Spinning, structure and properties of PP/CNTs and PP/carbon black composite fibers

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Abstract. In this paper, the effect of the compatibilisers-dispersants and other nanofillers on melt spinning of the polypropylene (PP) composites, containing carbon nanotubes (CNTs), and carbon black pigment (CBP) has been investigated. Further, the structure and selected properties of composite fibers, such as mechanical and electrical have been studied. The results revealed, that percolation threshold for PP/CBP composite fibres was situated within the concentration of 15 - 20 wt%, what is several times higher than for PP/CNTs fibers.

1. Introduction

The polypropylene (PP) fibers containing inorganic or organic fillers represent a large part of the synthetic fibre production. The knowledge and experience from the developments in mass pigmented, delustered and filled fibers have been widely involved in practice. The new formulations of PP concentrate dispersions (concentrates, masterbatches) and modified spinning methods have been developed to guarantee an acceptable spinning conditions and new or improved properties of fibres such as high colour strength and colour uniformity [1], enhanced mechanical properties [2], thermal and UV stability [3] and electrical conductivity [4].

The developments in inorganic and organic nanoparticles with one size below 100 nm have opened up a new ways for investigation and use of PP (nano) composite fibers. [5, 6]. Specially carbon nanotubes and other kinds of carbon particles are very attractive for new materials based particularly on PP/CNTs composites and composite fibers. A large number of original papers and numerous overview articles, focussed on developments in the polymer/carbon nanotubes (CNTs) (nano)composites [6-8] and (nano)composite fibers [9-11] have been published in the last two decades. In structural composites CNTs acts as effective reinforcing nanofibrous filler and enhances mechanical properties of polymers such as tensile strength and elastic modulus [12-14]. Polymer/CNTs functional composites improve the electrical and thermal conductivity [15, 16] and other properties such as electromagnetic and microwave absorption.

In this paper, the effect of the the MWCNTs functionalisation, spinning equipments, conditions and compatibilisers-dispersants on rheological properties, and melt spinning of the polypropylene (PP), containing carbon nanotubes (MWCNTs), and CBP has been investigated. Further, the structure and selected properties of composite fibers, such as mechanical and electrical properties are presented and discussed.
2. Experimental

2.1. Materials used

Polymers: PP HF 500R (PP500R), MFR 25 g/10 min, flakes; PP Moplen HP 561N (PP561N), MFR 11 g/10 min, produced by Basell Polyolefins, Italia.

PP Tatren TH 1810 (PP1810), MFR 20.8 g/10 min, produced by Slovnaft Plc., Slovakia.

Nanofillers: Multi-Wall Carbon Nanotubes - Nanocyl® 7000 (MWCNT), average diameter 10 nm, length 0.1-10 μm, surface area 250-300 m²/g, carbon purity 90%, metal oxide impurity 10%, produced by Nanocyl S.A., Belgium.

Carbon Black Pigments (CBP): Vulcan XC 605 (V605) and Printex L6 (PL6), produced by Degussa GmbH, Germany.

Compatibilisers: Slovacid 44P (S44P), ester of stearic acid and polypropylene glycol, Sasol GmbH, Germany; Tegopren 6875 (TEG), alkyl ester polydimethylsiloxane, Degussa GmbH, Germany; Novanik 3010 (NOV), copolymer of ethylene oxide and propylene oxide, Sasol GmbH, Germany; PP-g-MA – polypropylene grafted by maleic anhydride, Clariant GmbH, Germany; Polypropylene glycol 2000 (PEG), Aldrich. Oxazoline derivative, (ALOXA), synthesised in laboratory.

2.2. Preparation of PP/MWCNT composite fibres

Two-step technology was used for preparation of PP/MWCNT nanocomposite fibres:

1. Preparation of the dispersion of MWCNT in PP500R: Powdered PP500R, MWCNT (and compatibilisers) were mixed in high rpm mixer for defined time. Powder mixture was melted and kneaded using twin screw corotating extruder Φ 28 mm. Temperature of extruder zones were 80, 150, 220, 225, 225, 225, 232°C, Temperature of extrudated melt was 229°C. Extrudate was cooled and cut.

2. The PP/MWCNT chips were dried at 80°C and then they were melted and spun using extruders Φ 16 mm and Φ 32 mm. The temperatures of extruder zones were 80, 240, 250, 250°C and spinning temperature was 250°C. Metering of the melt 16g/min; spinning speed 150m/min.

Fibres were drawn using laboratory drawing machine at 120°C.

