

Anton Marcinčin,
Marcela Hricová,
Anna Ujhelyiová,
*Ondrej Brejka,
*Peter Michlík,
Mária Dulíková,
Zuzana Strecká,
**Štefan Chmela

Department of Fibres and Textile Chemistry,
Institute of Polymer Materials, FCHFT,
STU in Bratislava,
Radlinského 9, 812 37 Bratislava, SK

*Research Institute for Man-Made Fibres,
Štúrová 2, 059 21 Svit, SK

**Polymer Institute, Slovak Academy of Science,
Dúbravská cesta 9, 842 36 Bratislava, SK
E-mail: anton.marcincin@stuba.sk

Effect of Inorganic (Nano)fillers on the UV Barrier Properties, Photo and Thermal Degradation of Polypropylene Fibres

Abstract

Barrier properties against ultraviolet radiation and the light stability of polypropylene (PP) fibres are very important for light-weight summer fabrics as well as for leisure and sport wear. What is more, the thermal stability of PP composites is required in the spinning process and in the thermal treatment of fibres and fabric. In this paper the effect of selected inorganic nanofillers, such as boehmites (aluminas), organoclays, nano TiO₂ and multiwall carbon nanotubes (MWCNT) on the UV barrier properties, photo-oxidation and thermal stability of PP composite fibres was studied. Correlations between the UV barrier properties, light stability and thermal stability of PP composite fibres are also discussed.

Key words: inorganic nano-fillers, UV barrier properties, photo degradation, thermal degradation, polypropylene fibres.

Introduction

The UV barrier properties and light stability of PP composite fibres are extremely important for textile products, light-weight summer fabric and leisure and sports wear. Furthermore, the thermal stability of PP composites is required in the spinning process as well as in the thermal treatment of fibres and fabric. Many papers have also dealt with the photo (light - induced) and thermooxidation of nanocomposites, but relatively poor information related to the effect of sunlight and elevated temperature on nanocomposite fibres and fabrics appears in periodic literature.

The UV radiation of sunlight can be divided into UV-C (100 – 280 nm), UV-B (280 – 315 nm) and UV-A (315–400 nm) components, which denote the effect on living organisms. The human skin has to be protected against UV-B type radiation only, while the most dangerous UV-C type is absorbed by the atmosphere. UV-A radiation is essentially less dangerous than the other two [1]. UV transmittance by textiles consists of both contributions: transmission through the space between yarns and transmission through fibres. The retardation of the transmittance is expressed by the ultraviolet protection factor (UPF) [1 - 4]. The UPF is affected mainly by the thickness and density of textiles, as well as by dyes, pigments and other compounds in fibres and textiles, such as pectin, wax, water, etc. [5]. Fabric construction is affected by both the fineness and density of the yarn in the wrap and weft. Furthermore, the transmission of UV radiation through fibres can be changed by the absorption

and reflection of ultraviolet beams. The mass pigmentation of fibres with suitable inorganic pigments, carbon black pigment, or inorganic (nano)filler may provide a permanent improvement of the UV protection of fibres with high fastness in washing [2]. Organic UV absorbers, such as monochlorotriazine derivatives, proved to be effective compounds for the improvement of the protective properties of cellulose fabric [3].

However, the improvement of the UV barrier properties of textile fibres with solid nano particles incorporated into the matrix of the PP fibres also requires them to be environmentally durable in their processing and utilisation. Photo and thermal degradation, especially of PP nanocomposites and composite fibres, has been a very attractive area of research in recent years [6 - 10]. The papers most often deal with the effect of UV irradiation on the photostability of PP/organoclay composites as well as with the role of pristine montmorillonite (MMT), compatibilisers and organic ammonium compounds in the oxidative degradation of polymers. The main negative effect on the photo degradation of PP was found for pristine MMT (catalytic active sites), PP grafted with a maleic anhydride compatibiliser (photoresponsive carboxylic and anhydride groups) and for alkyl ammonium compounds (the decomposition of ammonium ion leads to catalytic acidic sites) [6, 7]. Much faster natural photooxidation was found for PP/nano-CaCO₃ and PP/nano-SiO₂ in comparison with pristine PP. The higher photooxidation rate corresponded with a higher concentration of nanofillers [9].

Furthermore, an organically untreated inorganic boehmite filler decreases the photostability of PP/boehmite composites due to the absorption of stabilisers on the hydrophilic surface, which prevents their antioxidant action [10, 11]. The oxidative behaviour of organically modified boehmites in PP matrix depends on organic substituents. The oxidation rate is accelerated e.g. by a long-chain alkyl benzenesulfonate [10]. On the other hand, the enhancement of the photostability of polymers by some metal oxides, functionalised nanofillers and UV stabilisers has been reported [12 - 14].

Inorganic nanoparticles in polymer composites can also affect their thermal stability and fire retardancy. The improved thermal stability and fire retardancy of PP/organoclay composites (5 wt% of organoclay) were found. The suppression of the thermooxidation of PP composites is explained by the diffusion barrier and reduction in mass loss [8]. The photooxidation of PP/organoclay composites dramatically decreases the originally improved thermal properties. In this case the weak points are formed from the photooxidation reactions that take place mainly on the sample surface [8, 15].

In this paper the effect of inorganic nanofillers, such as organoclays, boehmites (aluminas) multiwall carbon nanotubes (MWCNT) and nano-sized TiO₂ on the UV barrier properties, photooxidation and thermal stability of PP composite fibres was studied. Correlations between the UV barrier properties, light stability and thermal stability of PP composite fibres are discussed.

