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POLYPROPYLENE COMPOSITES WEAR RESISTANCE PROPERTIES DUE TO SPELT AND OAT GRAIN HUSKS SHORT FIBER PREPARATION TECHNOLOGY

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Abstract: This work presents several results of the investigations about mechanical properties and wear resistance of polypropylene based short fibre composites, reinforced with spelt and oat husk fibres. The spelt and oat short fibre material both sieved and unsieved is used to characterise sieving effect on the properties of the end material, analogous to wood polymer composites that already are in use in different applications. The developed composites of polypropylene matrix with and without organoclay powder also are investigated in order to enhance thermal as well as moisture absorbing characteristics and barrier properties. To get more information about wear resistance of such materials and effects of the different components and the fibre preparation technology on wear resistance Taber wear test is applied using CS10 abrasive.

Keywords: wear, Taber, grain husks, density.

1. INTRODUCTION

This investigation is a second part of test series made on wood polymer composites previously [1]. Main interest for previous study was commercial products of wood flour for wood-polymer composites (WPC) and it use possibility in different "hard" wear applications such as floor covering materials. Knowing model system for wood-polymer composites it become possible to make wear test on the husk-polymer composite that is the main interest of our research. As previously, polypropylene (PP) is used as a polymer matrix for this composites. Typical reinforcement for WPC are short fibres in size less than 0.75 mm that it would be possible to use such materials for standard injection moulding processing technology [2]. Grain husks could be an alternative to wood flour for such polymer composites due to the much lower application. It is possible to use wood flour in automotive, building and constructions industries and, of course, energetics [3–4]. Grain husk application is on very low level and more connected with some aspects of agro technical sector (food supplement, energetics). When grains come to mill they are separated from husks, straw and other impurities. All these residues, if not used properly used, produce great amount of waste. Consequently, grain husks can be perspective alternative for wood flour [5–8]. That's why main interest of this work is spelt and oat husks with as small as possible cleaning and pre-processing to make the material cheaper. Industry is more interested in a short time processing technology at the same time it is clear that high quality fibres with a better reinforcement effect is possible to obtain only by using clean and uniform fibre with small size deviation. On other hand in order to enhance mechanical (flexural, tensile, impact properties), thermal as well as moisture absorbing characteristics and barrier properties it is possible to use clay [9, 10]. There is quite high quantity of such publications, but only few of them are related to evaluation of wear resistance of such systems.

With new European Union directives and strategy "The Single-Use Plastics Directive" and "EU Plastics Strategy" use of plastic material will be greatly restricted [11, 12]. It is big part of economy

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that's why it is very important to change the application of traditional plastic materials from short life cycle to long life cycle materials. Use of husks renewable material with the harvest every year looks more promising than wood flour rejuvenated once per 20–40 years.

2. 2. EXPERIMENTAL

2.1. Materials

As matrix we used injection moulding grade polypropylene homopolymer HP400R from Basell-Orlen Polyolefins, Poland, with high flowability, MFR = 25 g / 10 min (230°C / 2.16 kg). As filler we used spelt (Triticum spelta) and oat (Avena sativa) husks from JSC "Rigas Dzirnavnieks" (Latvia) and UAB "Malsena Plius" (Lithuania) respectively. Husks were sieved to separate different impurities and crushed to short fibres with higher aspect ratio. A polypropylene to grain husk short fibres weight ratio of 60/40 was used for composite manufacturing in this investigation. As a compatibilizer between the non-polar matrix and the polar cellulosic fibers maleic acid anhydride grafted PP wax (MAH–g–PP) TP Licocene PP MA 6452 from Clariant, Germany, was applied in the amount of 3.3 wt.% in relation to the matrix. We also used organo modified nanoclays I.44P from Nanocor Inc to develop hybrid composites consisting of 57 wt.% polypropylene (PP+MAH–g–PP), 40 wt.% grain husks fibers and 3 wt.% organo clays.

