DETERMINATION OF PHYSICO-MECHANICAL AND RHEOLOGICAL PROPERTIES OF SILANE-TREATED WOOD FLOUR POLYPROPYLENE COMPOSITES

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ABSTRACT

Polypropylene composites with untreated and silane-treated wood flour in amounts from 1 to 50 mass % were obtained and characterized. The functionalization of the initial and pre-treated with NaOH wood flour was carried out in 0.003 % solution of vinyltrimethoxysilane. To estimate the effect of the different treatments on the chemical structure, the state and the morphology of the wood flour surface were studied by SEM, XRD and FT-IR analyses. The melt flow index, die swell effect, tensile properties, water absorption and Shore hardness of the materials obtained containing untreated and treated fillers were determined.

Keywords: *polypropylene, wood flour, surface treatment, properties, structure.*

INTRODUCTION

Despite that the natural wood fillers have a number of advantages, there are certain limitations by the development of polymer-wood composites with good mechanical properties. The main disadvantage is the low compatibility between the polar wood fillers with the non-polar polymer matrices such as polypropylene [1, 2]. To achieve acceptable material properties and form a composite with good interfacial bonding and effective stress transfer throughout the interface, adhesion must be improved practically all the time [3, 4].

Numerous approaches to the physical and chemical modification of the filler or the matrix have been attempted aiming to improve the compatibility and the bonding between the wood filers and the polymers [5]. What they have in common is that the wood flour hydrophilicity is reduced and its wettability by the polymer matrix is improved which actually ensures the adhesion between the components of the composite material. The following methods used to treat wood fillers have been reported in the literature: coupling with functional silanes, enzymatic, heat, esterification, mercerization, acetylation treatment, coating the wood flour with stearic acid, etc. [5 - 9].

Significant interest attracts the use of coupling agents, e.g. alkoxysilanes, aiming to improve the adhesion between the wood fillers and the polyolefin matrices and minimize the adverse effects on the mechanical properties of the composites. After the treatment of the filler surface with alkoxysilanes, the alkoxy groups (–Si–O–CH_3) hydrolyze to form silanol groups (–Si–OH). The latter react with the cellulose hydroxyl groups and from covalent bonds (–Si–O–C–) between the silane coupling agent and the surface of the filler [4, 6, 9]. The modifying effect of the silanes (with amino, thiol or acrylate functional groups) used as wood flour modifiers for preparation of composites with improved mechanical properties was confirmed [10]. In one of their publications where six different silanes were discussed, Li et al. established that vinyltrimetoxysilane (A-171) is the best coupling agent for wood flour (WF)/ high density polyethylene (HDPE) composites [11]. The influence of the silane treatment on the surface properties

e.g. wettability, surface chemistry was studied, as well as their relation to the physico-mechanical properties of the wood-plastic plywood [12, 13]. Compared to the non-treated WF/HDPE composites, both the mechanical properties and water resistance of the composites were improved. The concentration of the A-171 solution had no significant effect on the mechanical properties of the composites [11]. In another work, the bond-modifying properties of three silane coupling agents were studied. Again, the most effective agent turned out to be vinyltrimetoxysilane (VTMS). Applied together, the surface modification (with NaOH and H_2SO_4) and coupling agents (silanes) showed synergetic effect which contributes for the improvement of the bond between PE and wood [14]. As reported in another paper, 3-aminopropyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane and VTMS were used for modification of WF. The treatment with silanes significantly improved the tensile strength, bending strength and impact strength of the polypropylene (PP) composites but the authors did not find unambiguous differences between the silanes [15]. Sohn et al., observed an improvement of the impact strength up to 55.8 %, tensile strength up to 33.8 % and insignificant decrease of the bending modulus in improvement of the compatibility between PP matrix and WF by initiating hydrophobic modification of WF using alkali treatment and silane coupling process [16]. In another work Ichazo et al., treated the WF filler with sodium hydroxide and vinyl-tris-(2-methoxyethoxy)-silane. They observed the same tendency of a slight increase in the modulus and tensile strength of the composites. Morphological studies show that the use of PP functionalized with maleic anhydride and silane improves particle adhesion and dispersion, while alkaline treatment only improves dispersion [17].