■ Experimental

Materials used

Polypropylene:

- PP Moplen 500R (PP 500R), MFI 25 g/10 min, flakes; PP Moplen HP561R (PP 561R), MFI 25 g/10 min; PP Moplen HP561N (PP 561N), MFI 11 g/10 min, (all from Lyondell Basell Co., Italy)
- Polypropylene HPF (PP HP) with a melt flow index (MFI) of 8.0 g/10 min, in powder form, and Polypropylene TG 920 (PP TG) with a MFI of 10.5 g/10 min (both from Slovnaft a.s., Slovakia)

Fillers:

- Disperal 40 (D40), Al₂O₃ content 82.5 wt%, surface area 105 m²/g, (from Sasol Co., Germany)
- Cloisite 15A (C15A), Montmorillonite ion exchanged organoclay with dimethyl dihydrogenated tallow quaternary ammonium ions (from Southern Clay Product, USA)
- Multi-Wall Carbon Nanotubes - Nanocyl® 7000, (MWCNT), average diameter 10 nm, length 0.1 - 10 μm, surface area 250 - 300 m²/g, carbon content 90%, metal oxide impurity 10%, (from Nanocyl S.A., Belgium)

Nano TiO₂ fillers: Hombitec S 100, (TiO₂ S100), TiO₂ content 89.0 wt%, particle size 15 nm, specific surface 68 m²/g, (from Sachtleben, Inc., Duisburg, Germany), and UV Titan P160 (TiO₂ P160), content 80.0 wt%, particle size 17 nm, specific surface 59 m²/g (from Kemira Pigments Oy, Helsinki, Finland).

Compatibilisers:

- Slovacid 44P (S44P), ester of stearic acid and polypropylene glycol, (from Sasol Co),
- Tegopren 6875 (TEG), alkyl ester of polydimethylsiloxane, (from Degussa Co),
- PP-g-MA – PP grafted with maleic anhydride, (from Ciba Specialty)

Light (thermal) stabilisers

Commercial stabilisers: Uvasorb HA 88 (from 3V Sigma S.p.A, Bergamo, Italy), Irgafos 168 (from Ciba Co), Eversorb 90 and Eversorb 91 FD (both from Everlight Chemical Industrial Corporation, Pineville, NC USA)

Preparation of polypropylene nanocomposite fibres

The following two-step method was used for the preparation of PP nanocomposite fibres.

Preparation of masterbatches of nanofillers in PP (flakes, powder):

The PP HP, nanofiller and compatibiliser were mixed in a mixer of high r.p.m. for 3 min. The powder mixture was melted and kneaded using a twin screw corotating extruder (φ 28 mm). The temperatures of the extruder zones from the feedstock to the head were 80, 150, 220, 225, 225, 225 and 232 °C. The temperature of the extrudated melt was 229 °C. The extrudate was then cooled and cut. The concentration of the nanofiller in the PP HP was 10.0 wt%. The content of the compatibiliser was 4.0 wt%.

Melt mixing of PP nanocomposite:

C-spinning: Chips of the PP and PP/nanofiller masterbatch were mixed and spun using a single screw extruder (φ 15 mm) and spinneret with 13 orifices. The spinning temperature was 250 - 280 °C, the metering of the melt 11 g/min, the spinning speed 150 m/min, and the fineness of the as-spun multifilament was about 680 dtex. Fibres were drawn using a laboratory drawing machine at various drawing ratios, λ, at a drawing temperature of 120 °C.

D-spinning: The chips of the PP and PP/nanofiller masterbatch were mixed and spun using a single screw extruder (φ 30 mm) and spinneret with 40 orifices. The spinning temperature was 250 - 280 °C, the metering of the melt 30 g/min, the spinning speed 360 m/min, and the fineness of the as-spun multifilament was 840 dtex. Fibres were drawn using the laboratory drawing machine at various drawing ratios, λ, at a drawing temperature of 120 °C.

Methods used

Mechanical properties of the nanocomposite fibres

An Instron (Type 3343) was used for measurements of the tensile strength (T) and elongation at break (E), according to Standard ISO 2062:1993, as well as the Young's modulus (YM), according to Instron 3343 software.

Barrier against the UV radiation of PP nanocomposite fibres

The barrier properties of PP fibres modified with nanofillers were measured using a "Libra S12" spectrophotometer and evaluated on the basis of modified Standard STN EN 13758-1:2001. The modification of the method was in the preparation of the sample for measurement.

Before the measurement the nanocomposite PP fibres were wound on small metallic windows with cuts. The distance between cuts was 0.75 mm. Afterwards the transmittance through the layer of fibres was measured in the UV range. Consequently, the UPF was calculated by standard specification using the following equation:

$$UPF = \frac{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times S(\lambda) \times \Delta(\lambda)}{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times S(\lambda) \times T(\lambda) \times \Delta(\lambda)}$$

where: UPF – ultraviolet protection factor, $E(\lambda)$ – relative erythermal spectral effectiveness in W/m²·nm), $S(\lambda)$ – solar UVR spectral irradiance (Melbourne), $T(\lambda)$ – spectral transmittance of the sample, $\Delta(\lambda)$ – bandwidth in nm, λ – wavelength

Light stability of the PP nanocomposite fibres

The light stability of the PP nanocomposite fibres was investigated by two methods. The measurements consisted of the UV exposure of the fibres using two types of standard devices and the evaluation of changes in the basic mechanical properties of the fibres. The tenacity, elongation and Young's modulus of the fibres in dependence on the UV exposure time were evaluated according to ISO norms.

