

Anna Ujhelyiová,
Zuzana Strecká,
E. Bolhová,
M. Dulíková,
Peter Bugaj

Polypropylene Fibres Modified by Polyvinyl Alcohol and Nanoadditive. Structure and Properties

Slovak University of Technology in Bratislava,
Faculty of Chemical and Food Technology,
Institute of Polymer Materials,
Radlinského 9, 812 37 Bratislava
e-mail: anna.ujhelyiova@stuba.sk

Abstract

The modification of polypropylene (PP) by nanoadditives (NA) is an effective way to prepare the fibres with advanced properties for textile and technical application. The modification of polypropylene fibres by NA exhibit the change in morphology of modified PP fibres. This paper studies the influence of Cloisite 15A and polyvinyl alcohol on the properties of modified polypropylene/polyvinyl alcohol (PP/PVA) as well as modified polypropylene/polyvinyl alcohol/Cloisite 15A (PP/PVA/CL) fibres. The thermal, mechanical and barrier properties as well as the dyeability of modified PP fibres were evaluated. The results show that the thermal properties of semicrystalline modified PP fibres depend on used additives (PVA and CL) as well as on the conditions of their preparation or treatment. The changed morphology of modified PP fibres provides them with better dyeability.

Key words: modified fibres, polypropylene, polyvinyl alcohol, Cloisite 15A, nanoadditives, mechanical properties, thermal properties, barrier properties, dyeability, blended fibres, montmorillonite.

small inclusions that a large amount of interfacial phase is now included in the bulk of these nanocomposites. A complete transformation of the material's chemical, mechanical and morphological domain structure can be achieved by the addition of nanoparticles. Much of today's research activities have focused on the development of organic polymer-based nanocomposites.

Polypropylene (PP) is a most common commodity of organic polymers, which has a practical use in many areas, such as human and home appliances, automotive, construction, and other industrial applications. Other utilisation of PP like fibres is the improvement of its properties by modification with inorganic nanoadditives, which leads to the preparation of PP nanocomposites or nanocomposite PP fibres with better mechanical [2, 3] and barrier [4 - 6] properties, flame retardancy [7] as well as improved dyeability by the classical method (from a dyebath), with a low amount of nanoparticles [8 - 10].

The final structure and properties of PP nanocomposite materials are dependent on the morphology created, which is affected by the conditions of the preparation (temperature and rate of spinning and drawing, kinetics and thermodynamics of PP crystallisation at cooling, etc.) and the shape, particle size, aggregate size, surface characteristics and dispersion degree of nanoparticles in the polymer matrix. The crystallisation of PP is one of the effective processes which provides control of the morphology of PP nanocomposite fibres during their preparation, which is also influenced by

the type and structure of nanoparticles used. The presence of the inorganic or modified inorganic nanoadditives-nanoparticles causes a change of thermal behaviour and a great increase in the crystallinity of the polymer matrix because these nanoparticles behave more of as nucleating agents [11]. It was demonstrated that the ability of montmorillonite (MMT) to nucleate PP crystallisation depends on the clay deposit and the organo-treatment of the clay. Clays are usually modified by cationic surfactants like organic ammonium salts or alkyl phosphonium [12 - 15].

The improved dyeability of PP fibres by the classical method (from a dyebath) has remained a very important challenge to all polymer and textile chemists for many decades. Many researchers have explored the dyeing of PP fibres using polyblends, copolymers, plasma treatment and specially designed dyes. Dyeable PP fibres can be produced via nanotechnology using nanoparticles which form the place into the polymer matrix in with the dyes can be located. One of the commonly available nanoparticles is purified or surface modified nanoclay. Such modified nanoclay, with some chemical groups introduced onto their surface, would provide an increase in the dye affinity of PP nanocomposite fibres. In practice, PP fibres with cationic surfaced modified nanoclay would be dyed with acid dyes. Another possibility to create the dyesites needed for the dyeability of PP fibres is the creation of tortuous pathways formed by oriented nanoparticles in the polymer system, which is very good for PP dyeing with