2.2. Processing

Short fiber preparation technology in this study was similar for spelt and oak husks. Using mechanical sieves, the supplied material was cleaned from straws, husks with grains inside, small grain particles, dusts etc. Thus obtained material was conditioned at RH=50±5% and T=23±2ºC for at least 24 h. Completely dried husks were not optimal for milling process, because the material become brittle and the aspect ratio of the obtained products was considerable reduced. For milling we used Retsch SM300 cutting mill with sieve 0.75 mm. This type of material we encoded as ON and WN, oat husks none sieved and spelt husks none sieved, respectively. The products after previous milling operation were sieved by using 0.05 mm and 0.5 mm sieves to clean the product from all dust type impurities on the one hand, and to ensure optimal husks aspect ratio on the other hand. To obtain the end products we used Multiserv LPzB–2e, Poland, pneumatic sieves. These products were encoded as OS and WS, oat husks sieved and spelt husks sieved, respectively. Husks short fibers were dried for 16 hours at 103ºC in a vacuum chamber, but clays were dried for 8 h. All components were weighted with precision 0.01 g. After drying process finished materials were immediately placed in the desiccator with $CaCl_2$ and stored till extrusion. Extrusion was made using two-screw co-rotating extruder/compounder L/D 16 PRISM TSE 16 TC, from Thermo Electron Corporation. Thermal profile was 170, 175, 180, 185, 190ºC. Screw rotating velocity 50 min^{-1}. After extrusion material was cooled down in a water bath and cut into pellets, after than extruded material was dried once more for 4 hours and then rectangular plates were produced using compression moulding machine Scientific LP–S–50/ASTM, from Labtech Engineering, Thailand. Compression moulding was done at 200ºC with preheating time 5 min, pressing time 5 min, pressure 5 MPa and ramp cooling till 40ºC temperature at cooling rate of 15ºC / min. 2 mm thick square plates with side dimension 10 cm were obtained. In the center of the sample 6.3 mm hole was drilled for the wear test. The obtained materials are shown in table 1.

Table 1. Samples for Taber test**.**

Code	**PP**	**MAH–g–PP**	**Oat husks fibers milled**	**Oat husks fibers sieved**	**Spelt husks fibers milled**	**Spelt husks fibers sieved**	**Organo clay**
	wt.%	wt.% of PP	wt.%	wt.%	wt.%	wt.%	wt.%
PP	100	–	–	–	–	–	–
ON	60	3.3	40	–	–	–	–
OS	60	3.3	–	40	–	–	–
ONC	57	3.3	40	–	–	–	3
OSC	57	3.3	–	40	–	–	3
WN	60	3.3	–	–	40	–	–
WS	60	3.3	–	–	–	40	–
WNC	57	3.3	–	–	40	–	3
WSC	57	3.3	–	–	–	40	3

2.3. TESTING METHOD

Wear test was made using Taber rotary abraser 5135, from Taber Industries, USA. Two series of experiments were made under load of 1000 g using CS10 abrasive for mild-medium abrasion. Rotating speed was 72 min^{-1} and rotating distance – 1000, 1500, 2000 cycles.

Weight loss was measured using laboratory balances with precision 0.00001 g from Sartorius KB BA 100. Density determination by using additional equipment, YDK 01 Sartorius by LVS EN 1183 A.

3. RESULTS AND DISCUSSION

Taber wear test was made in dry condition at room temperature. Weight loss was calculated according to equation (1). Taber index was calculated according to equation (2). Samples were weighted before and after the test. Density of composites calculated according to equitation (3).

$$W_l = m_0 - m_1 \tag{1}$$

W_l – weight loss;

m_0 – weight before test;

m_1 – weight after test.

$$I = \frac{w_l * 1000}{test\ cycle} \tag{2}$$

W_l – weight loss, mg;

test cycle – 1000, 1500, 2000.

$$\rho = \frac{m_0 * \rho_l}{m_0 - m_1} \tag{3}$$

ρ – sample density, g/cm^3;

m_0 – sample mass in air, g/cm^3;

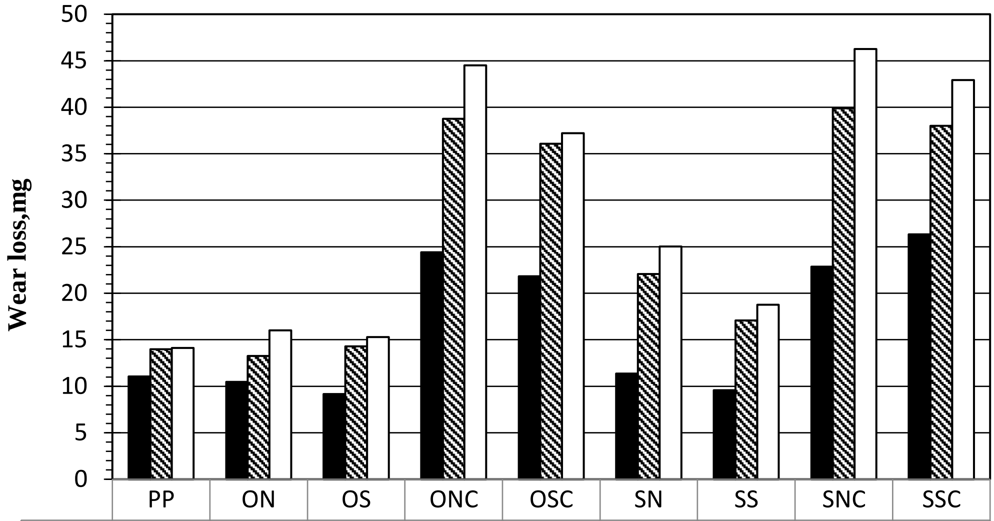
ρ_l – immersion liquid density, 0,806 g/cm^3 ethanol;

m_1 – sample mass in liquid, g.