CAROUSEL TEST apparatus (the merry-go-round type set up) – method **A** and

Xenotest 450 – method **B** were used for the irradiation of fibres

Photo-oxidation of the PP nanocomposite films

PP composite films were prepared from masterbatch chips in an electrically heated laboratory press (Fontune, The Netherlands) at 190 °C for 1 min. The thickness of the films was ca. 0.1 mm. Photo-oxidation was performed on a merry-go-round type setup. The irradiation source was a medium pressure 250 W mercury arc with luminophore envelope (RVL, Tesla Holešovice, Czech Republic) with

$\lambda > 310$ nm. The temperature of photo-oxidation was 30°C. The progress of chemical changes was followed by FTIR spectroscopy (NICOLET-400 Germany). The shape of the carbonyl band was broad, since it indicated the presence of several carbonyl products. The course of degradation is represented as the dependence of the degree of carbonyl absorption (measured as the area of CO absorption bands divided by the film thickness) on the irradiation time.

Thermal stability of PP nanocomposite fibres

The thermal stability of nanocomposite polypropylene fibres was evaluated by DTA using Derivatograf Q-1500D apparatus according to the following procedure: A sample of the fibre was heated to 600 °C at a rate of 10 K·min⁻¹ under air atmosphere. The temperature of the half-weight loss T_1 as well as the destruction temperature T_d could be obtained from thermograms according to Standard STN EN ISO 11358.

Results and discussion

Characterisation of the PP composite fibres and their mechanical properties

The PP composite fibres were prepared at laboratory scale. The difference in spinning conditions (methods C or D), methods of evaluation of the photo-oxidation (methods A or B) and mechanical characteristics of the fibres are presented in **Tables 1 - 3**. The fibres were drawn at a middle drawing ratio. The mechanical properties of the fibres, mainly the tenacity, elongation and Young's modulus, correspond with fibres for textile use. Two kinds of fibres were prepared and examined: fibres spun using a laboratory spinning line with an extruder of D=16 (C) mm, and with an extruder of D=32 mm (D). The linear density of drawn multifilaments amounted to 80-110 dtex (individual fibre 6-9 dtex) and 260-300 dtex (individual fibre 6-7 dtex). An acceptable level of spinability was exhibited in the case of fibres based on PP/D40, PP/TiO₂ and PP/C15A compositions, while the spinning of the PP/MWCNT composite was at a substantially lower level. A higher tenacity of fibres was obtained at a low concentration of nanofiller in the polymer matrix, up to 1.0 wt%. A higher content of the nanofiller led to a decrease in the tenacity and Young's modulus of the fibres. Some additives and compatibilisers have a positive effect on mechani-

Table 1. List of the PP/Disperal composite fibres. T_1 – linear density of drawn multifilaments, T – tenacity, E – elongation, YM – Young's modulus, S – stabilisers in a total amount of 1.0 wt% of Uvasorb HA 88 and 0.1 wt% of Irgafos 168.

No.	PP/filler composition	Content of filler, %	Content of additives	T_1 , tex	T , cN/tex	E , %	YM , N/tex	Irrad. method A/B	Spinn. method C/D
1	PP 561N/D40	0.0	-	9.1	72.1	21.9	6.1	A	C
2		0.02	-	8.6	74.3	21.4	7.3		
3		0.05	-	9.0	75.4	20.6	7.2		
4		0.1	-	8.9	76.2	20.5	7.1		
5		0.3	-	9.8	69.0	22.9	6.6		
6		1	-	10.5	56.9	23.4	6.0		
7		3	-	12.2	43.8	30.5	4.6		
8	PP 500R/D40	0.0	-	11.2	63.0	21.2	7.6	A	C
9		5.0	-	16.3	38.1	41.1	4.9		
10		5.0	3% S44P	13.5	47.0	21.1	5.9		
11		5.0	5% S44P	14.1	40.7	25.4	5.0		
12		5.0	8% S44P	12.3	47.0	25.8	5.2		
13		5.0	3% TEG	12.3	55.7	21.7	6.2		
14		5.0	5% TEG	13.0	51.2	23.2	5.5		
15	5.0	8% TEG	14.2	36.4	21.3	4.1			
16	PP 500R/D40	0.0	S	14.3	38.4	40.7	5.2	A	C
17		5.0	S	14.9	37.3	46.9	5.2		
18		5.0	3% S44P + S	13.3	42.6	28.6	5.8		
19		5.0	5% S44P + S	14.1	37.6	43.6	5.1		
20		5.0	8% S44P + S	12.2	46.0	30.3	5.6		
21		5.0	3% TEG + S	11.9	50.6	20.5	6.7		
22		5.0	5% TEG + S	12.7	40.3	20.3	4.9		
23	5.0	8% TEG + S	12.3	46.4	21.8	5.5			

Table 2. List of the PP/C15A and PP/MWCNT composite fibres. T_1 – linear density of drawn multifilaments, T – tenacity, E – elongation, YM – Young's modulus.

No.	PP/filler composition	Content of filler, %	T_1 , tex	T , cN/tex	E , %	YM , N/tex	Irrad. method A/B	Spinn. method C/D
24	PP 561N/C15A	0.0	10.6	68.13	22	9.3	A	C
25		0.01	11.3	58.05	23	6.8		
26		0.1	12.1	54.29	23	6.1		
27		1.0	11.6	57.05	22	6.5		
28		3.0	11.1	53.11	23	6.5		
29	PP TG/C15A	0.0	27.8	33.50	94	3.3	-	D
30		0.02	28.9	32.00	94	3.2	-	
31		0.1	28.0	31.60	95	3.1	-	
32		1.0	27.9	30.80	102	3.2	-	
33		3.0	28.3	2.74	98	3.0	-	
34	PP TG/MWCNT	0.02	28.3	19.99	102	3.0	A	D
35		0.05	27.6	19.85	104	3.1	-	
36		0.1	27.4	20.01	115	2.9	-	
37		0.3	27.5	16.49	103	2.8	A	

Table 3. List of the PP/nanoTiO₂ composite fibres. T – tenacity, E – elongation.