■ Introduction

Nanocomposites are a distinct form of composite material, which involve imbedding nano or molecular sized domain particles into organic polymer, metal or ceramic matrix materials. In all cases, it is perceived that the intimate inclusion of these nanoparticles in these matrices can completely change the properties of these materials [1, 16, 17]. The nanoparticles can serve as matrix reinforcement as well as change other properties such as mechanical, sorptive and colour, barrier or electrical of these base materials. The reason for the impact of these

disperse dyes. Distributed nanoparticles into the polymer matrix can provide chemical and/or physical linkages to the dyes. In this case, it should carry or be able to develop charged groups or other functional groups that can form chemical and/or physical linkages with dyes. The thermal stability of nanoparticles should retain its property for dye sorption after extrusion. It must be able to resist at least 200 °C. Moreover, they are stable in wet processing and other conditions. The nanoparticles should remain in the fibre and retain their ability in a high temperature aqueous medium. They should also be stable in UV light, weak acids and alkalis, oxidising/reducing agents, detergents and chemicals commonly associated with textile applications [9].

In today's world, there has been an alarming increase in the incidence of skin cancer worldwide. A primary reason for this disease is attributed to the depletion of stratospheric ozone layer, resulting in sun exposure. The production of textiles with increased absorption, reflection or scatter of solar UV radiation during the preparation of appropriate clothing is one possibility of how to protect human skin from harmful sun exposure [4]. There are many factors based on physical and chemical aspects which relate to the construction of fabrics (thickness, weight, density of weft and warp, density of knitted loops) and yarns (linear density, number of twists, construction of yarns) as well as the chemical (type of fibres, dyes used, UV stabilisers) and physical (supermolecular structure of fibres, concentration and distribution of agents) which change the properties of fibres, influencing the barrier properties of fibres. The change of some factors lead to positive or negative changes of the barrier properties in textiles [5, 6]. The modification of PP fibres by nanoadditives is also one of a number of very interesting areas regarding the improvement of the barrier properties of textiles. Nanoadditives which are able to absorb, reflect or scatter radiation affect the processability, supermolecular structure, morphology as well as thermal, physical mechanical and final properties of PP fibres [6].

This paper presents the influence of polyvinyl alcohol and the influence of the different treatments of nanoadditives Cloisite 15A on the crystallisation of PP, on physical-mechanical and barrier properties as well as on the dyeability of modified PP fibres.

■ Experimental

Material used

- Polypropylene CF 331 (PP) - Slovnaft, a.s., Bratislava, (Slovak Republic), melt flow index MFI = 11 g/10 min
- Polyvinyl alcohol POVAL 205 (PVA) - Kuraray (Japan), viscosity (4% water solution, 20 °C) = 4.6 - 5.4 mPas, degree of hydrolysis = 86.5 - 89.0%, pH = 5 - 7
- Glycerine (GL) - plasticiser for the PVA
- Nanoadditive - Cloisite 15A (CL) is a natural montmorillonite modified with a quaternary ammonium salt, Southern Clay Products, Inc., Texas, USA, typical dry particle sizes: 50 10% less than 2 μ, 50% less than 6 μ and 90% than 13 μ.

The unmodified polypropylene (PP), modified polypropylene/polyvinyl alcohol (PP/PVA) and modified polypropylene/polyvinyl alcohol/Cloisite 15A (PP/PVA/CL) fibres were prepared in three steps – the treatment of PVA and the preparation of PP/PVA and PP/PVA/CL concentrates and fibres. The first step: PVA was plasticised with the glycerine at a temperature of 130 °C for 40 min. Plasticising using the glycerine was also used for the different treatment of nanoparticles. The CL was treated in glycerine at various conditions (different times of mixing: 5, 10, 15 min, different processes of mixing: B - only mixing and C - mixing with ultrasound) and then the glycerine with Cloisite 15 A was used for the plasticising of PVA. The PP/PVA and PP/PVA/CL concentrates were prepared using a two screw extruder in temperature zones – 190, 210, 230, 215 and 190 °C. Next, the modified PP/PVA (97/3 wt. %) and PP/PVA/CL (96.5/3/0.5 wt.%) fibres was spun by the classical procedure, using a laboratory pilot plant with a single screw extruder $\phi = 16$ mm at 250 °C. The draw ratio was $\lambda = 3$ at a temperature of 110 °C.

