Properties of composite polypropylene fibers for technical application

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Abstract

This work focuses on the properties of polypropylene concentrates and fibers modified by inorganic additive. Polypropylene staple fibers are assigned as reinforcement of concrete to transform and absorb deformation energy. Modification of polypropylene fibers is necessary to ensure more intense anchoring of fibers in cement matrix. In this work the impact of inorganic additive on the rheological properties of polypropylene and polypropylene concentrate as well as on thermal, thermomechanical and mechanical properties of composite polypropylene fibers is investigated.

At rheological properties the index pseudoplasticity of polypropylene and polypropylene concentrates were comparable. Thermomechanical analysis shows, that temperature of fiber deformation was higher at higher drawing ratio of composite polypropylene fibers containing inorganic additives. Mechanical properties of modified fibers without stabilization and stabilized at 95°C for 1 minute achieved higher values at drawing ratio 4.0. Surface modification of fibers containing inorganic additives was noticeable.

Keywords: polypropylene fibers, modification, inorganic additive, rheological, thermal, thermomechanical and mechanical properties

Introduction

The modern era of research and development of fiber reinforced concrete (FRC) was initiated in the early 1960´s by Romualdi, Batson and Mandel. In the present fiber reinforced concrete is firmly established as worldwide most commonly used construction material. The expression fiber-reinforced concrete is by AC1 116R, Cement and Concrete Terminology defined as concrete containing dispersed randomly oriented fibers (Sideris 2009, Zollo 1997, Banfill et al. 2006). This three-dimensional reinforcement of the concrete provides that by usage of fibers concrete becomes more tough and durable. The practical function of fibers is from a constructional point of view, to protect composite against sudden failure at the crack initiation in matrix. The tension is transferred to the fibers until the ultimate strength of fibers is reached (Noumowe 2005, Singh 2004).

Modern engineer have as a main objective the attempts to modify the properties of concrete by the inclusion of fibers to improve rheology or plastic cracking characteristics of the material in the fresh state or up to about 6 hours after casting, tensile or flexural strength, impact strength and toughness, durability and to control cracking and the mode of failure by means of post-cracking ductility (Hannant 2003).

Properties and character of fiber reinforced concrete depend on the type of material, fiber geometry, binder formulation, fiber distribution, fiber orientation and fiber concentration. Based on used material type there are four categories of fibers used for concrete reinforcing: steel fiber, glass fiber, synthetic fiber including carbon fibers, and natural fiber (Zollo 1997). Although glass, carbon and steel fibers have been extensively used in cement matrices, this paper focuses on the addition of polypropylene fibers.

Polypropylene fibers are used as a reinforcing agent in construction applications for many years. In concrete PP fiber is used in a wide variety of applications in general constructions and specifically in ground-floor slabs. Specific uses have included precast products and situations where fire resistance is important. The latter is achieved by the fibers melting and leaving channels in the concrete though which steam can escape, thus improving the spalling resistance. Utilization of polypropylene fibers alters characteristics of concrete in a very beneficial way. Result is, that PP fibers have effectively improved concrete's flexural strength, compressive strength, bonding strength, dynamic performance, while reduced the

water penetration and mass loss due to abrasion. The fatigue life of concrete is also prolonged (Hannant 2003, Sun 2009, Tapkin 2006).

Extensive use has been applied in the construction industry of small quantities (0.1 pre cent by volume) of short (<25 mm long) fibrillated monofilament polypropylene fibers to alter the properties of the fresh concrete, notably to reduce the extent of plastic shrinkage cracking should it occur (Hannant 2003).

More intense anchoring of polypropylene fibers in cement matrix is reached by physical and chemical modification. Addition of sufficient additive ensures that fibers are consistently fixed in matrix. This leads to expressive improve of functional of PP fibers in relation to transmission and absorption of deformation energy to form and load silica composites.

In this work the rheological properties of polypropylene (PP) and PP concentrate (PP/C) modified by inorganic additives were studied. This PP/C concentrate was used at the preparation of composite polypropylene (PP/CF) fibers modified with 6.4 wt. % content of inorganic additive in fiber. The processability of PP/C concentrate and thermal, thermomechanical and mechanical properties of PP and PP/CF fibers were studied.