No.	PP/filler composition	Content of filler, %	T , cN/tex	E , %	Irrad. method A/B	Spinn. method C/D		
38	PP TG/TiO ₂ S100	0.0	52.2	38.7	B	D		
39		0.05	52.1	47.3				
40		0.1	5.00	54.5				
41		0.2	48.9	54.6				
42		0.4	48.1	51.5				
43		0.6	47.7	51.1				
44		1.0	43.2	37.9				
45		2.0	39.5	21.3				
46		0.0	52.4	38.7			B	D
47		0.05	50.3	42.6				
48	0.1	50.1	44.8					
49	0.2	48.3	50.0					
50	0.4	44.9	53.5					
51	0.6	44.3	52.4					
52	1.0	41.4	56.3					
53	2.0	37.2	60.4					
54	0.0	52.3	38.7	B	D			
55	0.1	47.8	62.5					
56	0.4	44.9	61.5					
57	0.6	44.4	60.6					
58	1.0	42.9	59.0					
59	2.0	38.1	51.4					
60	3.0	37.5	52.3					
61	0.1	47.2	55.2			B	D	
62	0.4	45.8	59.4					
63	0.6	44.3	55.2					
64	1.0	42.9	54.5					
65	2.0	40.0	48.6					
66	3.0	36.1	29.2					

Table 4. Ultraviolet protection factor (UPF) of the PP/D40 ($T_1 \approx 10.5 \times f_{13}$) and PP/TiO₂ S100 composite fibres ($T_1 \approx 12.0 \times f_{40}$).

PP/filler composition	Content of D40, %	UPF	PP/filler composition	Content of TiO ₂ S100, %	UPF
PP 561N/D40	0.00	5.3	PP TG/TiO ₂ S100	0.0	4.8
	0.02	5.4		0.2	5.2
	0.05	6.1		0.4	5.3
	0.10	5.9		0.6	6.4
	0.30	6.1		1.0	5.7
	1.00	7.9		2.0	6.8
	3.00	8.3		3.0	8.5

Table 5. UV barrier properties (UPF) of the PP/D40/filler composite fibres; S – fibres with stabilisers in total amount of 1.0 wt% Uvasorb HA 88 and 0.1 wt% of Irgafos 168.

PP/filler composition	Content of filler, %	Content of additives	UPF	UPF (S)	PP/filler composition	Content of filler, %	Content of additives	UPF
PP 500R/D40	0.0	-	5.47	7.08	PP 561R/D40	0.0	-	7.83
	5.0	-	8.04	6.66		0.2	0.8% PP-g-MA	5.23
	5.0	3% S44P	6.09	7.31		1.0	4.0% PP-g-MA	5.56
	5.0	5% S44P	6.28	8.17		0.1	0.04% TEG	9.50
	5.0	8% S44P	7.39	7.05		0.5	0.2% EG	8.48
	5.0	3% TEG	6.92	7.54		5.0	2.0% TEG	9.22

Table 6. UV barrier properties (UPF) of PP/MWCNT and PP/C15A composite fibres.

PP/filler composition	Content of filler, %	UPF	PP/filler composition	Content of filler, %	UPF
PP 561R/MWCNT	0.0	~28.5	PP TG/C15A	0.0	~29.0
	0.02	32.6		0.02	33.4
	0.05	31.8		0.10	35.3
	0.10	36.3		1.00	39.4
	0.30	48.4		3.00	44.3

cal properties at an optimum concentration (data in Table 1 are for PP/D40 composite fibres). The fibres were examined from the point of view of the UV barrier properties, photo-oxidation stability and thermal properties.

UV barrier properties of the PP composite fibres

The results of the UV barrier properties of PP composite fibres confirmed the expected positive impact of nanofillers in the form of a reduction in the transmittance of UV irradiation through a thin defined layer of fibres. The results in **Table 4** show a gradual increase in the UV barrier properties of PP fibres containing dispersed D40 and TiO₂ S100 particles. The UPF factor increased for both nanofillers, by about 20% for a content of 0.3 wt% and by 50% for 3.0 wt% of solid particles in the PP matrix. The increment of the UPF factor decreased for a higher concentration of nanofillers, and at a content above 3.0 wt% of solid particles in the PP fibres, there was a negligible, positive effect of the modification on the UV barrier properties of the fibres. Very effective concentrations of fillers D40 and TiO₂ S100 were found within 0.1 -

1.0 wt%, where the enhanced UPF factor corresponded with higher or non-reduced tensile properties (**Tables 1, 3 & 4**).

The positive effect of oligomeric additives (non-ionogenic surfactants) on the UPF factor of PP composite fibres was expected because of the higher degree of dispersion of solid particles in the polymer matrix. This expectation was confirmed for alkyl polydimethyl siloxane (TEG). The synergistic effect of this additive shifted the UPF factor to higher values for both lower and higher concentrations of nanofiller D40 (**Table 5**). The oligomeric surfactant S44P exhibited a negligible impact on the barrier properties of the fibres, and the reactive compatibiliser PP-g-MA decreased the UPF value of the composite fibres below that of the original unmodified ones. On the other hand, the PP/D40/S44P fibres stabilised using a Uvasorb HA 88 light stabiliser and Irgafos 168 thermal stabiliser exhibited slightly improved UV barrier properties, but they did not achieve those of fibres containing the TEG additive.

Outstanding UV barrier properties were exhibited by PP composite fibres con-

taining MWCNT and organoclay Cloisite 15A at low concentrations. A gradual increase in UPF was found within a concentration of MWCNT of up to 0.3 wt% and C15A up to 3.0 wt% in PP fibres (**Table 6**). The higher UPF values in **Table 6** correspond with a higher total linear density of the fibres in comparison with those in **Table 4**. The increment of the UPF for PP/C15A fibres is in harmony with the UPF of the PP/D40 and PP/TiO₂ fibres. Comparing the nanofillers examined, an apparently higher UV barrier efficiency exists with the presence of MWCNT fibrous nanofiller in the PP fibres.

