1.0                  | 43.8 ± 1.4                 | 44.7 ± 14.2      | 4.75 ± 0.23     |             |
|                  | 3.0                  | 45.8 ± 2.9                 | 25.8 ± 4.0       | 4.46 ± 0.17     |             |

Table 3 Tensile strength $\sigma$, elongation at break $\varepsilon$ and Young’s modulus E of PP/C30B nanocomposite fibres

| Fibres           | $C_{OC}$ in fibre, % | Draw ratio $\lambda_{max}$ | $\sigma$, cN/tex | $\varepsilon$, % | $E$, N/tex |
|------------------|----------------------|----------------------------|------------------|-----------------|-------------|
|                  |                      |                            |                  |                 |             |
| -                | -                    | 41.6 ± 0.7                 | 33.8 ± 4.1       | 4.73 ± 0.17     |             |
| PP/C30B          | 0.02                 | 52.5 ± 1.9                 | 29.4 ± 4.0       | 4.99 ± 0.19     |             |
|                  | 0.1                  | 49.4 ± 2.3                 | 27.2 ± 3.3       | 4.83 ± 0.16     |             |
|                  | 1.0                  | 43.9 ± 1.6                 | 20.3 ± 1.3       | 4.78 ± 0.18     |             |
|                  | 3.0                  | -                          | -                | -               |             |
| PP/C30B/S44P     | 0.02                 | 44.4 ± 1.7                 | 43.4 ± 11.9      | 4.56 ± 0.16     |             |
|                  | 0.1                  | 56.7 ± 0.8                 | 24.6 ± 1.7       | 5.38 ± 0.14     |             |
|                  | 1.0                  | 38.1 ± 3.4                 | 24.7 ± 6.2       | 4.57 ± 0.27     |             |
|                  | 3.0                  | 12.3 ± 0.7                 | 58.5 ± 13.3      | 1.49 ± 0.10     |             |
| PP/C30B/TEG      | 0.02                 | 56.3 ± 0.8                 | 25.2 ± 1.0       | 5.31 ± 0.22     |             |
|                  | 0.1                  | 55.1 ± 0.9                 | 26.0 ± 1.4       | 4.73 ± 0.35     |             |
|                  | 1.0                  | 44.0 ± 2.4                 | 28.3 ± 3.2       | 4.68 ± 0.18     |             |
|                  | 3.0                  | 22.4 ± 1.5                 | 81.8 ± 11.2      | 2.25 ± 0.14     |             |
Analysis of the mechanical properties of fibers shows predominant effect of supermolecular structure and orientation of fibers on both tensile strength and Young’s modulus (Tables 1, Figure 2). The orientation of fibers results from the deformation of fibers in drawing. The positive effect of low concentration of organoclay and compatibilisers on mechanical properties of PP composite fibers resides in the favourable deformation during the drawing process. The higher $\lambda_{\text{max}}$ at drawing of fibers was achieved in this case.

4. Conclusions
The analysis of the thermal properties, supermolecular structure, orientation and mechanical properties of PP/organoclay composite fibers obtained in the experimental work allow to draw the following conclusions:
- Tensile strength and Young’s modulus of the PP/organoclay composite fibers correspond with their DSC-CLM melting temperature (orientation of non-crystalline regions) and melting enthalpy (total crystallinity).
- Tensile strength and Young’s modulus of PP/organoclay fibers increase gradually with higher total crystallinity obtained by WAXS method, lower $\alpha$-form fraction, higher fraction of mesophase crystallites and lower size of both the $\alpha$-form and mesophase crystallites. These parameters were found for PP/organoclay composite fibers containing 0.02-1.0 wt% of organoclay C15A (C30B with TEG dispersant, only).

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References
[1] Wang K et al 2005 Shear amplification and re-crystallization of isotactic polypropylene from an oriented melt in presence of oriented clay platelets Polymer 46 pp 9022-9032
[2] Ma J et al 2002 Crystallization behaviors of polypropylene/ montmorillonite nanocomposite J. Appl. Polym. Sci. 83 pp 1978-1985
[3] Zhang QX et al 2003 Multiple melting and crystallization of nylon-66/montmorillonite nanocomposites J. Polym. Sci. Part B: Pol. Phys. 41 pp 2861-2869
[4] Nowacki R et al 2004 Spherulite nucleation in isotactic polypropylene based nanocomposites with montmorillonite under shear Polymer 45 pp 4877-4892
[5] Grebowicz JS et al 2001 Deformation of undrawn poly(trimethylene terephthalate) (PTT) fibers Polymer 42 pp 7153-7160
[6] Marcinčin A et al 2008 Spinning of Polypropylene/Organoclay Composites, Thermal and Mechanical Properties of Fibres Tekstil 57 pp 141-148
[7] Marcinčin A et al 2009 Study of Rheological, Thermal and Mechanical Properties of Polypropylene/Organoclay Composites and Fibres Fib. and Tex. in EE 17 pp 22-28