Dyeing

Dyeing conditions

In order to remove the lubricants, the fibres were washed in a bath of 1.5 g/l Slovapon and 1 g/l Na₃PO₄ at 75 °C for 20 min.

The fibres were dyed in a laboratory dyeing machine - Ahiba ↑↓ AG CH 4127 Birsfelden (Switzerland). The following bath composition was used: dispersant 1 g/l Kortamol NNO, 2 g/l (NH₄)₂SO₄, 0.17 g/l Texavin and disperse dye C.I. Disperse Red 86 2% o.w.f. The fibres were dyed at 120 °C.

Reduction clearing

The dyed fibres were washed in a solution consisting of 3 ml/l NaOH 38°Be, 0.3% Perigen THD and 2 g/l Na₂S₂O₄, at 75 °C for 30 minutes.

Method used

Thermal properties

The thermal properties of the fibres were measured using a DSC 7 Perkin Elmer apparatus as follows: 1st heating from 70 to 220 °C, cooling from 220 to 70 °C and 2nd heating from 70 to 200 °C with a heating or cooling rate of 10 °C/min. The melting and crystallisation temperatures as well as the melting and crystallisation enthalpies were evaluated.

$$DH = \Delta H_{mexp} - (\Delta H_{mPP} \cdot w_{PP}) \quad (1)$$

where DH is the difference between the experimental melting enthalpy and additive melting enthalpy of modified PP fibres, ΔH_{mexp} – experimental melting enthalpy of modified PP fibres, ΔH_{mPP} – melting enthalpy of pure PP fibres, w_{PP} – weight percentage of PP in modified PP fibres.

Mechanical properties

The mechanical properties (tenacity, elongation at break, Young's modulus) of unmodified, and modified – PP/PVA and PP/PVA/CL fibres were measured using 1112 Instron 1112 tensile tester in accordance with Standard Specification ISO 2062:1993. The coefficients of variation of these parameters were calculated as well.

Barrier properties

The barrier properties of the fibres were estimated on the basis of the transmittance from model samples of fabric prepared from the fibres used, measured by a Libra S12 spectrophotometer with deuterium lamp and the UPF, UVA and UVB were calculated according to Standard Specification STN EN 13758-1:2001. A model textile fabric was prepared by reeling on the metallic small rectangular frame, which has the same distant cuts (0.75 mm) on all edges.

Colour characteristics

The colour characteristics of dyed fibres were evaluated by the CIE Lab method. The colour parameters were estimated by the measurement of the reflectance curves using Ultrascan XE spectrophotometer equipment.

Morphology of surface

The morphology of the surface of unmodified PP and modified PP/PVA/CL was measured by Olympus BX 56 optical

microscope with use of the “analySIS” software for scanning the fibre surface.

Results and discussion

The PVA and PVA/CL affect the thermal behaviour of the PP matrix in anisotropic oriented PP/PVA and PP/PVA/CL fibres in their preparation as well as in isotropic PP/PVA and PP/PVA/CL systems (Table 1).

PP in anisotropic PP/PVA and PP/PVA/CL fibres forms a more stable α -modification with higher melt temperature, as observed during the 1st heating, than in pure PP fibres (Table 1). The melting temperature of PP in PP/PVA and PP/PVA/CL fibres is increased by about 4 °C and in the PP/PVA/CL fibres which had the same composition of PP, PVA and CL and were prepared at the same conditions, with only different treated conditions of nanoadditive, were increased by about 3 - 5 °C. The mixing of CL with ultrasound in glycerine provides the crystallisation of a more stable α -modification of PP with higher melting temperatures, but with a lower content of crystalline phase - crystallinity of PP. The melting enthalpies of anisotropic PP/PVA/CL fibres are lower approx. 2 - 8 J/g than the melting enthalpy of pure PP fibre. The PVA in anisotropic PP/PVA fibre practically does not influence the content of the crystalline phase of PP. On the basis of the results obtained, it can be observed that the addition of Cloisite 15A into the PP/PVA system, and the behaviour of PP during crystallisation is changed. Cloisite 15A behaves like a solvent of PP in this system because it decreases the ability of PP crystallisation (lower DH – Table 1) in oriented anisotropic PP/PVA/CL fibres.