Density and hardness of tested samples shown in table 2. Density results shows highest values for sieved husk samples and hybrid samples with organo clays. Sieved cleaned short husk fibers can make more regular distribution in PP matrix that wide broad distribution in size and form in none sieved samples. Usually hardness of inorganic filler contained composites greater that of neat polymer material, in our case hardness of PP based composite increased by adding husks, and decreased after introducing of organo clays. The interesting result is that ON and SN sample hardness in greater than that of OS and SS samples respectively on other hand difference in 1 point could be possible deviation. Check of structure by meaning of microscopy of this sample could help in future data analysis of this such composites.

Table 2. Samples density and hardness mean values**.**

Sample	**PP**	**ON**	**OS**	**ONC**	**OSC**	**SN**	**SS**	**SNC**	**SSC**
Density g/cm^3	0.911	1.033	1.061	1.073	1.064	1.045	1.047	1.054	1.061
Shore D	72	76	75	72	73	77	76	73	74

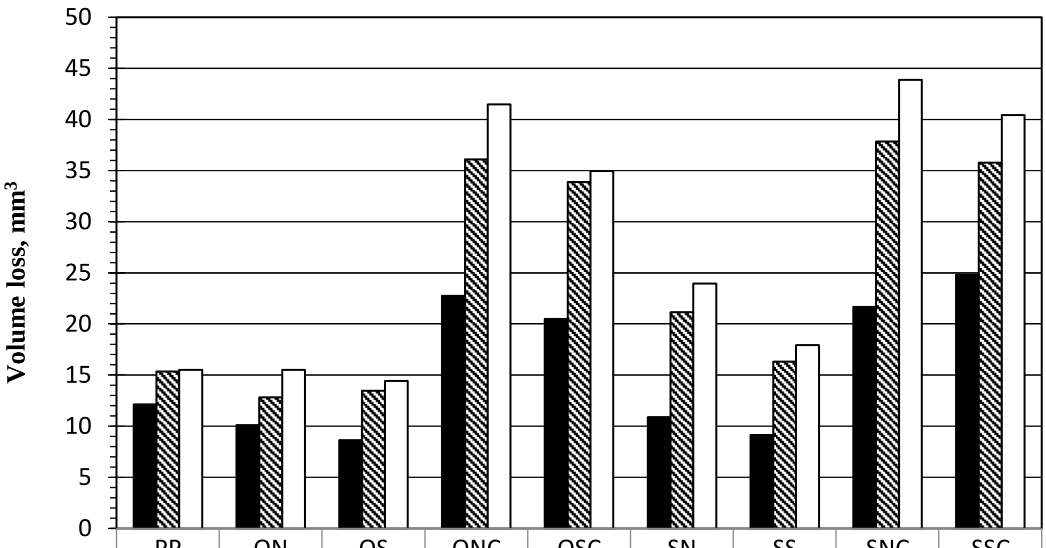


	PP	ON	OS	ONC	OSC	SN	SS	SNC	SSC
■ 1000	11,050	10,450	9,160	24,420	21,810	11,360	9,561	22,870	26,345
▧ 1500	13,990	13,260	14,300	38,750	36,080	22,080	17,091	39,890	37,990
□ 2000	14,130	16,020	15,300	44,510	37,220	25,040	18,751	46,270	42,910

Figure 1. Wear loss for PP and different husk composites at 1000, 1500 and 2000 of wear cycle.