Regardless of the previous research in this direction, there are still divergences in the scientific literature. The results reported do not allow making firm conclusion about the most effective kinds of silanes. The available data revealing the influence of the filling with WF and the different treatments with silanes on the mechanical, thermal and other properties of the materials are quite unconvincing. Nevertheless, the silane coupling agents have certain potential in their use to improve the interaction in wood-polymer composite materials. The considerations above determined the aim of the present work, namely to study the effect of the surface treatments and the degree of filling with wood flour on the basic properties of polypropylene based composites.

EXPERIMENTAL

Materials

Wood flour (WF) was supplied by Kronospan Bulgaria Ltd, polypropylene (PP) grade 6531, commercial product of Lukoil Neftochim Burgas with melt flow index 3.5 g 10 min^{-1} (230°C/2.160 kg); sodium hydroxide (NaOH) with molecular mass 40.00 g mol^{-1} and purity 98 %, product of Marvin Ltd, Dimitrovgrad and vinyltrimethoxysilane (VTMS) with chemical formula $C_5H_{12}O_3Si$, boiling point 123°C, molecular mass 148.23 g mol^{-1}, density 0.968 g mL^{-1} and purity 98 %, product of Sigma-Aldrich.

Preparation of the filler

The wood flour was dried in a laboratory dryer at temperature 60°C for 24 h. The fraction composition of filler was determined on laboratory analytic vibro sieves. The set of sieves used contained sieves with opening diameters 0.8; 0.63; 0.315; 0.25; 0.16; 0.1 and less than 0.1 mm. The selected fraction with a particle size between 0.25 - 0.16 mm was stored in containers for further characterization and chemical modification.

Wood flour surface treatments

Alkali treatment (NaOH)

For this treatment, 2M NaOH solution was used. The volume of the solution was equivalent to 1.5 times the volume of the wood flour. The filler was kept in the solution for 30 min and then it was washed with distilled water to remove the residual NaOH. The treated wood flour was dried for 24 h [17].

Silane treatment

The treatment of the initial wood flour and the one pre-treated with NaOH was carried out in 0.003 % solution of VTMS in distilled water. The solution obtained was stirred with magnetic stirrer for 5 min. Further, the wood flour was soaked in silane solution at ratio 1 : 5 for 15 min and drying at temperature of 100°C to hydrolyze the coupling agent [18]. After treatment with the above reagents, the resulting treated fillers were stored at room temperature in glass containers. Untreated

and treated wood flour samples with NaOH and VTMS were designated as WF, Na-sWF and sWF, respectively.

Preparation of silane-treated wood flour polypropylene composites

The mixing of the polymer with treated and untreated wood flour was carried out in laboratory rolls at temperature 170°C and mixing duration of 5 min. The compositions prepared were pressed on a laboratory press PHI (England) between aluminium foils under the following conditions: samples thickness about 1 mm, temperature 180°C, melting period 10 min at 180°C, pressing pressure 9 MPa for 5 min, followed by cooling to 40°C at cooling rate 20ºC min^{-1}. The series of polypropylene composites obtained had filler contents as follows: 1; 3; 5; 10; 20; 30; 40 and 50 mass %, respectively.

Characterization of the fillers

Loose density

The loose density was determined by free and uniform filling of a cylinder with volume of 25 cm^3. After weighing the amount of wood flour (WF, sWF and Na-sWF), the loose density was calculated by the formula: $\rho = m/V$, where: ρ - is the loose density of the material, g cm^{-3}; m - mass of the material, g; V - volume of the material, cm^3.

Fourier Transform Infrared Spectroscopy (FT-IR)

The effect of the different treatments on the chemical structures of the wood flour was studied by FT-IR analysis. The infrared spectra of the fillers before and after the chemical treatment were registered in the wavenumber region from 4000 cm^{-1} to 400 cm^{-1} on spectrophotometer Nicolet iS 50 FT-IR Thermo Scientific equipped with DTGS KBr detector (4 cm^{-1}) at scan number of 32.

Scanning electron microscopy

SEM analyses were performed on a JSM 6390 electron microscope (Japan) in conjunction with energy dispersive X-ray spectroscopy (EDS, Oxford INCA Energy 350) equipped with ultrahigh resolution scanning system (ASID-3D) in regimes of secondary electron image and back scattered electron image. Before attempting SEM characterization, the sample must be clean and completely dry. Surface oils or dirt must be removed with solvents such as methanol or acetone. The sample is mounted on a double coated conductive carbon tape that holds the sample firmly to the stage surface and can be used as a ground strap from the sample surface to sample holder. The samples were gold coated for ~ 40 s. Gold at that thickness will have little or no effect on elemental analysis. The accelerating voltage was 20 kV, I ~ 75 mA. The pressure was of the order of 10^{-4} Pa.