Similar behaviour of PP in the PP/PVA and PP/PVA/CL isotropic systems evaluated on the basis of results from the 2nd heating was obtained. The melting temperatures of PP in isotropic PP/PVA and PP/PVA/CL fibres are identical to the melting temperature of pure PP fibre. PP crystallisation in PP/PVA or PP/PVA/CL fibres is greatly influenced by oriented stress during the spinning and drawing of the fibre, which does not affect the PP crystallisation of the isotropic system. The PP in isotropic PP/PVA and PP/PVA/CL systems, without oriented stress, forms similar crystal modifications, such as in pure PP, but the content of crystalline PP phase in the PP/PVA blend is higher than in pure PP, whereas

Table 1. Thermal properties of PP, PP/PVA and PP/PVA/CL fibers at 1st and 2nd heating and cooling; B – mixing, C – mixing with ultrasound.

PP/PVA/CL composition, wt. %	Symbol of fibres	Type of treatment	1 st heating			2 nd heating		
			T _m , °C	ΔH_m , J/g	DH, J/g	T _m , °C	ΔH_m , J/g	DH, J/g
100/0/0	A1	-	158.6	94.8	-	159.5	80.2	-
97/3/0	A2	-	162.7	92.3	0.3	159.4	98.2	20.4
96.5/3/0.5	A3	B15	162.5	88.9	-2.6	159.4	75.2	-2.2
96.5/3/0.5	A4	B30	161.0	85.8	-5.7	158.9	74.9	-0.5
96.5/3/0.5	A5	C5	163.2	90.3	-1.2	161.1	73.6	-3.8
96.5/3/0.5	A6	C15	163.5	83.6	-7.9	160.9	69.9	-7.5
96.5/3/0.5	A7	C30	164.0	82.3	-9.2	160.9	64.3	-13.1

Table 2. Tenacity (σ), elongation (ϵ), Young modulus (E) of PP, PP/PVA and PP/PVA/CL fibers.

PP/PVA/CL composition, wt. %	Symbol of fibres	Type of treatment	σ , cN/tex	ϵ , %	E, N/tex	UPF
100/0/0	A1	-	26.5	21	4.03	9.25
97/3/0	A2	-	18.6	65	1.97	9.81
96.5/3/0.5	A3	B15	19.0	104	1.76	11.82
96.5/3/0.5	A4	B30	18.5	115	1.72	9.45
96.5/3/0.5	A5	C5	22.4	59	1.88	10.47
96.5/3/0.5	A6	C15	22.2	66	1.76	10.25
96.5/3/0.5	A7	C30	22.5	74	2.01	12.99

the content of crystalline phase in the PP/PVA/CL is lower than in pure PP. The amount of PP crystalline phase in the PP/PVA fibre rose very significantly due to the affect of PVA during the 2nd heating. The lower melting enthalpies of the PP/PVA/CL fibres were measured, which decreases much more during the treatment of nanoparticles (Table 1). It again confirms that Cloisite 15A behaves like a solvent for the PP crystallisation in the PP/PVA/CL blend. Its effect with the time of treatment of Cloisite 15A in glycerine before the preparation of the fibre.

The mechanical properties of fibres relate to their morphological structure. Therefore it is necessary to evaluate the mechanical properties of all fibres prepared with different additives, which change their structure. Results of measurements of the mechanical properties (tenacity, elongation and Young's modulus) of the PP, PP/PVA and PP/PVA/CL are in Table 2. Taking the results into consideration, it is possible to say that the tenacity and Young Modulus of the modified fibres decreased or the elongation of these fibres increased. The results obtained are in harmony with the theory of tenacity of oriented systems – fibres with the addition of a very small content of any compound in the oriented fibre-forming system essentially decrease the tenacity of the fibre additive fibre in comparison with the tenacity of pure polymer fibres. Next, the difference in the mechanical properties of the PP/PVA/CL fibres was

found with different treated nanoadditives. The decrease in tenacity of the PP/PVA/CL fibres with the nanoadditive, treated using mixing with ultrasound, was lower by half than the decrease in the tenacity of the PP/PVA/CL fibres with nanoadditives, treated with mixing without ultrasound. Better dispersion of the nanoparticles of Cloisite 15A induces more evenness of structure and in the mechanical properties of the PP/PVA/CL fibres prepared with Cloisite 15A, treated using mixing with ultrasound.