The dependences in **Figure 1** indicate the higher UV prevention efficiency of knitted fabric prepared at a lower tension of fibre during knitting, i.e. when the density of the fabric is not so compact. The difference between modified and unmodified fabric is smaller for more compact fabric (higher knitting tension).

The positive impact of the solid particles of nanofillers in the matrix of oriented PP composite fibres at a low concentration on the UPF results from two contributions: the direct interaction of solid particles with UV irradiation, and the changes in the supermolecular structure of fibres during deformation and orientation. In all cases the highest UPF increment corresponds with the highest orientation of fibres, i.e. their highest tenacity and modulus as well as the highest crystallinity and structure density assumed (excluding PP/MWCNT fibres).

Light stability of the PP composite fibres

The effect of D40, C15A, nanoTiO₂ and MWCNT in PP composite fibres on the photo-oxidation of PP as well as the possibility of stabilising the fibres using commercial light stabilisers were inves-

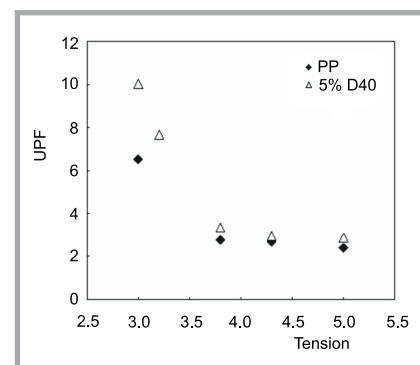


Figure 1. Dependence of UPF on the tension in the preparation of the knitted fabrics from pure PP fibre and PP fibre with 5% wt. D40.

tigated. The change in the tenacity of the fibres during irradiation was taken as a measure of their resistivity against UV photo-oxidation and degradation (**Figures 2 - 6**). The results reveal a gradual decrease in the tenacity of PP fibres with an increase in the concentration for all nanofillers examined (**Figures 2 - 4**), excluding MWCNT (**Figure 6**). At a higher concentration of inorganic nanofillers D40 and C15A, similar effects on the photo-degradation of the PP composite fibres were obtained (**Figure 2**). The decrease in the tenacity of irradiated fibres of 1 - 3 wt% was sharp after a relatively short irradiation time, about 200 hours. The negative effect of a lower concentration, up to 0.1 wt% of solid particles, appeared at a longer UV exposure time, over 300 hours. In any case, the degradation of PP composite fibres due to dispersed D40 and C15A nanofillers is already apparent at a low content in the PP fibres, up to 0.1 wt%. The extremely negative effect of these solid nanoparticles on the light stability of the PP composite fibres was found above a concentration of 1.0 wt%, in spite of using originally stabilised PP 561N and PP 561R for the spinning of the fibres examined (**Figure 2**).

An extremely negative effect of the D40 nanofiller on the light stability of PP fibres was found for a content of 5.0 wt%, with a negligible effect of compatibilisers-dispersant (**Figure 3.a**). The total degradation of the fibres occurred after up to 200 hours of UV irradiation. The negative interactions of the D40 nanofiller, leading to a decrease in fibre tenacity after UV irradiation, were suppressed when commercial light and thermal stabilisers were incorporated into the PP matrix together with a nanofiller (**Figure 3.b**). It seems that introducing a suitable stabiliser into the polymer composite together with a nanofiller, as with the concentration, is an effective way of stabilising the fibres against photo-oxidative degradation.

A similar negative effect on the degradation of PP composite fibres was found for nano TiO₂ S100 and P160 (**Figure 4**). Xenotest apparatus was used for the accelerated ageing of fibres (Method B). The tenacity of both samples of fibres exposed gradually decreased when the concentration of nano TiO₂ in the fibres increased. The results of UV barrier properties (UPF) (**Table 5**) and degradation of these fibres under UV irradiation

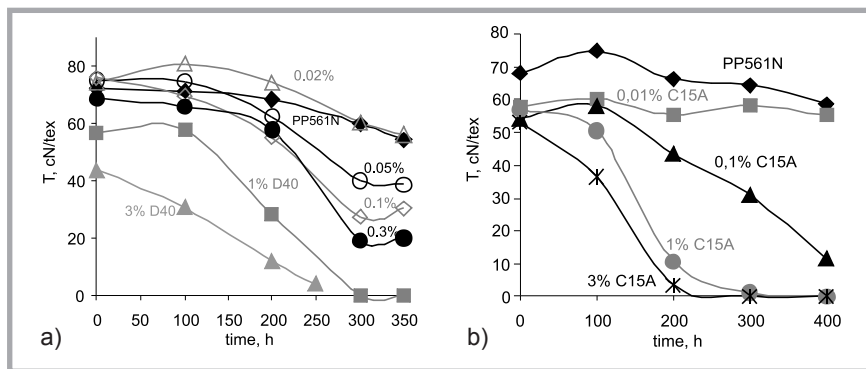


Figure 2. Dependence of the tenacity on the UV exposure time for PP/D40 (a) and PP/C15A (b) composite fibres containing various amounts of D40 and C15A (irradiation by method A).