X-ray Diffraction analysis

The X-ray diffraction patterns were taken by using a PANalytical Empyrean apparatus at atmospheric pressure, room temperature, Ni-filtered Cu target K_α radiation in the interval $2\theta = 5 - 80°$.

Characterization of the composite materials

Melt flow index

The melt indices of the initial PP and the composition based on it, containing wood flour, were determined by the melt flow index (*MFI*, g 10 min^{-1}) method on an apparatus MFI 3350 Prodemat (France) at temperature of 230ºC and load 2.160 kg according to standard EN ISO 1133.

Die swell effect

The die swell effect of the composites and pure polypropylene, expressed by the coefficient of expansion (B) which is calculated by the formula: $B = D/d$, where: d - die diameter, mm; D - diameter of the extruded samples, mm, measured after cooling the extrudates to temperature 23°C.

Water absorption

Samples of each composite type were weighted to a precision of 0.001 g. The samples were then placed in distilled water and kept at room temperature. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. Weights of the specimens were measured after 24 h. The values of the water absorption in percentage were calculated using the following equation [19]:

$$WA_t = \frac{W_t - W_0}{W_0} \times 100$$

where: WA_t is the water absorption at time t; W_0 is the oven dried weight and W_t is the weight of specimen at a given immersion time t.

Tensile Properties

The tensile strength (σ, MPa), elongation at break (ε, %) and the Young modulus (E, MPa) for the initial polypropylene and its composites with untreated and silane-treated wood flour were measured according to EN ISO 50527-1 on a dynamometer INSTRON 4203 (England) at speed of 50 mm min^{-1} and room temperature.

Hardness by Shore

The hardness by Shore of the composites was determined on an apparatus „Stendal" (Germany), scale A.

RESULTS AND DISCUSSION

To improve the interaction on the interface WF - PP matrix, two approaches are commonly used: modification of the filler or modification of the matrix by introduction of additives (coupling agents). The first approach was used in the present work, i.e. the WF surface was treated with organofunctional silane coupling agent (VTMS). The following procedures were carried out: (i) preliminary alkali (NaOH) treatment of the surface followed by functionalization with silane coupling agent and (ii) simple functionalization of WF with VTMS. The loose density of the treated and untreated WF (iii) was determined and the products obtained were characterized by SEM, XRD and FT-IR analysis.

The fractionation analysis of the initial powdery wood flour carried out indicated that the predominating fraction had laboratory sieve opening diameter of 0.25 - 0.16 mm (Table 1). It was nearly 53 % of the total mass analyzed and for this reason it was selected for further treatment and preparation of the polymer compositions. The use of the coupling agent VTMS and NaOH for treatment of the initial wood flour, as described in the Experimental section, lead to a decrease of the filler loose density from 0.1989 g cm^{-3} (for WF) to 0.1967 and 0.1794 g cm^{-3} for Na-sWF and sWF, respectively.

The state and the morphology of the surface are important factors determining the wetting of the filler by the PP matrix and strongly affect the degree of dispersion and the properties of the composite materials obtained [20]. Fig. 1 shows SEM images of untreated wood flour, as well as sWF and Na-sWF functionalized with silane. Before the treatment, the wood flour has fibrous structure and smooth surface (Fig. 1(a)). After treatment of the WF with silane, the surface morphology changed (Fig. 1(b)). The changes observed are probably due to the formation of silane coating on the surface of wood flour [21]. The mercerization or filler treatment with NaOH can be used single process or for activation of the surface for further treatment [8]. The alkali treatment of the wood flour results in partial removal of the lignin and hemicellulose

Table 1. Fractional composition of wood flour.