Experimental

Material used

Polypropylene (PP) TATREN HT 1810 with MFI = 20.9 g/min produced by Slovnaft a.s., Bratislava (SR) was used for the preparation of PP/C concentrate, PP and PP/CF. Polypropylene concentrate (PP/C) consists of pure polypropylene and 6.4% wt. of micronized inorganic additive was prepared by melting of PP with inorganic additive using the twin screw extruder with diameter of ø = 32 mm. PP fibers were used in a form of standard (PP) fibers and composite (PP/CF) fibers. Content of inorganic additive is 6.4 wt. % in composite fibers. PP and PP/CF fibers were drawn on the different draw ratio (λ) in the range 2.0 − 4.0.

Methods used

Rheological properties of PP and PP/C concentrates were measured using the capillary rheoviscosimeter Göttfert N 6967 with hole diameter ø = 2 mm, hole length l = 30 mm at temperatures 240 °C, 260 °C and 280 °C. Basic rheological parameters were estimated by Newton and Ostwald de Waele rule:

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad (1)$$

$$\tau = K \cdot \dot{\gamma}^{n} \qquad (2)$$

where η is viscosity, $\dot{\gamma}$ – shear rate, τ – shear strain, n – index pseudosplasticity, which characterize the Newtonian behavior of melting, K – coefficient.

The characteristics as shear rate $\dot{\gamma}$ and shear strain τ of PP and PP/C concentrates were calculated from measured parameters (weight flow and pressure), and used on estimation of viscosity η at defined values of shear rate $\dot{\gamma}$. Viscosity was specified at four shear rates 100, 300, 500 a 1000 s^{-1} mostly used in production technologies. Pseudoplasticity index n, characterizing the deviation from Newtonian behavior was evaluated from logarithmic dependence of shear strain on shear rate.

$$log\,\tau = f\!\left(log\,\dot{\gamma}\right) \qquad (3)$$

Thermal properties of PP/CF fibers were carried out using the DSC 7 fy Perkin-Elmer apparatus. Method was used to study of the temperature and structural transformations of samples. Conditions of DSC measurements of fibers were following: 1st heating: $50 \rightarrow 220$ °C, cooling: $220 \rightarrow 50$ °C a 2nd heating: $50 \rightarrow 200$ °C. The heating or cooling rates were 10 °C/min. Measurements were realized at nitrogen atmosphere. From obtained thermograms melting temperatures (T_m) for 1st and 2nd heating were specified. Melting temperatures were deducted from maximum of the peak. Melting enthalpies (ΔH_m) for 1st and 2nd heating were estimated too. Melting enthalpies were indicated as endothermal or exothermal peak areas, valued from thermal interval. Measurements were interpreted by program DSC 7 – Pyris Manager v. 2.0.

Thermomechanical properties of PP and PP/C fibers were performed using Shimadzu Thermomechanical Analyzer TMA-50. Temperature (T_D) at which the fiber is deformed as well as total deformation – shrinkage (l_D) of fiber at 90 °C was determined using the TMA dependences. Conditions of measurement were following: heat from room temperature to 90 °C at the heating rate 5 °C/min, and fiber length 9.8 mm.

Mechanical properties (tenacity, and Young's modulus) were measured by Instron 3343 device and evaluated using Instron program. Measuring conditions were the length of fiber 125 mm and rate of clamp 500 mm/min.

Surface evaluation was provided using microanalyzer JXA-840A with EDS and WDS system, produced by JEOL, Japan. Measurement conditions were following: accelerating voltage 15 kV, sample current 1.10^{-10} A.

