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Composite Materials Based on Thermoplastic Matrix

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Abstract—The results of studies of the properties of composite materials that are obtained on the basis of low-pressure polyethylene and wheat husk with additives of quartz flour, adhesion promoter, and lubricants are given. The influence of the prescription composition of composite materials on the physicomechanical properties of products is determined. Regression dependences of the effect of the composition of composites with wheat husks and polyethylene matrix on physicomechanical characteristics of the products, such as static bending strength, elasticity, and impact toughness, are obtained. The possibility of replacing wood flour with wheat husk for the production of wood–polymer composites is established.

Keywords: composites, production, properties, polyethylene matrix, wheat husk, quartz flour, adhesion promoter, lubricants

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INTRODUCTION

Products made of wood–polymer composite materials with thermoplastic polymer matrices (WPCt), compared with similar products made of solid wood, have significant advantages in terms of water resistance, durability, and microbiological destruction. The main areas of application of products made of WPCt are currently the construction, automotive, and furniture manufacturing industries. In the industrial production of WPCt, polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) are mainly used as a thermoplastic polymer matrix. The most common filler is coniferous wood flour. To improve the adhesion between filler and thermoplastic polymers, adhesion enhancers (compatibilizers) are used, the most common of which are copolymers of olefins that contain groups of maleic anhydride [1]. The development of production and consumption of products made of WPCt on world and domestic markets is being restrained due to their higher cost and significantly lower mechanical strength in comparison with solid wood products. One way to reduce the cost of WPCt is replacement of wood flour with cheaper filler. However, it is necessary to experimentally select a formulation and technological parameters for the production of WPCt with necessary physical and mechanical properties.

One potential cheap raw material for the production of WPCt is represented by plant resources, including wastes of agricultural origin. Application of rice husk and straw [1–5], buckwheat husk [6], wheat straw [7–15], and rye straw [16] is known for the production of WPCt from agricultural wastes of recycling of cereal crops. Products made of WPCt, in which, instead of wood flour, seed shell (husk, pods) of rice are produced in great quantities in the world [1, 2]. In Russia, which is one of the world leaders in wheat production, wheat-processing wastes are not used in WPCt production.

In its chemical composition, rice husk is fundamentally differs from wheat husk by being up to 19% silica [1, 2, 17], and it has approximately the same content of pulp (28–48%) and lignin (12–30%) as does wheat husk [2, 17]. It is known that the introduction of mineral fillers into WPCt increases their strength and flexural modulus, fire resistance, and antioxidant capacity [1].

The purpose of this work was to evaluate the effect of the composition on physicomechanical properties of the composites with a polyethylene matrix and a filler made of a mixture of wheat husk and silica with additives of the METALEN F-1018 adhesion promoter.

MATERIALS AND METHODS

In preparing laboratory samples of composite materials (CM), the main filler was an industrial sample of wheat husk provided by the training and experimental farm of Ural State Agrarian University (Yekaterinburg). The wheat husk contained 6.8 wt % of mineral inclusions. As a mineral component of the filler, quartz flour with an average particle diameter of 8 μm made by Russkii Kvartz LLC was used. High-density

Table 1. Composition of composite material

No. of mixture	Content of components, wt %					
	lubricants		quartz flour (Z_3)	METALEN (Z_4)	wheat husk (Z_5)	HDPE (Z_6)
	total (Z_1)	including stearic acid (Z_2)				
1	4.2	3.528	1.6	0.8	48.4	45.0
2	4.2	3.528	1.6	4.2	48.4	41.6
3	4.2	3.528	1.6	0.8	48.4	45.0
4	4.2	3.528	8.4	4.2	41.6	41.6
5	4.2	0.672	8.4	0.8	41.6	45.0
6	4.2	0.672	8.4	4.2	41.6	41.6
7	4.2	0.672	1.6	0.8	48.4	45.0
8	4.2	0.672	1.6	4.2	48.4	41.6
9	0.8	0.672	1.6	0.8	48.4	48.4
10	0.8	0.672	8.4	4.2	41.6	45.0
11	0.8	0.672	8.4	0.8	41.6	48.4
12	0.8	0.672	8.4	4.2	41.6	45.0
13	0.8	0.128	8.4	0.8	41.6	48.4
14	0.8	0.128	8.4	4.2	41.6	45.0
15	0.8	0.128	1.6	0.8	48.4	48.4
16	0.8	0.128	1.6	4.2	48.4	45.0
17	5	2.500	5	2.5	45	42.5
18	0	0	5	2.5	45	47.5
19	2.5	2.500	5	2.5	45	45.0
20	2.5	0	5	2.5	45	45.0
21	2.5	1.250	10	2.5	40	45.0
22	2.5	1.250	0	2.5	50	45.0
23	2.5	1.250	5	5	45	42.5
24	2.5	1.250	5	0	45	47.5
25	2.5	1.250	5	2.5	45	45.0
26	2.5	1.250	5	2.5	45	45.0