Laboratory sieve d, mm	Fraction m_i, g	Granulometric composition, %
0.8	0.12	0.24
0.63	0.35	0.70
0.315	0.29	0.58
0.25	2.73	5.46
0.16	26.41	52.81
0.1	4.35	8.70
< 0.1	15.24	30.48
total	49.48	98.96
Loss of material	0.52	1.04

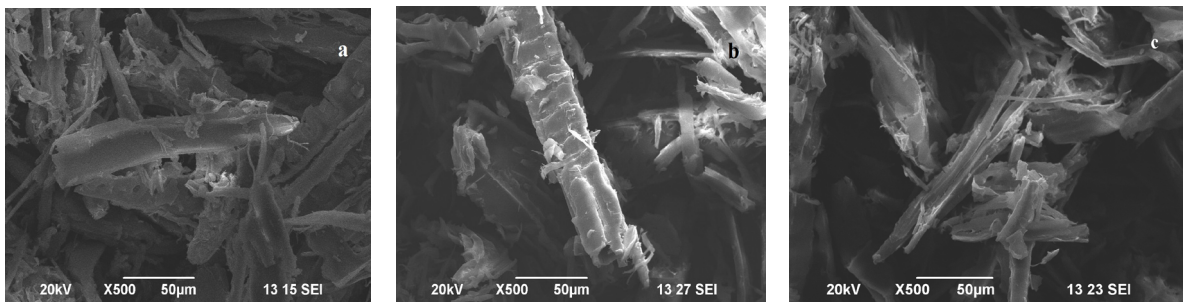

Fig. 1. SEM images of untreated (a); silane-treated (b); and alkali treated wood flour with subsequent silane functionalization (c).

[6] thus creating rough surface topography (Fig. 1(c)).

Fig. 2 shows the X-ray diffraction (XRD) patterns of pure WF, Na-sWF and sWF. It can be seen that all the diffractograms contain three diffraction peaks at 2θ = 16.0° (101), 22.5° (002) and 34.7° (040), which originated from the crystalline region of the cellulose in the wood flour [22]. The peak at 2θ of 18° represents the amorphous region of cellulose [23].

The results showed that the crystal structure of WF was not destroyed after the functionalization with VTMS. As can be seen in Fig. 2, the intensity of the three crystal surface characteristic peaks decreased as a result from the filler surface treatment carried out. The intensity of the diffraction peaks (101, 002) that mainly affected the wood flour crystallinity decreased most significantly for sWF. In the process of the wood flour silane treatment, some of the VTMS atoms probably enter into the void of wood flour and penetrate the amorphous area of the wood cell wall. This, in turn, leads to increase of the amount and decreases the crystallinity of the wood flour [24]. The relative crystallinity of Na-sWF was higher than that of sWF since the alkali treatment results in removal of the natural and artificial impurities from the surface, as it has been confirmed by SEM (Fig. 1(c)), which increases the amount of crystalline cellulose.

The modifying effect of the VTMS additive on the filler surface was confirmed by FT-IR analysis. Fig. 3 shows the changes observed in WF spectra before and after its treatment. It can be seen in Fig. 3(a) that the IR spectrum of untreated WF has intense bands localized at 604, 1640 and 3383 cm^{-1} which characterize off-plane vibrations, bending vibrations and stretching vibrations of O–H fragments present in the wood flour [25], respectively. The pronounced peaks at 1056 and 1270 cm^{-1} are related to C–O stretching vibrations in the lignin and cellulose structures. On the other hand, the bands shaped like shoulders and localized at 1106 and 1153 cm^{-1} indicate for the C–O–C bending vibrations in lignin composition [26]. The bands in the range from 1300 to 1500 cm^{-1} characterize off-plane vibrations, bending vibrations of C–H bonds in the structures of methyl ($–CH_3$) and methylene ($–CH_2$) fragments. Beside off-plane and bending vibrations, the presence of C–H stretching vibrations in cellulose were also registered in the infrared spectrum of WF, indicated by the intense peak at wavenumber value of 2898 cm^{-1}. The absorption band at 1730 cm^{-1} is due to the C=O stretching vibrations in carbonyl groups present in lignin composition. The bands at 1510 and 1592 cm^{-1} show in-plane vibrations of C=C in aromatic rings contained in the compositions