The barrier properties of the PP, PP/PVA and PP/PVA/CL fibres were measured by spectrophotometer on the basis of Standard Specification STN EN 13758-1:2001 and the UPF results obtained are in Table 2. The PVA and PVA/CL have a positive effect on the barrier properties of PP/PVA and PP/PVA/CL fibres in comparison with PP fibre (Table 2). The higher growth of UPF was observed by the addition of PVA with nanoadditive Cloisite 15A in comparison without Cloisite 15A. The highest increase in UPF in the PP/PVA/CL fibre was found after it had been prepared with Cloisite 15A treated using mixing with ultrasound for 30 min. From this it would be reasonable to expect the best dispersion of nanoparticles, which provides sufficient barrier protection against UV radiation.

Next, the PP, PP/PVA and PP/PVA/CL fibres were dyed with disperse dyes by the classical process from the bath. The

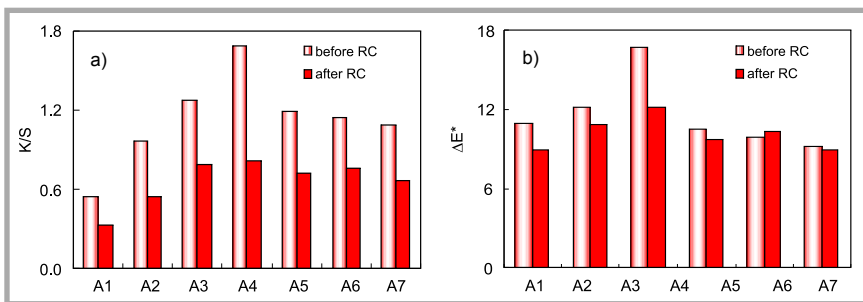


Figure 1. K/S (a) ΔE^* (b) of PP, PP/PVA and PP/PVA/CL fibers; Symbol of fibres as in Table 1.

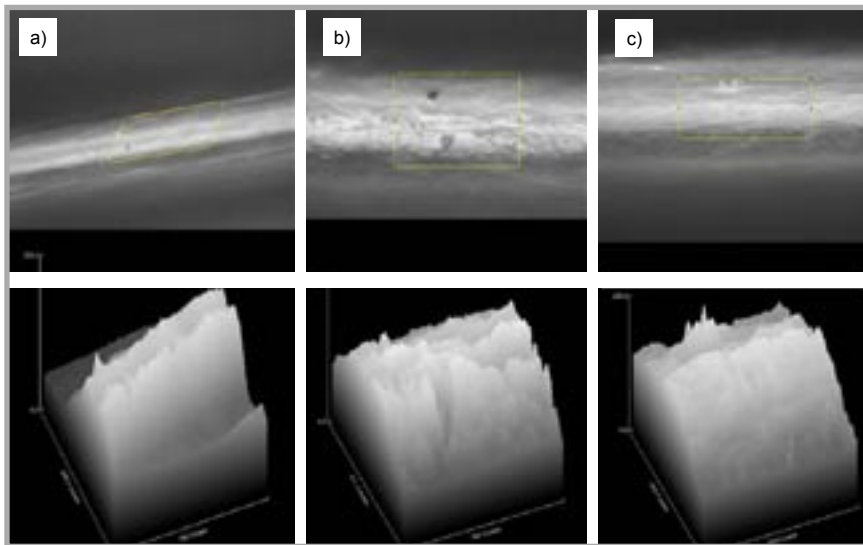


Figure 2. Surface of unmodified PP (a) and modified PP/PVA/CL (with mixing – b, with mixing and ultrasound – c) fibers.