Results and Discussion

The obtained dependences of shear strain and viscosity on shear rate of PP and PP/C concentrate measured at temperatures 260°C are on the Fig. 1. The addition of inorganic additive to the PP increases the share strain at the same share rate (Fig. 1a). But, the shifting of dependence viscosity on the share rate is very little (Fig. 1b) therefore the increase of share strain after the addition of inorganic additive did not make worse the processability of PP/C concentrate at the spinning of composite PP/CF fibers. The same result was obtained for the dependence of share strain and viscosity on shear rate measured at the temperatures 240°C and 280°C, too.
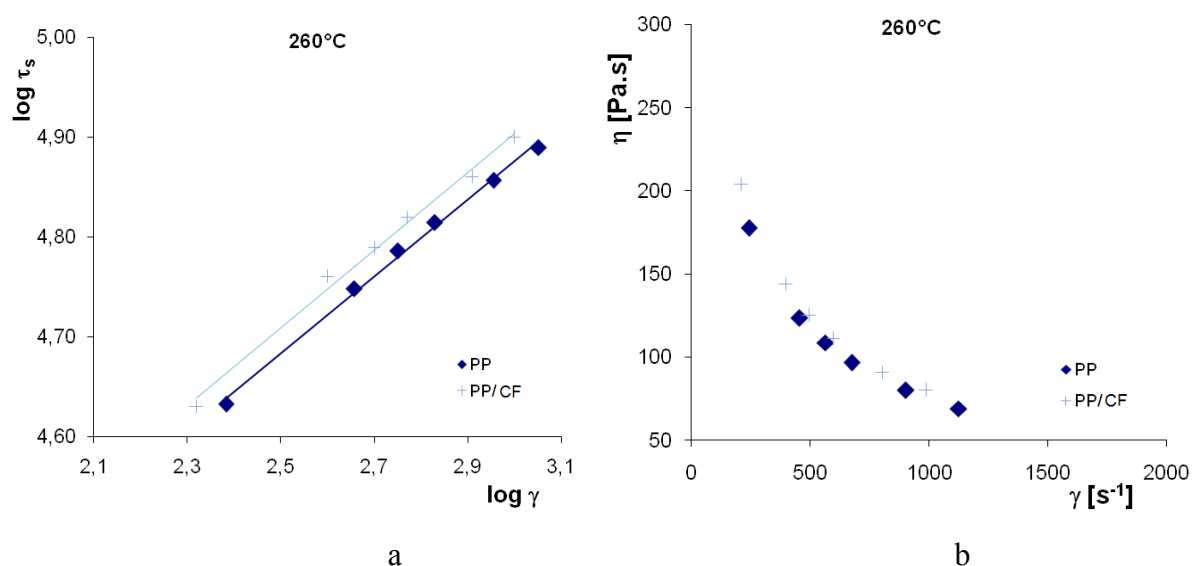

a

b

Figure 1:   Dependencies of share strain (a) and viscosity (b) on share rate of PP and PP/C concentrate at temperature of 260°C

There were calculated the index pseudoplasticity n, coefficient K and viscosity at the four share rates (Tab. 1). At higher temperatures the index pseudoplasticity n of PP/C concentrate was higher in comparison with index pseudoplasticity of pure PP and increased with the increased temperature. It means that at the higher temperature the melt of PP/C concentrate

has lower deviation from the Newton liquid. The viscosities of PP/C concentrate are also higher in comparison with the pure PP and decrease with the increase of measured temperature.

Table 1: Index pseudoplasticity n, coefficient K and viscosity η of PP and PP/C concentrates at various shear rates $\dot{\gamma}$

SAMPLE	[T°C]	K	n	η [Pa.s]			
				$\dot{\gamma}$ 100 [s⁻¹]	$\dot{\gamma}$ 300 [s⁻¹]	$\dot{\gamma}$ 500 [s⁻¹]	$\dot{\gamma}$ 1000[s⁻¹]
PP	240	6973	0,36	373	185	134	86
	260	5277	0,38	310	158	115	75
	280	4485	0,39	272	139	102	67
PP/C	240	8318	0,34	407	198	142	90
	260	5426	0,39	327	167	123	80
	280	3935	0,42	274	145	108	72

Table 2: Melting (T_m) temperatures and melting (ΔH_m) enthalpies of PP and PP/C fibers obtained at 1st and 2nd heating