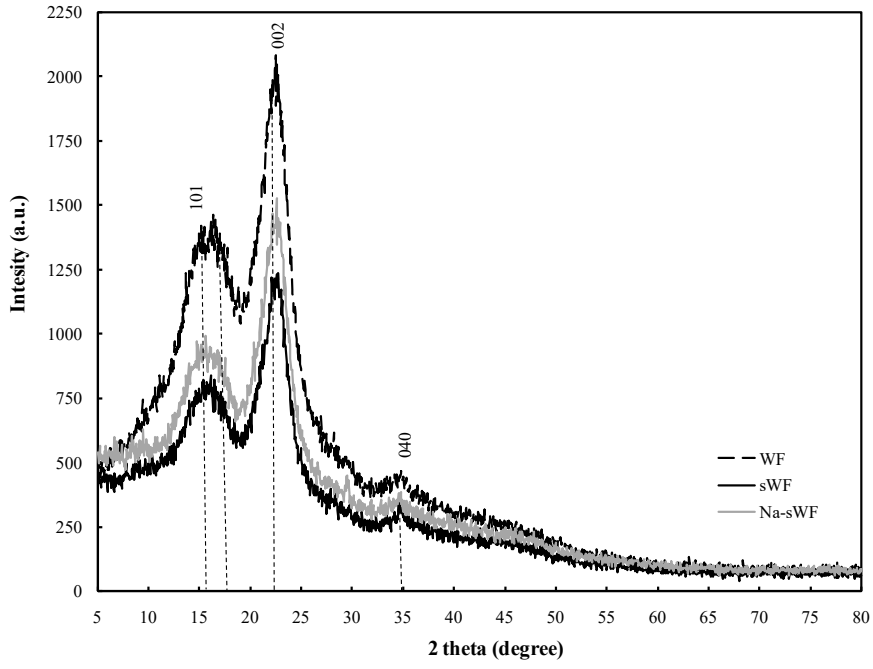

Fig. 2. XRD diffraction patterns of untreated (WF); silane-treated (sWF); and alkali treated wood flour with subsequent silane functionalization (Na-sWF).

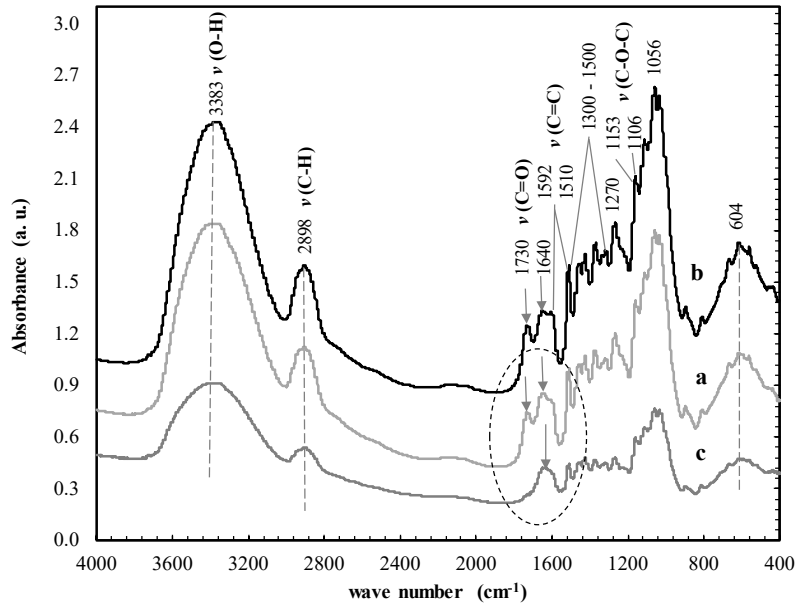

Fig. 3. FT-IR spectra of untreated (a); silane-treated (b); and alkali treated wood flour with subsequent silane functionalization (c).

of both cellulose and lignin [27].

It was found that the profile of the WF infrared spectrum underwent certain changes after the treatment with VTMS (Fig. 3(b)). The changes can be described as slight increase of the intensities of the absorption bands at 604, 1106, 1153, 1640, 2898 and 3383 cm^{-1} in the spectrum of the wood flour after the treatment. This might be due to the superposition of additional vibrations of C–O and C–H in the structure CH_2=Si$(OCH_3)_3$ [28]. Since the bands at 604, 1640 and 3383 cm^{-1} characterize O–H groups, the surface effects are probably related to the formation of intermolecular hydrogen bonds (Si–O···C–O(H) and C–O···H–C) by the interaction of oxygen atoms present in the WF/VTMS structure with the hydrogen atoms present in the structure VTMS/WF. The lack of widening of the infrared bands after the modification of the wood flour could be connected to the low number of newly formed intermolecular bonds, probably due to the low content of the modifier (< 1 wt. %). After the pre-treatment with NaOH followed by functionalization of filler surface with silane, the intensities of all the peaks registered in the IR spectrum decreased (Fig. 3(c)). It means that the reagents used reacted with the surface of the initial wood flour. The peak observed at 1730 cm^{-1} for WF and sWF (Figs. 3(a) and 3(b)) is not present in the spectrum of Na-sWF (Fig. 3(c)). This is due to the partial delignification of the WF surface as a result of the alkali treatment carried out.