polyethylene (HDPE) of 273–83 grade (*GOST* (State Standard) *16338–85*) that was manufactured by OJSC Kazanorgsintez was a polymer matrix of composites. Lubrication functions were performed by stearic acid of T-32 grade and oxidized polyethylene wax (OPW) (LLC RuskhimNeft’). To improve the compatibility of components, METALEN F-1018 adhesion agent manufactured by METAKLEI (Karachev) was used, which is an ethylene–hexene copolymer with grafted anhydride and carboxyl functional groups.

Mixing of CM components in a given ratio (Table 1) was carried out on a laboratory extruder of LERM-1 brand at 180–190°C.

The mixture obtained after extrusion (MM) in the form of strands was cooled to room temperature, then the strands were cut into pellets. CM samples in the form of disks (90 mm in diameter, 4–5 μm in thickness) were obtained with each mixture composition from grains by compression pressing for 20 min at 180°C and a maximum pressure of 10 MPa.

To obtain thermogravimetric curves of fillers, a TGA/SDTA 851^e instrument for thermogravimetric analysis made by Mettler Toledo was used.

The melt flow index of the obtained MM was determined on an IIRT-A instrument with a capillary inner diameter of 4 mm at 190°C and a load of 37.3 N.

The Brinell hardness (*HB*), contact modulus (CME), and number of elasticity (E) of the samples were determined on a BTShPSP U42 hardness tester by pressing a ball with a diameter of 5 mm under a load of 132 N for 30 s.

To determine the toughness of WPCt (*a*), samples 15 × 10 mm in size were prepared. To determine the toughness with a notch (a_n,) a 0.7-mm-wide notch was applied by a metal cutting sheet to a depth of 1.5 mm across the sample of the composite. The tests were carried out on a Dinstat-Dis instrument.

To determine the index of flexural strength (σ), samples 15 × 10 mm in size were prepared. Tests were carried out on a Dinstat-Dis instrument with a cantilever restraint for the sample.

To study the morphology of composted chips by scanning electron microscopy (SEM), a JSM-6390LA scanning electron microscope made by JEOL (Japan) additionally equipped with an EDAX (energy dispersive analyzer of characteristic X-ray) attachment was used.

RESULTS AND DISCUSSION

To assess the effect of processing temperature on wheat husk, a thermogravimetric analysis (TGA) was performed (Fig. 1). According to the data shown in Fig. 1, wheat husk heated to 200°C behaves similarly to rice husk and wood flour of 180 grade. In the temperature range from 200 to 370°C, the weight loss when wheat husk is heated is 10–13% than those for rice husk and wood flour. When the temperature rises above 400°C, the mass loss dynamics of the wheat husk is identical to the weight loss of rice husk. According to the TGA data, the maximum temperature of the processes for obtaining CM with wheat husk was chosen to be 190°C.

From the mixtures obtained by compression pressing of the mixtures, disks were obtained, the physical and mechanical properties of which are given in Table 2.

According to the data of Table 1, the content of polyethylene in MM is a multicollinear factor, since the content of this component functionally depends on the content of all other components ($Z_6 = 100 - Z_1 - Z_2 - Z_3 - Z_4 - Z_5$). The content of oxidized polyethylene in CM is functionally dependent on the content of stearic acid and total amount of lubricants.

The obtained results of the correlation analysis of the content of other components in MM showed that the contents of wheat husk and quartz sand in the mixture are collinear in the composition given in Table 1 with a confidence level of at least 0.95 (Pearson's paired linear correlation coefficient $r_{Z_3Z_5}$ is –1.00), as well as the total content of lubricants and the stearic acid content ($r_{Z_1Z_2} = 0.65$). For Z_2 and Z_4, the pairwise linear correlation is absent ($r_{Z_1Z_4} = 0$), and for the remaining pairs of components the correlation is weak ($r < 0.3$) [18].