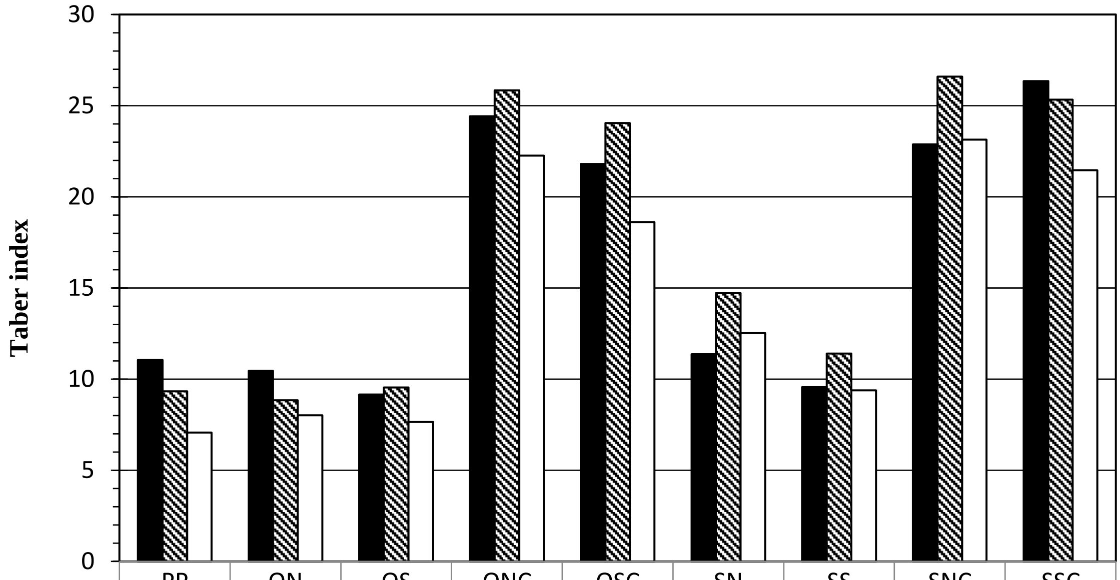
As demonstrated in figure 1 wear test weight loss data show similar result for PP and husk composites at 1000 wear cycles. This could be connected with structure of the composite. Surface area mainly consists of PP and PP "laminated" husk fiber. On the one hand, rigid husks fibers may contribute to increased wear resistance, mainly due to cellulose part of the fibers, but, on other hand, lignin and waxes may work as lubricants in polymer husk composite. For higher wear cycles wear is greater for the samples with husks fibers, however, wear depends on the husks type. At 1500 and 2000 wear cycles ON and OS samples result near PP data, at the same time SN and SS show much higher wear loss values. Spelt fibers composite have lower density that oat husk composites resulting in higher wear. ON and SN samples have greater wear values then OS and SS samples in the end of the test because of the increased dust and grain particle content that easily separates from the composite, facilitating wear. Hybrid composites wear losses at all wear cycles are 2–4 times greater than those of neat PP. At the lowest wear duration, increased wear values may be connected with thinner PP outer layer. Clay structure of very thin thickness plates, that enhance mechanical stiffness, hardness etc. of hybrid composites, stiffens PP macromolecule, however contributes to increased wear of the samples. Similarly, to previously obtained data on binary composites, cleaner and more homogeneous OSC and SSC composites demonstrate better wear resistance than ONC and SNC samples.

Volume loss results calculated from density and weight loss of tested materials (figure 2) mainly changes in same tendency as weight loss, as density of all composites near 1 g/cm^3 and doesn't affect result in a wide range. Taber index results calculated for all samples for 1000, 1500 and 2000 wear cycles (figure 3) decreases with higher cycle number. As Taber wear index results are calculation from the wear data. ON and OS samples more or less in the PP region of wear index. Main tendency in decrease of taber index by increasing of wear cycle and it could be connected with change in contact surface its roughness and homogeneity. For other composites wear index increases till 1500 wear cycles and then drops down. Wear loss of this materials decrease after wearing outside surface, abrasive surface become full of sample material dust faster wear process changes to sliding process of similar surfaces.



	PP	ON	OS	ONC	OSC	SN	SS	SNC	SSC
■ 1000	12,124	10,112	8,636	22,752	20,495	10,870	9,136	21,688	24,821
▨ 1500	15,350	12,831	13,483	36,103	33,905	21,127	16,331	37,829	35,792
□ 2000	15,503	15,501	14,425	41,470	34,976	23,959	17,918	43,879	40,427

Figure 2. Volume loss for PP and different husk composites at 1000, 1500 and 2000 of wear cycle.



	PP	ON	OS	ONC	OSC	SN	SS	SNC	SSC
■ 1000	11,050	10,450	9,160	24,420	21,810	11,360	9,561	22,870	26,345
▨ 1500	9,327	8,840	9,533	25,833	24,053	14,720	11,394	26,593	25,327
□ 2000	7,065	8,010	7,650	22,255	18,610	12,520	9,376	23,135	21,455

Figure 3. Taber index for PP and different husk composites at 1000, 1500 and 2000 of wear cycle.

4. CONCLUSIONS

Wear tests of grain husk polymer samples showed that they have good surface wear resistance. Sieved samples with longer preparation technology finished test with better results than none sieved samples, but this difference is not great. Sieved samples are brighter and with homogeneous texture color that none sieved samples. Filled composites shoved higher roughness that pure polypropylene on wear contact surface. Result data scatter could be connected with husk inhomogeneity at high wear, wear of inner surface of sample. Volume change in the level of wear loss data because of comparably similar density of composites. Hybrid composites with clay addition showed highest wear and volume loss and taber index results. For further tests it would be interesting to try smaller clay amount and make test with clay containing master batch for better clay dispersion in composite. Test could be effected by intercalation or exfoliation process of clay nano layers and husk short fiber homogeneity and surface regularity, SEM and other structure and morhhology check methods would be on high priority.

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