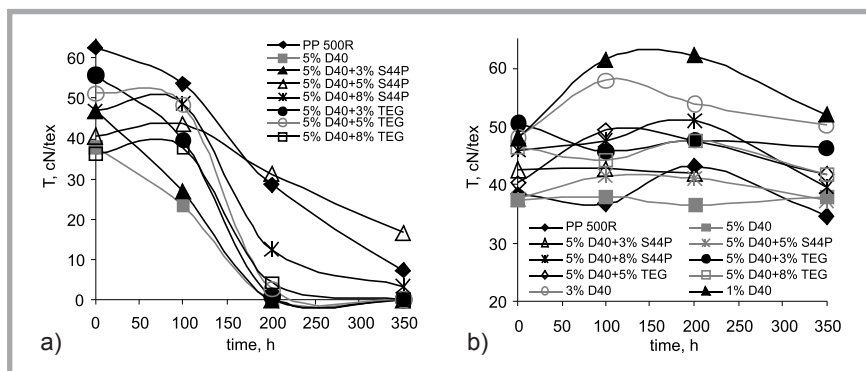


Figure 3. Dependence of the tenacity on the time of UV exposure for PP/D40 and PP/D40/compatibiliser composite fibres without stabilisers (a) and with stabilisers (b) in the total amount of 1.0 wt% of Uvasorb HA 88 and 0.1 wt% of Irgafos 168, (irradiation by method A).

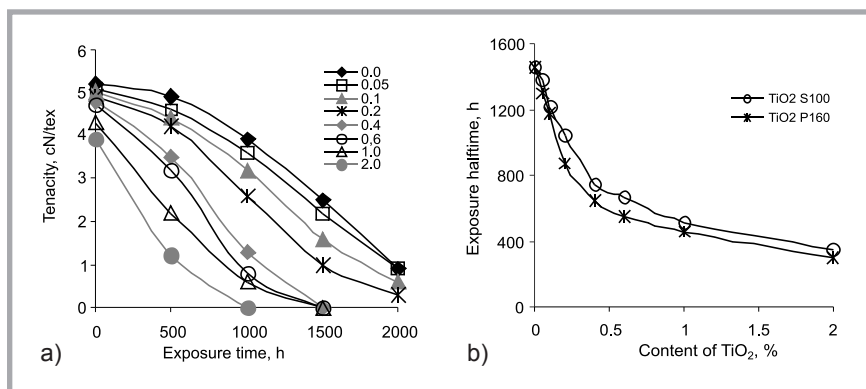


Figure 4. Dependence of the tenacity on the UV exposure time for PP/TiO₂ S100 fibres (a) and dependence of the UV exposure halftime on the TiO₂ content for PP/TiO₂ fibres (b); (irradiation by method C).

(**Figure 4**) are comparable with those obtained for PP/D40 and PP/C15A composite fibres (**Figure 2**). The positive effect of nano TiO₂ on the UV barrier properties of PP composite fibres is accompanied with accelerated degradation of fibres at the same environmental conditions. The efficient light stabilisers were meant to prevent the negative influence of nano TiO₂ on PP fibres. The most efficient stabilisers from the HALS series, Eversorb 90 and Eversorb 91FD, were selected on the basis of experimen-

tal results. The positive effect of these stabilisers, leading to the retardation of photo-degradation in PP/nanocomposite fibres, is given in **Figure 5**. Both stabilisers, used in the amount of 0.3 wt%, were efficient at lower concentrations of the nanofiller, up to 1.0 wt%. Their efficiency sharply decreases at a concentration of nano TiO₂ above 1.0 wt%. It can be assumed that certain higher concentrations of the stabiliser could ensure the required light stability of fibres containing over 1.0 wt% of nano TiO₂.

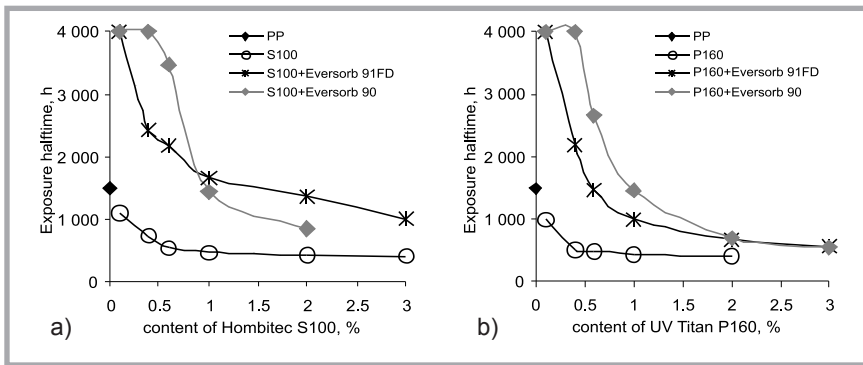


Figure 5. Dependence of the UV exposure half-time on the content of nano-TiO₂ in the fibres: (a) nanoTiO₂ S100 and (b) nanoTiO₂ P160 were used with and without 0.6 wt% of Eversorb stabilisers, (irradiation by method B).

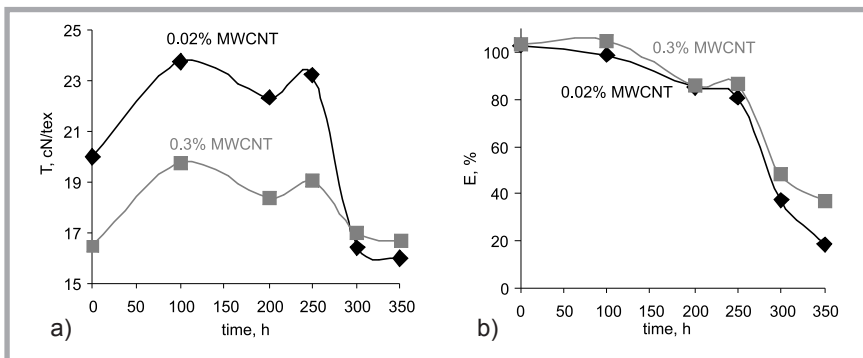


Figure 6. Dependence of the tenacity (a) and elongation (b) of PP/MWCNT fibres on the UV exposure time, (irradiation by method A).