results obtained, which were evaluated before as well as after reduction cleaning of the dyed fibres, are in the Figures 1, 2. These results of the colour properties of the fibres observed correspond with the previous results of the thermal and mechanical properties. The colour strength K/S and colour difference ΔE^* before and after reduction cleaning are higher in PP/PVA and PP/PVA/CL fibres than PP fibre. The PVA increases the K/S or ΔE^* of PP, which significantly rises with the addition of Cloisite 15A. The various treatments (time, mixing and mixing with ultrasound) of Cloisite 15A influence the K/S and ΔE of PP/PVA/CL fibres differently. The sorption of dye by fibre with Cloisite 15A, only with mixing without ultrasound, can be caused by the creation of more attractive dye places for the dyed molecules (Figure 1). The K/S and ΔE^* of these fibres after reduction cleaning markedly decrease which relates to the low fixation of dye in the fibre. Irrespective that the colour strength K/S and colour difference ΔE before the reduction cleaning of the dyed PP/PVA/CL fibres, which were prepared using nanoparticles

treated by mixing without ultrasound, are lower than fibre treated only by mixing, the fixation of dye in the fibre is better, because the loss of dye from the fibre during the reduction cleaning was very little. From these results it follows that more attractive places for the dye sorption in PP/PVA/CL fibres were created with mixing, but these places insufficiently fixate the sorptive dye molecules in the fibres.

Conclusions

1. The thermal properties of semicrystalline modified PP fibres depend on the additives used (PVA, PVA/CL) as well as on the conditions of treatment of the nanoadditive;
2. PVA including CL decreased the PP crystallisation in the preparation of the modified oriented (1st and 2nd heating) PP fibres in comparison with the PP fibre;
3. The crystallisation temperatures of modified PP/PVA and PP/PVA/NA fibres are higher in comparison with PP fibres;

4. The treatment of Cloisite 15A by mixing and ultrasound processing improves the evenness of the mechanical properties of PP/PVA/CL fibres in comparison with fibres which contain the Cloisite 15A which was only mixed;
5. PVA and PVA/CL improve the barrier properties of modified PP/PVA and PP/PVA/CL fibres;
6. The dyeability of PP/PVA/CL fibres dyed with dispersed dye and modified Cloisite 15A, treated only with mixing, is better than the dyeability of PP/PVA/CL fibres modified with Cloisite 15A, treated by mixing and ultrasound.

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References

1. <http://www.ntcresearch.org/pdf-rpts/AnRp02/M00-MD08-A2.pdf>.
2. Tjong Z. S. C., *Material Science and Engineering*, R 53, 2006, pp. 73-197.
3. Marcinčin A., Hricová M., Hoferiková A., *Vlákná a textil (Fibres and Textiles)*, Vol. 13(1-2), 2006, pp. 3-8.
4. Sarkar A.K., *Textiles for UV protection*. Vol. 13. 2005, Colorado: Woodhead Publishing, pp. 354-377.
5. Palacin F., *Textilvervedlung*, Vol. 31, 1996, p. 235.
6. Hliffker R. et al., *Textile Research Journal*, 66(2), 1996, pp. 62-69.
7. Vaera-Zaragoza M. et al., *Polymer Degradation and Stability* Vol. 91(2006) pp. 1319-1325.
8. Wang C.C. et al., *Journal of Colloid and Interface Science*, Vol. 273(2004) p. 80.
9. <http://www.ntcresearch.org/pdf-rpts/AnRp01/C01-D20-A1.pdf>.
10. <http://www.ntcresearch.org/pdf-rpts/AnRp02/C01-D20-A2.pdf>.
11. Chan C. M. et al., *Polymer*, Vol. 43(2002) p. 2981.
12. Benetti E. M. et al., *Supramolecular Polymer Assemblies*, Vol. 46(2005) p. 8275.
13. Li J., Zhou Ch., Gang W., *Polymer Testing*, Vol. 22(2003) pp. 217-223.
14. Chan C.M. et al., *Polymer*, Vol. 43(2002) p. 2981.
15. Benetti E.M. et al., *Supramolecular Polymer Assemblies*, Vol. 46(2005) p. 8275.
16. Bogun M. et al., *Fibres and Textiles in Eastern Europe*, Vol. 14(2006) No. 2(56) pp. 13-16.
17. Mikolajczyk T. et al., *Fibres and Textiles in Eastern Europe*, Vol. 12(2004), No. 3(47) pp. 19-23.

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