λ	1st heating				2nd heating			
	T_m [°C]		ΔH_m [J/g]		T_m [°C]		ΔH_m [J/g]	
	PP	PP/CF	PP	PP/CF	PP	PP/CF	PP	PP/CF
2.0	158.8	158.7	79.1	72.1	159.2	158.9	69.1	62.3
2.5	161.0	163.8	71.6	80.2	158.7	158.4	61.7	61.5
3.0	159.5	161.7	85.4	75.2	158.9	159.4	65.9	59.1
3.5	162.3	162.3	82.9	71.8	158.7	158.2	70.0	57.5
4.0	162.2	162.2	83.0	75.9	158.0	158.5	64.8	65.6

Thermal properties of PP and PP/CF fibers with drawing ratio of 2.0 – 4.0 were evaluated by DSC (Tab. 2). From obtained results it is obvious, that at 1st heating the melting temperatures and enthalpies of PP as well as PP/CF fibers are higher in comparison with 2nd heating. The higher melting temperatures reflect the formation of more stabil modification with major content of α-modification. The melting enthalpies of PP and PP/CF fibers increase with the increase of drawing ratio, too. It confirms that the crystallization ability of PP at the one-direct oriented process during the spinning and drawing is higher than without orientation.

Thermomechanical analysis (TMA) was used for the investigation of dimensional stability of PP and composite PP/CF fibers in dependence on temperature. Results are in Tab. 3. From dependence of deformation of fiber on temperature (at heating rate 5°C/min from room temperature to 90°C) deformation temperatures of fibers and shrinkage at 90°C were evaluated.

Table 3: Temperature (T_D) and shrinkage (l_D) of PP and composite PP/CF fibers

λ	T_D [°C]		l_D [%]	
	PP	PP/CF	PP	PP/CF
2.0	53.2	52.9	-1.9	-2.9
2.5	57.3	56.3	-1.2	-2.2
3.0	56.3	59.8	-2.5	-1.8
3.5	57.1	57.6	-1.1	-2.5
4.0	55.3	62.4	-3.8	-2.0

Shrinkage was detected at all measured fibers (Tab. 3). Higher shrinkage of PP was detected at higher draw ratio. But the addition of inorganic additive in PP/CF fibers defends the shrinkage. It confirms the higher temperature at which the fiber deforms as well as the lower shrinkage.Tenacity (σ) and Young's module (E) of PP and composite PP/CF fibers were measured without and after stabilization at 95°C for 1 minute (Tab. 4).

Table 4: Tenacity (σ), and Young's module (E) of PP and composite PP/CF fibers with different drawing ratio without stabilization (WTS) and with stabilization (WS) at 95 °C during 1 min

λ	σ[cN/tex]				E[N/tex]			
	WTS		WS		WTS		WS	
	PP	PP/CF	PP	PP/CF	PP	PP/CF	PP	PP/CF
2.0	16.9	15.5	16.8	16.5	1.14	1.10	0.85	0.91
2.5	22.3	20.1	22.4	19.9	1.62	1.52	1.53	1.40
3.0	27.8	26.4	23.4	22.9	2.34	2.48	2.12	2.02
3.5	31.8	24.3	29.5	22.9	3.24	2.89	3.28	2.91
4.0	33.9	30.3	30.9	27.7	3.53	3.25	3.48	3.20

Mechanical properties of PP/CF fibers with addition of inorganic additives achieved slightly lower values than mechanical properties of PP fibers even though at higher draw ratio the difference between values was increasing before stabilization. After the stabilization

mechanical properties tenacity and Young's module were found to be lower than it was at fibers without stabilization. Percentage decrease of tenacity and Young's module of PP and PP/CF fibers after stabilization are growing until draw ratio $\lambda=3.0$ and then decreasing. However, decrease is more significant at pure PP fibers. Inorganic additives defend to movement of macromolecular chain, what leads to lower decrease of tenacity and Young's module of PP/CF fibers in compare to PP fibers at all range of draw ratio.