Table 7. Temperature at 50% weight loss (T_1) and the degradation temperature (T_d) of the PP/D40 composite fibres.

PP/filler composition	Content of filler, %	Draw ratio λ	T_1 , °C	T_d , °C
PP 561N/D40	0.00	8.0	459	501
	0.02	8.0	438	499
	0.02	8.5	445	499
	0.05	8.5	430	499
	0.10	8.5	438	498
	0.30	7.5	439	499
	1.00	7.0	445	499
	3.00	7.0	455	498

The quite different behaviour of MWCNT as a nanofiller in PP fibres was found during the irradiation of PP/MWCNT composite fibres in comparison with previous inorganic nanofillers. A negligible decrease in tenacity after 350 hours of irradiation was indicated for 0.3% of MWCNT, and a slightly greater one (4 cN/tex) was found for 0.02% of the nanofiller (Figure 6.a). On the other hand, the elongation of PP/MWCNT fibres in the exposure time investigated changes considerably from 100% to 20% for 350 hours of irradiation (Figure 6.b), which means that interactions of UV irradiation with PP/MWCNT fibres lead to the creation of a rigid net that prevents

the elongation of fibres under external tension, in spite of retaining the original level of fibre tenacity. The mechanism of net formation can be explained by chemical interactions of PP chains with active sites on the MWCNT surface. This can lead to chemical bonding between PP and MWCNT. The rigid structure of fibres can also result from the arrangement of the supermolecular structure. MWCNT acts as an efficient nucleating agent for PP.

The different behaviour of PP/D40 and PP/MWCNT fibres under UV irradiation (Figure 2, 6) results from the extremely accelerated photo-oxidation of fibres containing D40 and from the re-

tardation of the photo-oxidation of the PP matrix in the presence of MWCNT nanofiller, expressed e.g. by concentration of carbonyl groups (Figure 7). The very short induction period for PP/D40 (100-200 hours) and the longer one for PP/MWCNT fibres (250 - 300 hours) in comparison with unmodified PP fibres (300 - 350 hours) correspond with their light stability (Figure 2 & 6.a).

Thermal stability of the PP composite fibres

The thermal stability of PP/D40 and PP/MWCNT composite fibres was investigated using TG analysis. The experimental results are given in Figure 8, which reveal that the thermal stability of PP/D40 composite fibres without thermal and light stabilisers is acceptable up to 3.0 wt% of D40 in the PP matrix, including compatibilisers. The temperature at a 50 % weight loss is, on average, 20 °C lower when compared with unmodified PP fibres (Figure 8.a, Table 7). The stabilisation of PP/D40 composites with common thermal and light stabilisers leads to an improvement in the thermal stability of composite fibres and to an almost negligible decrease in weight loss in comparison with standard PP fibres (Results are not given here). The destruction temperature T_d of PP/D40 composite fibres does not depend on stabilisation, and for all the samples it has practically the same value.

In spite of the similar shape of thermograms, the PP/MWCNT composite fibres exhibited apparent higher thermal stability, evaluated on the basis of the temperature at 50% weight loss of the sample in comparison with PP/D40 fibres, (Figure 8.b).

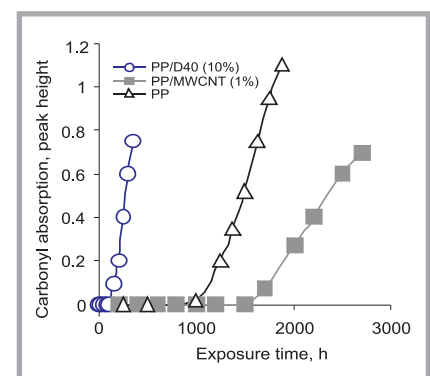


Figure 7. The dependence of the concentration of carbonyl groups in the PP and PP nanocomposite films on the UV exposure time (photo-oxidation study).

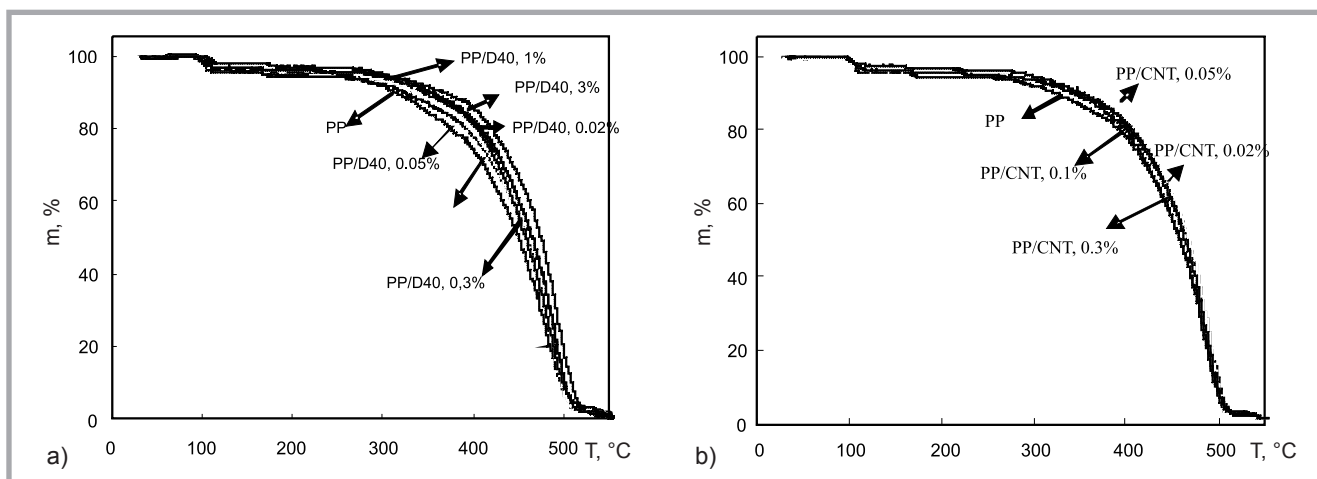


Figure 8. TG thermograms of PP/D40 (a) and PP/MWCNT (b) composite fibres for various contents of nanofillers.