PP/CBP composite fibres were using the same two-step process. Masterbatch, containing of 30 wt% of V605 or PL6 prepared in the first step, was mixed with PP1810 on final concentration of the pigment and simultaneously spun at 270°C in the second step. Fibres were drawn at 120°C.

2.3. Methods used

The capillary rheoviscosimeter Göttfert (with extruder Φ=20 mm) for measurement of the rheological properties of concentrates was used. The Newton equation τ = ηγ and Ostwald de Waele power law τ = Kγⁿ, where K – coefficient, n – deviation from the Newtonian flow (power law exponent), for evaluation of the basic rheological characteristics of concentrates were used.

DSC 7 (Perkin Elmer) was used for evaluation of thermal properties of the PP/CNT fibres, for estimation of their supermolecular structure and interactions of components at the interphase. The heating and cooling rate was 10°C/min, temperature range of 50-280°C.

Mechanical properties: An Instron (Type 3343) was used for measurements of the tensile strength and elongation at break according to ISO 2062:1993 as well as Young’s modulus.

Electrical properties:a) Direct current electrical conductivity of the PP composites (strings) and fibres was measured by the standard four-contact method (FCM). b) The resistivity of the linear textiles method (RLT) according to accredited test (CSN 800059) is suitable for measurement of the electrostatic and electroconductive properties of the fibres. Resistivity was expressed in [Ω.m].

3. Results and discussion

3.1. PP/MWCNT fibres with improved mechanical-physical properties
The favourable conditions at preparation of PP/MWCNT composites (masterbatches), optimal spinning and drawing conditions with suitable compatibilisers and selected nanofillers in addition, contribute to high draw ratio of LOY PP composite fibres, to their higher tenacity and Young’s modulus and to very low breaking elongation (Table 1).

The results reveal enhanced tenacity and Young’s modulus of selected composite fibres about 25-30% compared with unmodified fibres. The similar effect of MWCNT wit other additive was achieved for dynamical-physical properties e.g. dynamical modulus of fibres.

DSC analysis (results are not in the short paper) of composite fibres indicates, that effect of solid particles and dispersants within the investigated concentration on thermal properties (on phase structure) of fibres is negligible. MWCNT fibrous particles act as medium nucleating agents.

Table 1 The tenacity $\sigma$, elongation at break $\varepsilon$, Young’s modulus $E$ and their coefficients of variation for PP561N/ MWCNT (0.1%) composite fibres

| Fibre composition         | Draw ratio $\lambda$ | $T_1$ [tex] | $\sigma$ [cN/tex] | CV$\sigma$ [%] | $\varepsilon$ [%] | CV$\varepsilon$ [%] | $E$ [N/tex] | CV$E$ [%] |
|---------------------------|----------------------|-------------|-------------------|----------------|-----------------|-----------------|------------|----------|
| PP561N+PP500R             | 7.0                  | 10.9        | 64.8              | 2.9            | 22.6            | 7.6             | 7.2        | 2.8      |
| PP+0.1% CNT               | 7.0                  | 10.8        | 65.1              | 7.6            | 22.6            | 8.1             | 7.3        | 5.3      |
| PP+0.1% CNT+0.1% D40      | 7.2                  | 9.9         | 76.1              | 6.8            | 20.7            | 6.9             | 8.7        | 7.2      |
| PP+0.1% CNT+0.1% C15A     | 7.5                  | 9.9         | 72.8              | 5.3            | 21.6            | 5.5             | 7.9        | 5.3      |
| PP+0.1% CNT+0.1% C15A+S44P| 7.5                  | 10.1        | 71.7              | 8.3            | 20.3            | 5.0             | 8.2        | 8.8      |
| PP+0.1% CNT+0.1% C15A+TEG | 7.5                  | 9.7         | 81.2              | 2.1            | 21.7            | 6.2             | 9.5        | 4.5      |
| PP+0.1% CNT+0.1% C15A+S44P+TEG | 7.5        | 8.9         | 77.0              | 2.3            | 21.7            | 4.4             | 9.1        | 5.7      |
| PP+0.1% CNT+0.1% PP-g-MA+TEG | 7.2         | 10.3        | 76.6              | 6.2            | 22.0            | 9.3             | 8.9        | 6.0      |
| PP+0.1% CNT+0.05% ALOXA+S44P | 7.5         | 9.3         | 74.0              | 5.8            | 20.0            | 4.4             | 8.8        | 6.4      |

The following technology and equipment is necessary to keep, to ensure acceptable spinning of PP/MWCNT composite fibres with enhanced mechanical properties:

- Two step process: a) preparation of polymer composite (concentrate) and b) melt spinning of polymer composite with final concentration of MWCNT and additive in chips form is recommended.