Preparation and analysis of regression mathematical dependences of the properties of MM (Y) on their composition was performed according to the data of classical regression analysis in the form of nonlinear second-degree polynomials with the coefficients of linear, pairwise, and quadratic influence of the content of components in the composite [18].

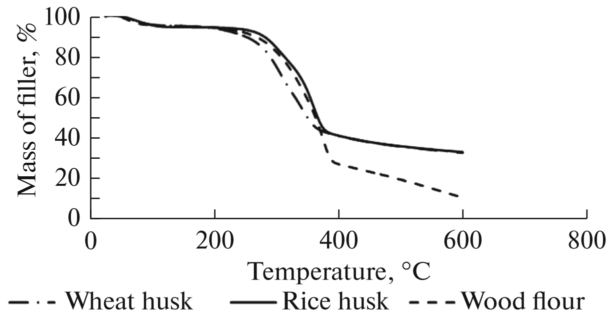

Fig. 1. Change in mass of filler while heating.

Regression analysis was performed with a confidence probability of 0.95 with successive inclusion into a regression equation of its members with significant coefficients.

For more accurately assessing the effect of the content of components in MM on the properties of CM, collinear factors were excluded from statistical analysis that have the least effect on the property under study, according to the value of the partial linear correlation coefficients.

When assessing the effect of the component content on the melt fluidity of MM at 190°C and a load of 37.3 N, the quartz flour content has the smallest value of the partial linear correlation coefficient of the collinear factors of Z_3 and Z_5 [19] ($r_{\mathrm{MFI}Z_3Z_1Z_2Z_4Z_5} = 0.07$; $r_{\mathrm{MFI}Z_5Z_1Z_2Z_3Z_4} = 0.38$). From the collinear factors of Z_1 and Z_2, total content of lubricants has the smallest value of the partial linear correlation coefficient ($r_{\mathrm{MFI}Z_1Z_2Z_3Z_4Z_5} = 0.00$; $r_{\mathrm{MFI}Z_2Z_1Z_3Z_4Z_5} = 0.11$). Therefore, the regression equation for the dependence of MFI on the content of MM of three variables was obtained: stearic acid (Z_2), METALEN (Z_4), and wheat husk (Z_5). The greatest in magnitude of the normalized coefficient of determination $\left(R_N^2\right)$ is a regression equation without collinear variables that is presented in Table 3. From the obtained linear regression equation, it follows that in the studied range of concentrations of the MM components, its melt viscosity at 190°C decreases with an increase in the concentration of wheat husk in the mixture. The value of the calculated partial linear correlation coefficient $\left(r_{\mathrm{MFI}Z_5}\right)$ indicates a strong influence of the wheat husk content in MM on its melt flow index (Table 3).

It follows from the data in Table 3 that an increase in the wheat husk content in CM according to the obtained regression equation has a very strong positive effect on the strength of a composite under static bending and a strong influence on its elasticity number. At the same time, a positive synergistic contribution to the elasticity of the composite, although not

Table 2. Physical and mechanical properties of CM

No. of mixture	Melt flow index of MM, g/10 min	Flexural strength, MPa	Elasticity number, %	Contact modulus of elasticity, MPa	Brinell hardness, MPa	Impact strength, kJ/m^2	Notched impact strength, kJ/m^2
1	1.75	25.1	40.2	2706	209	5.0	5.5
2	1.69	25.7	64.2	1300	105	3.9	5.5
3	1.40	18.0	58.8	1748	202	4.3	6.9
4	2.07	21.9	75.6	3291	210	4.4	6
5	1.51	23.0	69.0	2835	158	4.1	5.9
6	1.66	22.2	60.3	2047	118	4.2	6.3
7	1.30	23.7	59.2	2005	142	4.0	5.8
8	1.77	23.1	67.1	1250	166	4.6	5.0
9	0.93	20.3	59.5	2504	134	5.2	5.6
10	0.40	25.0	49.7	1810	137	6.0	7.2
11	1.21	22.3	52.4	1842	152	6.8	8.9
12	1.62	23.1	56.4	1930	159	5.2	8.5
13	1.81	25.5	60.1	1891	148	6.6	7.8
14	1.65	24.5	58.7	1736	142	5.7	6.5
15	1.18	26.5	54.0	1677	126	6.7	7.5
16	1.30	23.7	67.5	1477	155	5.6	6.1
17	1.88	25.4	69.7	1368	140	5.7	7.1
18	1.30	27.8	62.2	1606	138	5.7	8.1
19	2.28	30.3	63.0	1699	156	5.6	6.8
20	1.31	24.84	69.7	1424	128	6.1	7.2
21	1.80	30.5	64.7	1761	139	6.4	8.8
22	1.24	30.9	69.6	1510	117	6.1	6.6
23	2.16	27.5	68.4	2042	181	5.5	6.9
24	1.36	21.4	62.2	1483	114	6.7	8.7
25	1.87	24.4	59.2	2107	106	5.2	5.3
26	0.93	22.56	63.0	2173	110	4.5	6.2