It was found that the treatments carried out affected the surface characteristics of the wood flour. It is important from practical point of view to find out the relationship between the different treatments of the filler, the degree of filling and the physico-mechanical and the rheological properties of the PP/WF materials. The melt flow index (*MFI,* g 10 min^{-1}) is an important technological indicator for the thermoplastics which is directly connected to their processing into products. With the addition of 1 mass % wood flour, the melt flow index of the pure initial PP (3.66 g 10 min^{-1}) decreased from 3.66 to 2.74 g 10 min^{-1} and then gradually changes until filling degree of 10 mass % (Table 2). The presence of coupling agent and the pre-treatment with NaOH during the second stage resulted in more gradual decrease of the *MFI* so it was measured to be 3.60 and 3.45 g 10 min^{-1} at 1 mass % content of sWF and Na-sWF, respectively. The same tendency was observed up to filling degree of 10 mass % for the composites filed with sWF and up to 20 mass % for these filled with Na-sWF. The values of the melt flow index determined for the compositions discussed here were 2.24 and 2.06 g 10 min^{-1}. The increase of the filler content to 50 mass % impedes polymer fluidity so the melt flow index for all the materials was in the range 0.61 - 0.19 g 10 min^{-1}. The different values of the *MFI* observed were due to the difference in the

Table 2. Melt flow index and die swell effect of PP composites with different contents of untreated and silane-treated wood flour.

Sample	Melt flow index, g 10 min^{-1}			Die swell effect		
	WF	sWF	Na-sWF	WF	sWF	Na-sWF
Initial PP	3.66			1.30		
PP + 1 mass %	2.74	3.60	3.45	1.25	1.25	1.30
PP + 3 mass %	2.48	3.16	2.97	1.10	1.10	1.20
PP + 5 mass %	2.46	2.97	2.78	1.10	1.10	1.20
PP + 10 mass %	2.43	2.24	2.54	1.05	1.05	1.10
PP + 20 mass %	1.66	1.69	2.06	1.00	1.00	1.00
PP + 30 mass %	1.20	1.12	0.98	1.00	1.00	1.00
PP + 40 mass %	0.71	0.60	0.83	1.00	1.00	1.00
PP + 50 mass %	0.43	0.19	0.61	1.00	1.00	0.90

dispersed compositions of the fillers [29 - 31]. The finer dispersed silane treated WF possesses larger active area which facilitates the establishment of adhesion interactions on the phase border between the filler and the polymer and the result is that the fluidity of the composites decreased more gradually.

The preliminary treatment followed by functionalization and the simple use of VTMS for the WF improved the compatibility with the polymer. The sliding of the PP macromolecules was eased so the fluidity of the melts was more uniform (up to 10 - 20 mass % filling). At higher content of the filler - up to 50 mass %, equal saturation of the filler with polymer occurred, as a result of which the *MFI*s for the compositions with treated and untreated wood flour were closer to each other and the differences between them disappeared.

Table 2 shows the same that the increase of the filler content resulted in decrease of the Die swell (*B*) of the extrudates which is identical for all the composite materials made with treated and untreated wood flour. The change varied from 1.30 for the initial polypropylene to 0.90 - 1.00 for the filled with up to 50 mass % composites. This is most probably due to the restraining influence of the filler on the orientation of the PP macromolecules during the flow out from the die. Besides, the fillers exert steric hindrance because of the physical interactions taking place at the border between the two phases so the mobility of the polymer macromolecules is limited and the fluidity decreases which is confirmed by the results obtained for the melt flow index.

The influence of the WF and treated WF, as well as its amount on the tensile strength (σ, MPa) of the PP based composites was studied and the results obtained are summarized in Table 3. As can be seen from Table 3, the tensile strength of the composites containing 1 mass % filler WF, sWF and Na-sWF (24.08, 23.73 and 21.09 MPa) was higher than that of the pure PP (15.04 MPa). Further increase of the content of these fillers up to 30 mass % gave tensile strengths in the range from 16.86 to 20.66 MPa which is still higher than that of the initial PP. The retention of the tensile strength values of the composites at WF concentrations up to 30 mass % can be explained with the improved chemical compatibility between the wood flour and the PP matrix resulting from the filler treatment with VTMS. Thus, the adhesion between the two components of the composites can be significantly increased so the stress from the PP matrix to the filler can be distributed evenly. At 40 mass % content of untreated and silane-treated WF, the tensile strength of the compositions studied had values close to these of the initial PP - about 17 MPa. With further increase of filler contents, σ began to decrease and reached 14.02 and 9.78 MPa, respectively. The decrease of the tensile strength of the WF/PP composites observed is in accordance with the results reported by Bouza et al. [32].