- The powder form of PP for mixing with MWCNT and other additives before melt processing of concentrate (composite) is required

- The application of equipment with high kneading and homogenization effect (lower temperature) is crucial for preparation of PP/MWCNT composites (masterbatch), suitable for melt sinning. The twin screw extruder with diameter $\phi = 28$ mm and higher is needed.

- The low spinning speed process producing of LOY composite fibres is appropriated.

- The higher draw ratio in cold drawing at optimal conditions, the higher both tenacity and Young’s modulus can be achieved.

The knowledge and experiences obtained were utilized at spinning of PP/MWCNTs composite fibers with high content of fibrous nanofiller. The results are in the next chapter.

3.2. Electrically conductive PP/MWCNT composite fibres

3.2.1. Rheological properties and spinning of PP/MWCNT composites

The melt viscosity of the PP/MWCNT composites increases gradually with content of the MWCNT in PP matrix. Already 1.0 wt% of nanofiller in PP causes the first break on the dependences of both the power law exponent and viscosity on content of MWCNT. The second break is observed between 6 wt% and 8 wt% of MWCNT in the PP. This corresponds with qualitative change in number of contacts of fibrous particles, their mutual interactions and higher electrical conductivity (Table 2).
Table 2 Dependence of viscosity $\eta$, power law exponent $n$ and electrical conductivity $\sigma$ (four contact method) on concentration of MWCNT in PP500R/MWCNT composites.

| Concentrate composition | $n$  | $\eta$ [Pa.s] | $\gamma=100$ s$^{-1}$ | $\gamma=300$ s$^{-1}$ | $\sigma$ [S.cm$^{-1}$] |
|------------------------|------|---------------|------------------------|------------------------|-------------------------|
| PP561R+PP500R          | 0.41 | 329          | 173                    | -                      |
| 1% CNT                 | 0.40 | 302          | 156                    | $<1.9 \times 10^{-9}$ |
| 4% CNT                 | 0.39 | 378          | 194                    | $3.2 \times 10^{-5}$   |
| 6% CNT                 | 0.48 | 416          | 235                    | $5.6 \times 10^{-2}$   |
| 8% CNT                 | 0.29 | 777          | 357                    | $5.1 \times 10^{-1}$   |

3.2.2. Mechanical properties of PP/MWCNT composite fibres
Tenacity and Young’s modulus of PP/MWCNT composite fibres decrease gradually with content of the fibrous particles in PP fibres. The low elongation at break (about 15%) and high non-uniformity of the mechanical properties (CV) are characteristic for the fibres (Table 3). The compatibilisers-dispersants (PEG and NOV) have significantly improved spinability and deformation of the fibres in drawing. In addition, they have improved the non-uniformity expressed by lower CV$\sigma$ and CV$\varepsilon$ in comparison with the PP/MWCNT fibres without compatibiliser-dispersant.

The decrease of the tensile strength and elastic modulus of the PP/MWCNT fibres containing higher content of the fibrous nanofiller (MWCNT) is in contrary with the mechanical properties of the PP composite fibres with low content of nanofiller (Table 1).

Table 3 The tenacity $\sigma$, elongation at break $\varepsilon$, Young’s modulus $E$ and their coefficients of variation of PP500R/MWCNT composite fibres, drawn at low gradient of deformation

| Content of MWCNT [%] | Draw ratio $\lambda$ | $T_i$ [tex] | $\sigma$ [cN/tex] | $\sigma_{\%}$ [%] | $\varepsilon$ [\%] | $\varepsilon_{\%}$ [%] | $E$ [N/tex] | CV$E$ [%] |
|----------------------|---------------------|-------------|-------------------|-------------------|-------------------|-------------------|-------------|----------|
| 1.0                  | 7.6                 | 63.2        | 47.5              | 10.7              | 15.7              | 21.6              | 4.4         | 8.0      |
| 4.0                  | 6.8                 | 112.6       | 38.4              | 10.1              | 14.8              | 26.3              | 4.4         | 8.4      |
| 6.0                  | 9.3                 | 93.0        | 35.0              | 15.8              | 13.1              | 44.8              | 4.3         | 6.7      |
| 8.0                  | 7.0                 | 195.8       | 33.3              | 15.0              | 14.3              | 8.5               | 4.1         | 2.2      |

The microscopic observation of the PP/MWCNT fibres reveals a significant difference in the morphology of the fibres without compatibiliser-dispersant and that with dispersant. The MWCNT is uniformly distributed in the fine structure of the PP matrix without dispersant. On the contrary, the flocules of the MWCNT are formed in the abundance of the polyglycol based dispersant, immiscible with PP. The flocules are easy deformed at drawing and form of the oriented dispersed phase in the PP matrix.