Table 3. Statistical characteristics of the obtained regression equations adequate for a confidence level of 0.95

Property of CM	Regression equation	Normalized coefficient of determination	Private linear correlation coefficient
MFI of MM at 190°C, g/10 min	MFI = $0.033Z_5$	0.883	$r_{\mathrm{MFI}Z_5} = 0.939$
σ, MPa	$\sigma = 0.5438Z_5$	0.941	$r_{\sigma Z_5} = 0.984$
E, %	E = $1.242Z_5 + 0.05Z_4Z_5$	0.942	$r_{\mathrm{E}Z_5} = 0.950$ $r_{\mathrm{E}Z_{4,5}} = 0.281$
a, kJ/m^2	$a = 0.143Z_5 - 0.0095Z_1Z_5$	0.934	$r_{\mathrm{E}Z_5} = 0.953$ $r_{\mathrm{E}Z_{4,5}} = -0.630$

very significant compared to the content of wheat husk in the CM, is made by METALEN adhesion promoter content in the composite. With an increase in wheat husk and METALEN in CM, the elasticity of the composite increases (Fig. 2). An increase in the content of wheat husk in CM has a positive effect on the impact strength of the composite. However, there is a significant antagonistic effect of reducing the toughness of CM, while simultaneously increasing the content of lubricants in the composite (Fig. 3). For

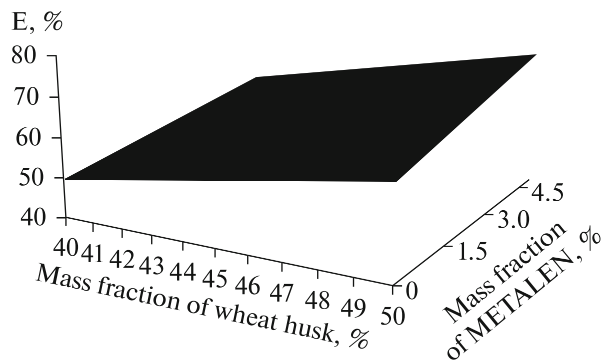

Fig. 2. Surface of dependence of elasticity of composite on content of components.

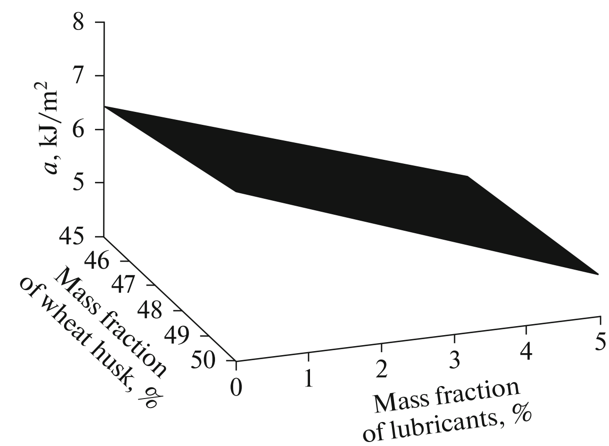

Fig. 3. Surface of dependence of impact strength of composite on content of components.

remaining properties of composites, their regression dependences on the studied prescription composition are not significant with a confidence level of 0.95.

The properties of disks that are obtained by the same method from the mixtures containing 47.5 wt % HDPE, 2.5 wt % METALEN, and 50 wt % various fillers are given in Table 4.