The change of the elongation at break (ε, %) of the materials obtained is also shown in Table 3. The initial PP had elongation of 42.8 %. The introduction of 1 mass % WF in the PP matrix resulted in elongations at break decreased to 19.3 % and 10.4 % for the materials

Table 3. Tensile properties of PP composites with different contents of untreated and silane-treated wood flour.

Sample	Tensile strength, MPa			Elongation at break, MPa			Young`s modulus, MPa		
	WF	sWF	Na-sWF	WF	sWF	Na-sWF	WF	sWF	Na-sWF
Initial PP	15.04			42.8			756		
PP + 1 mass %	24.08	23.73	21.09	19.3	10.4	26.2	855	948	683
PP + 3 mass %	23.35	22.44	20.95	9.7	10.0	25.8	931	950	685
PP + 5 mass %	23.92	22.87	19.86	6.9	6.4	16.9	984	951	705
PP + 10 mass %	22.78	22.35	19.13	6.8	5.6	14.9	999	963	709
PP + 20 mass %	21.02	22.37	18.39	5.3	4.2	7.9	1081	1149	795
PP + 30 mass %	18.53	20.66	16.86	3.6	3.0	6.4	1131	1215	838
PP + 40 mass %	17.00	16.54	14.99	2.9	2.6	4.9	1141	1251	923
PP + 50 mass %	14.67	9.78	14.02	2.2	1.8	2.9	1197	1251	1046

with untreated and silane treated WF, respectively. For the samples containing 1 and 3 mass % Na-sWF, the property studied had values of about 26 %. With further increase of the content of Na-sWF in the compositions, ε gradually decreased and at 10 mass % Na-sWF the elongation at break was ~ 15 %. The latter value is almost 2 and three times higher than these for the samples with WF and sWF containing the same amount of filler.

The use of higher amounts of fillers lead to additional decrease of the elongation and at filler contents in the range 20 - 50 mass % ε was almost independent on its amount and surface treatment and was found to be in the range from 2 % to 8 %. Similar behavior after adding natural fillers in PP have been reported by a number of researchers [32, 33]. The decrease of the elongation at break of the composites is probably due to decrease of macromolecules' mobility because of the formation of physical bonds between the filler and the polymer, as it has been concluded from the values of the melt flow index (Table 2).

It can be seen from the Table 3 that all the compositions containing sWF and non-modified wood flour had significantly higher Young modulus (E, MPa) compared to the initial PP - 756 MPa. It is well known that the value of the modulus of the filler is one of the main factors having certain effect on the modulus of the composites obtained, i.e. the high modulus of the wood flour compared to that of the pure PP can be the reason for the increase of the property studied after the introduction of WF in the PP matrix [33 - 35]. For the composites containing silane treated sWF, the Young modulus was higher even at only 1 mass % filler content and it was 948 MPa. This can be due to the better distribution of the wood flour in the PP matrix because of the silane treatment [17]. Significantly stronger was the increase of the elasticity modulus after the addition of sWF, especially for the materials containing 30 and 40 mass % filler. Thus, for the PP based materials with 40 mass % sWF, the modulus reached values of 1250 MPa. In this case, the higher elasticity modulus was probably due to the improved adhesion between the PP matrix and the VTMS functionalized wood flour [33]. This additional increase of the modulus was observed also for the materials with 50 mass % sWF which allows obtaining high hardness of the materials obtained. For all the compositions with untreated WF and sWF, the hardness was in the range 86 - 93.