TG thermograms with negligible changes, the weight loss being dependent on the nanofiller content, were also obtained for PP/C15 composite fibres (Results are not given here).

In any case, the dependence of the weight loss of PP composite fibres containing inorganic nanofillers D40 and MWCNT on the temperature shows the acceptable thermal stability of the fibres for common use.

Conclusions

On the basis of the experimental results, the following conclusions can be drawn:

- The positive impact of boehmite Disperal 40, organoclay Cloisite C15A, nano TiO₂ and MWCNT nanofillers in the matrix of oriented PP composite fibres on their UV barrier properties (UPF) at low concentrations of the nanofiller was found. For all the composite fibres, excluding the PP/MWCNT fibres, the highest UPF increment corresponds, with the highest orientation of the fibres, i.e. their highest tenacity and modulus.
- The unambiguous negative effect of the nanofillers investigated, excluding the MWCNT, on the light stability of PP composite fibres was found. This effect results in a gradual decrease in the tenacity of UV irradiated PP fibres with a higher content of solid additives.
- PP/MWCNT fibres exhibit a negligible decrease in tenacity over the exposure time, but there is a sharp decrease in elongation, creating a rigid net that prevents the elongation of fibres under external tension.
- An effective way of stabilising fibres against photo-oxidative degradation consists in adding a suitable stabiliser

to the polymer composite at the same time as the nanofiller with a similar concentration.

- The TG thermograms of PP composite fibres containing inorganic nanofillers D40 and MWCNT show the acceptable thermal stability of fibres for common use.

Acknowledgment

The experimental work was supported by EU FP6 Project: NMP3-CT-2005-516972 "NANOHYBRID", Slovak Agency APVV, project APVT 20-011404 and Agency VEGA, project 1/0444/09.

References

1. Reinert G., Hilfiker R., Schmidt E., Fuso F., Sonnenschutzigenschaften textiler Flächen und deren Verbesserung, *Textilveredlung* 31 (1996) pp. 227-234.
2. Hanke D., Hoffman K., Altmeyer A., Schindler G., Schon U., Wirppertal, Klotz M.L., UV Protection by Textiles, *Chemical Fiber International* 47 (1997) pp. 130-131.
3. Czajkowski W., Paluszkiwicz J., Stolarski R., Kaźmierska M., Grzesiak E., Synthesis of reactive UV absorbers, derivatives of monochlorotriazine, for improvement in protecting properties of cellulose fabrics, *Dyes and Pigments* 71 (2006) pp. 224-230.
4. Hoffmann K., Kaspar K., Gambichler T., Altmeyer P., In vitro and in vivo determination of the UV protection factor for lightweight cotton and viscose summer fabrics: A preliminary study, *J. Am. Academy of Dermatology* 43 (2000) pp. 1009-1016.
5. Palacin F., Textile finishing protects against UV rays, *Textilveredlung* 31 (1996) pp. 235-238.
6. Mailhot B., Morlat S., Gardette J. L., Boucard S., Duchet J., Gérard J. F., Photodegradation of polypropylene nanocomposites, *Polymer Degradation and stability* 82 (2003) pp. 163-167.

7. Qin H., Zhang S., Liu H., Xie S., Yang M., Shen D., Photo-oxidative degradation of polypropylene/montmorillonite nanocomposites, *Polymer* 46 (2005) pp. 3149-3156.
8. Diagne M., Gueye M. Vidal L., Tidjani A., Thermal stability and fire retardant performance of photo-oxidized nanocomposites of polypropylene-graft-maleic anhydride/clay, *Polymer Degradation and stability* 89 (2005) pp. 418-426.
9. Li J., Yang R., Yu J., Liu Y., Natural photo-aging degradation of polypropylene nanocomposites, *Polymer Degradation and stability* 93 (2008) pp. 84-89.
10. Bocchini S., Morlat-Thérias S., Gardette J.L., Camino G., Influence of nanodispersad boehmite on polypropylene photooxidation, *Polymer Degradation and stability* 92 (2007) pp. 1847-1856.
11. Chmela Š., Friedlerová A., Borsig E., Erler J., Muelhaupt R., Photo-oxidation and Stabilization of sPP and iPP/Boehmite-Disperal Nanocomposites, *Journal of Macromolecular Science. Pure and Applied Chemistry* 44 (2007) pp. 1027-1034.
12. Gordienko V. P., Dmitriev Y. A., The degradation and stability of polyethylene with small additions of metal oxides under UV-irradiation, *Polymer Degradation and stability* 53 (1996) pp. 79-87.
13. Lim Y. T., Lee T. W., Lee H. Ch., Park O.O., Enhanced photo-stability of conjugated polymer nanocomposites doped with functionalized nanoparticles, *Optical Materials* 21 (2002) pp. 585-589.
14. La Mantia F. P., Tzankova Dintcheva N., Malatesta V., Pagani F., Improvement of photo-stability of LLDPE-based nanocomposites, *Polymer Degradation and stability* 91 (2006) pp. 3208-3213.
15. Tidjani A., Wilkie Ch. A., Photo-oxidation of polymeric-inorganic nanocomposites: chemical, thermal stability and fire retardancy investigations, *Polymer Degradation and stability* 74 (2001) pp. 33-37.

Received 03.03.2008 Reviewed 11.06.2009