It follows from the data of Table 4 that disks from CM with wheat husk are superior in bending strength, impact strength than the composites with wood flour of 180 grade inferior to them in water absorption for 30 days. Introduction of quartz flour to the composites with wheat husk of 5 wt % approximates their strength values in bending and water absorption to the indicators of the corresponding properties of composites with rice husk and increases the toughness index by 40%.

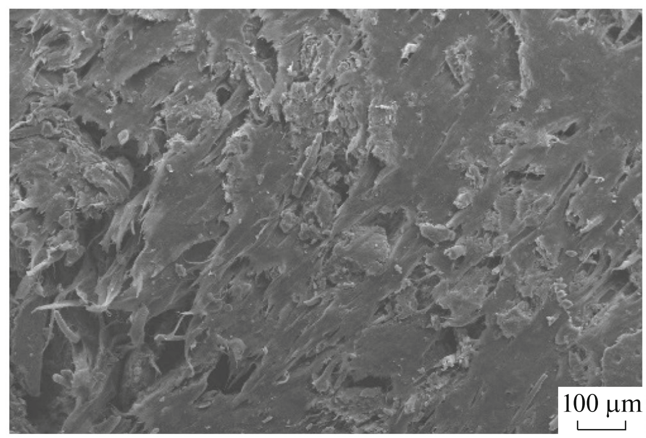

Fig. 4. SEM photo of composite fracture obtained according to recipe no. 23.

Data of scanning electron microscopy showed (Fig. 4) that, with the introduction of 10 wt % quartz flour to the composite in the presence of the METALEN adhesion promoter (mixture no. 23), the homogeneity of the composite structure is not disturbed: there are practically no areas in the break, where filler is not covered with a polyethylene layer. This can explain the high indices of mechanical properties of WPCt samples of this composition (bending strength, number and modulus of elasticity, hardness).

A crack in the WPCt sample (Fig. 5) that is obtained by recipe no. 8 looks heterogeneous: individual filler fibers, breaks, and hollows. Such a microstructure of the composite material explains the relatively low values of the indices of physical and mechanical properties of this sample: in terms of impact strength and impact strength with a notch,

Table 4. Properties of disks obtained from CM using the same technique

Name of the indicator	Filler			
	rice husk	wood flour of 180 grade	wheat husk	mixture of wheat husk and quartz flour (45 : 5, wt pts)
Flexural strength, MPa	23.0	18.8	19.6	21.4
Impact strength, kJ/m^2	4.8	3.7	4.5	6.7
Water absorption for 30 days, wt %	12	13	17	13

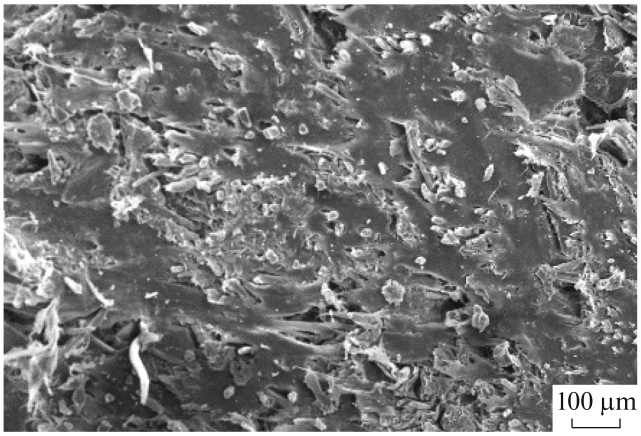

Fig. 5. SEM photo of composite fracture obtained according to recipe no. 8.

contact modulus of elasticity, and hardness, it is significantly inferior to the composite with wood flour and rice husk.

CONCLUSIONS

In the studied range of changing the composition of composites with magnification, the mass fraction of wheat husk proportionally increases the strength in static bending, elasticity, toughness.

Increase the content in the composite material of the adhesion agent METALEN leads to a synergistic increase in the elasticity of the composite.

The results of the studies performed showed that wood–polymer composites can replace valuable wood coniferous flour with wheat husks without loss of product quality in terms of flexural strength, impact strength, and water absorption.

The addition of wheat flour to the husk of wheat leads to an increase in the index of the impact strength of the composite compared with the composite containing rice husk.

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