The Young modulus of the samples with content 1 - 10 mass % Na-sWF, shows values lower than that of the PP matrix. NaOH treatment is possible to cause excessive delignification of the filler. In turn this can damage the treated wood flour and negatively affect the modulus of elasticity [5]. The reduced values of Young's modulus are consistent with the measured Shore hardness of materials with 1 - 10 mass % Na-sWF, precisely 63 - 69. When sufficiently large amounts of 20 to 50 mass % Na-sWF are used, the modulus of elasticity (795 - 1046 MPa), exceeds that of the polymer matrix, but still remains lower than this material with untreated and sWF. Above 20 mass % filling degree of Na-sWF,

a tendency to increase the hardness of the materials up to about 90 is observed.

Water absorption (*WA*) behavior of the samples with untreated and treated wood flour was measured by immersion in water for 24 h and the results are illustrated in Fig. 4. For all the compositions studied, *WA* increased with the increase of filler content from 1 to 50 mass % which is in accordance with the data published by other authors [36 - 39]. The PP based materials containing VTMS functionalized wood flour showed the lowest values of water absorption, e.g. it was 3.79 % at 50 mass % sWF. This value is lower than that for PP with WF at the same filler content (4.77 %). The reason for this difference is that, on one hand, the coupling agent used forms silane coating on the surface of the wood flour particles (Fig. 1(b)) which protects it and reduces the water absorption of the composites. On the other hand, the presence of higher number of hydroxyl groups with the higher content of filler stipulate the higher *WA* of the composites with untreated WF.

It was found that there is no big difference of the water absorption between the PP based composites with untreated WF and these with Na-sWF (Fig. 4). The shapes of the curves for these materials are quite similar up to 40 mass % filler content. The filler content of 50 mass %, *WA* of the materials with Na-sWF was higher than that of the materials with untreated WF - the values measured were 5.40 and 4.77 %, respectively. The difference in the *WA* can be attributed to the fact that the alkali pre-treatment of the wood flour creates porous and coarse surface (Fig. 1(c)) which can easily absorb water.

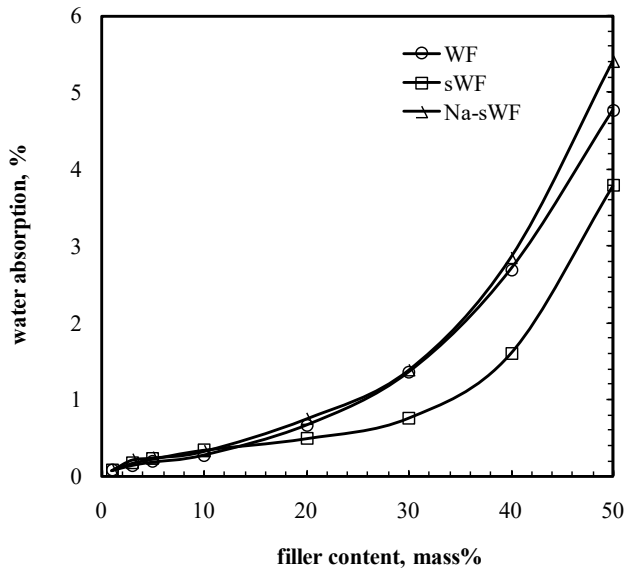

Fig. 4. Dependence of water absorption on the filler content in polypropylene composites.

CONCLUSIONS

Preliminary alkali treatment of the surface of wood flour followed by functionalization with silane coupling agent and simple functionalization with vinyltrimethoxysilane were carried out. It was found that treatments affected the surface characteristics of wood flour. The physico-mechanical and rheological properties of the resulting wood flour filled composites were determined and compared to these of polypropylene samples containing untreated filler. The presence of coupling agent and the pre-treatment with NaOH of the secondary phase gave more gradual decrease of the melt flow index of the compositions containing up to 10 and 20 mass % filler. The tensile strength at filler content of 40 mass % untreated and silane-treated wood flour in the compositions was higher than that of the pure polypropylene - 15.04 MPa. It was found that the elongation at break of the compositions with 10 mass % pre-treated with NaOH wood flour was almost 2 and 3 times higher compared to that of the samples with untreated and silane-treated wood flour, respectively, at the same contents of the filler. The use of wood flour contents from 20 to 50 mass % in the compositions resulted in decreased elongation and the latter was almost independent on the surface treatment and the amount of the filler used. For the polypropylene based materials containing 40 mass % silane-treated wood flour the Young reached value of 1250 MPa. Using pre-treated wood flour, this property had lower values than these observed for the materials with untreated and silane-treated wood flour. The lowest values of the water absorption 3.79 % possessed the compositions containing 50 mass % wood flour functionalized with vinyltrimethoxysilane.

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