3.2.3. Electrical properties of the PP composite fibres
Electrical properties of the PP/MWCNT composite fibres were measured using two methods: standard four contact method (FCM) and resistivity of the linear textile method (RLT). Results are presented in the Table 4. The percolation threshold is dependent on shape of sample measured and shifted from the PP composites to PP composite drawn fibres within the nanofiller concentration of 4.0–8.0 wt%. The electrically conductive composites was obtained already at 4.0 wt% of conductive particles, but 8.0 wt% was unsufficient for conductive drawn fibres (Table 4). Electrical conductivity of PP/MWCNT fibres is compared with conductivity of PP/CBP V605 (Table 5). The results reveal that percolation threshold for PP/CBP composite fibres is situated within the concentration of 15 - 20 wt%, what is two times higher than for PP/MWCNT fibres (Table 4). The decrease of the conductivity of drawn fibres was confirmed also for PP/CBP fibres.
Table 4 Electrical resistivity $\rho$ of the PP500R/MWCNT composite fibres evaluated by method of resistivity of linear textiles (RLT)

| Content of MWCNT [%] | $\rho$ [\(\Omega\cdot m\)] composites | $\rho$ [\(\Omega\cdot m\)] undrawn fibres | $\rho$ [\(\Omega\cdot m\)] drawn fibres |
|---------------------|--------------------------------------|----------------------------------------|-------------------------------------|
| 0                   | $1.1\times10^{13}$                  | $3.4\times10^{15}$                    | $9.2\times10^{15}$                  |
| 1.0                 | $1.3\times10^{13}$                  | $1.1\times10^{15}$                    | $8.6\times10^{14}$                  |
| 4.0                 | $2.5\times10^{7}$                   | $1.3\times10^{8}$                     | $3.1\times10^{7}$                   |
| 6.0                 | $5.4\times10^{3}$                   | $4.3\times10^{6}$                     | $6.7\times10^{5}$                   |
| 8.0                 | $1.4\times10^{3}$                   | $3.4\times10^{5}$                     | $2.2\times10^{4}$                   |

Table 5 Electrical resistivity $\rho$ of the PP1810/V605 composite fibres evaluated by method of resistivity of linear textiles (RLT)

| Content of V605 pigment [%] | $\rho$ [\(\Omega\cdot m\)] | undrawn fibres | drawn fibres |
|-----------------------------|-----------------------------|----------------|--------------|
| 0                           | $\sim 10^{13}$              | $\sim 10^{13}$ |              |
| 5                           | $4.0\times10^{13}$          | $5.1\times10^{12}$ |              |
| 10                          | $1.9\times10^{8}$           | $1.1\times10^{8}$ |              |
| 15                          | $2.6\times10^{4}$           | $5.7\times10^{4}$ |              |
| 20                          | $2.6\times10^{4}$           | $6.3\times10^{4}$ |              |
| 25                          | $6.8\times10^{4}$           | $1.2\times10^{5}$ |              |
| 30                          | $8.0\times10^{4}$           | $6.8\times10^{4}$ |              |

Improvement of the rheological properties and spinability of the PP/MWCNT/CBP L6 composite fibres by polar additives (PEG and NOV) led to decrease their electrical conductivity compared to PP/MWCNT fibres. This phenomena can be explained by separation and flocculation of the fibrous nanofiller in the PP matrix, what shifts the percolation threshold to higher concentration of electrically conductive additives.

4. Conclusions

On the basis of experimental results the following conclusions can be drawn:
- Two step process, preparation of polymer composite and melt spinning of polymer composite with final concentration of MWCNT and additives in chips form is recommended for acceptable spinning and properties of fibres.
- The application of equipment with high kneading and homogenization effect is crucial for preparation of PP/MWCNT composites suitable for melt sinning. The twin screw extruder with minimum diameter $\phi = 28$ mm is needed.
- The low spinning speed process producing of LOY composite fibres is appropriate, providing the high deformability of fibres in cold drawing.
- The MWCNT particles with high aspect ratio contribute in PP matrix to creating the electrically conductive net at essentially lower concentration than carbon black pigment. The percolation threshold corresponds with filler concentration at which the viscosity began to increase rapidly.
- The electrical conductivity of the composite fibres decreases with increase of their deformation and orientation.

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