It follows that the fibers with the better dimensional stability and mechanical properties for technical application to the concrete are able to obtain with the optimal conditions at the stabilization process after spinning and drawing.

Localization of inorganic additive in the surface of composite PP/CF fibers was observed using microanalyzer. The obtained pictures with relevant graphs of content of inorganic additives in composite PP/CF fiber surface are shown at Fig. 2. Surface of PP fiber is smooth but at the surface of composite PP/CF fiber can be seen roughage caused by participation of inorganic additive (Fig. 2 a, b). Presence of inorganic additive in composite PP/CF fiber is proven by relevant peak at graph (Fig. 2 d). The graph of PP fibers (Fig. 2 c) does not content the peak of inorganic additive.

Conclusion

- Rheological properties of PP concentrates containing inorganic additives is comparable to pure PP
- The orientation process causes the higher crystallization ability PP in the PP as well as PP/CF fibers.
- Composite PP/CF fibers with higher draw ratio are more resistant to temperature deformation.
- At draw ratio 4.0 the tenacity and Young´s module of composite PP/CF fibers achieved highest values.
- The inorganic additive is localized in the surface of composite PP/CF fibers and is able to provide for the better adhesion to the concrete at the preparation of fiber-reinforcing concrete composites.
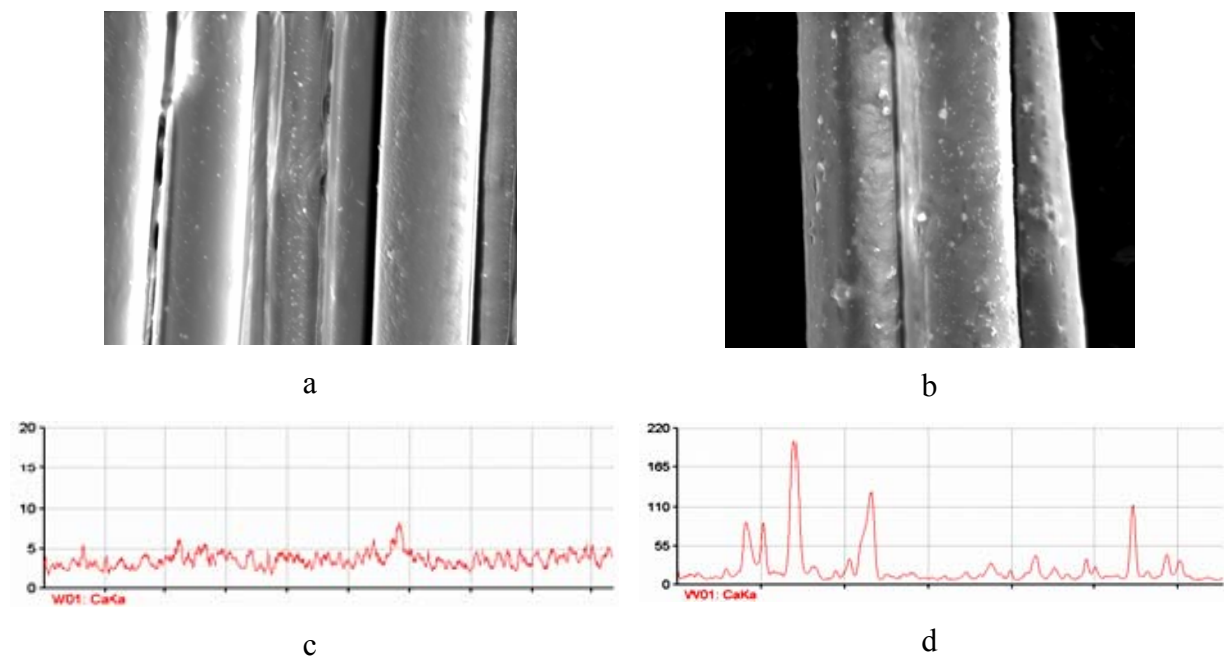
Figure 2: Surfaces (a, b) and contents of inorganic additive (b, d), d) of PP (a, c) and PP/CF (b, d) fibers with draw ratio 3.5.

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