Mineral filler effect on mechanical and rheological properties of thermoplastic HDPE/ barley straw composites

A. Kuzmin[1*], *Yu.* Goncharova[2], *V.* Slavkina[2], and *D.* Chalganov[1]

[1]National Research Mordovia State University, Bolshevistskaya st., 68, 430005 Saransk, Russia
[2]Federal Scientific Agroengineering Center VIM, 1st Institutsky st., 5, Moscow, Russia

Abstract. The paper is devoted to the properties of the wood-polymer composite based on polyethylene and barley straw. The effect of a mineral additive, namely shungite powder with a particle size of less than 20 microns, was studied. The developed composites were obtained on a laboratory two-rotor batch mixer. The mechanical and rheological properties of the composites (tensile strength and modulus of elasticity, water absorption, density, effective viscosity and modulus of elasticity) have been studied. It has been shown that the adding of shungite powder contributes to increase in the composites mechanical properties, in particular, the tensile strength increases. With an increase in the concentration of shungite, the viscosity of the composition melt decreases. The obtained thermoplastic materials can be used in construction and furniture production, as well as in the automotive industry. Key words: wood-polymer composite, polyethylene, barley straw, shungite, mechanical and rheological properties.

1 Introduction

The building material industry has a specific place in the national economy, determining the scale of capital construction, its efficiency and technical level, the construction timing of buildings and structures, as well as the quality of construction in certain regions.

Today, wood-polymer composites (WPC) are increasingly used in construction, furniture production, and the automotive industry [1–3]. WPC is both UV- and water-resistant, has good thermal insulation properties, and is able to be recycled [4-7].

The production of extruded wood-polymer composites is one of the most promising in the field of rational use of sawmill waste, furniture and woodworking industries, the use of low-grade wood, vegetable cellulose-containing waste and secondary plastics to process them into high-quality profile parts for a wide range of applications, including construction and furniture [8-13].

The polymer matrix of the WPC gives it such properties as high moisture resistance, strength and wear resistance, non-slip surface of the WPC product even when wet, heat resistance and the ability to withstand extreme weather conditions, inaccessibility for insects, fungi, and putrefactive bacteria, ease of processing and installation [14-17]. The hydrophobic

[*] Corresponding author: kuzmin.a.m@yandex.ru

additives into WPC structure make it possible to operate composite products in conditions of high humidity, and flame retardants and antiseptics protect them from fire and decay to the entire depth of the product (unlike the surface treatment of most wooden products).

Most manufacturers prefer low-pressure polyethylene (HDPE), because of a relatively low cost and processing temperature of such WPC, as well as they are environmentally friendly and frost-resistant [18-22]. The low adhesion of these thermoplastic polymers to organic fillers makes it difficult to obtain WPC with a high level of technological and operational characteristics. Therefore, to improve the adhesion of the polymer to the wood filler, binding agents are introduced into the composition of the WPC during the processing stage. WPC additionally contain functional additives that improve the operational properties of products, increase consumer qualities and presentation of products [23-26].

The operational properties of WPC depend on the initial compounds and the technological scheme of their production [27, 28]. WPC building products are mainly produced by direct extrusion or WPC granulate extrusion. The direct extrusion method involves the simultaneous loading of filler, polymer and certain additives into a twin-screw extruder using an automatic dosing system.

Thus, the objective of this study is to develop a formulation of a wood-polymer composite based on polyethylene and agro-industrial waste, as well as to establish the dependences of mineral filler effect on mechanical and rheological properties.

2 Method and materials

2.1 Materials

As a polymer matrix, low-pressure polyethylene of 273-83 grade, manufactured by PJSC Kazanorgsintez, was chosen (density is 0.950 ... 0.955 kg / m^3; tensile strength is of at least 29.4 MPa; relative elongation is of at least 700%; melt flow rate is 0.40 ... 0.65 g / 10 min).

Barley straw was ground in a rotary-knife mill and sieved using an A-20 sieve vibration analyzer (Vibrotechnik Ltd). We used a fraction of barley straw with an average particle size of less than 250 μm. The ground barley straw was dried in a Binder thermo-vacuum oven at a temperature of 80°C for 5 hours. Humidity of vegetable filler was less than 5%.

As mineral filler, shungite powder of the Novokarbon brand produced by Karbon-Shungit Ltd with an average particle size of less than 20 μm was used.

As a coupling agent, Maleid F was used, with a composition of 75% N,N-metaphenylenediamine and 25% binding additives.

Hexol HPI, a modifier based on hexachloroparaxylene, was used as a rheological additive.

Table 1 presents the formulations under development.

Table 1. Composites compound (mass fractions are indicated).

	WPC 1	WPC 2	WPC 3	WPC 4	WPC 5	WPC 6
HDPE	50	50	50	50	50	50
Barley straw	47	44,5	42	37	32	27
Shungite powder	-	2,5	5	10	15	20
Maleid F	2	2	2	2	2	2
Hexol HPI	1	1	1	1	1	1

2.2 Compositions making

Compositions were mixed with HAAKE PolyLab Rheomix 600 OS double-rotor laboratory mixer with Roller rotors. The load weight was 50 grams. The compounding temperature in three zones was 150°C, rotors speed was 50 rpm. Mixing was carried out in two stages. At the first stage, polyethylene granules were melted, at the second stage, barley straw, shungite and modifiers were introduced. Mixing was carried out for 15 minutes to constant values of temperature and rotor shaft torque.

The obtained compositions were pressed with Gibitre hydraulic thermal press to get plates 200×200×1 mm in size. The pressing temperature was 150°C, the pressing force was 2.5 MPa. From the obtained plates, standard samples for elastic-strength and rheological tests according to GOST 12019-66 were cut out.

2.3 Research Methods

The elastic-strength tests of the samples were carried out with universal machine UAI-7000 M at a temperature of 23 ± 2 °C and a clamping speed of 1 mm/min. The tests were carried out in accordance with GOST 11262-2017. 5 standard samples were tested for each composition.

The density of the composites was determined with H-200L density meter with a resolution of 0.001 g/cm^3 according to GOST 15139-69. The method is based on hydrodynamic weighing of samples.

Water absorption values were determined according to GOST 4650-2014. 3 samples of each composition were kept in distilled water for 24 hours.

For a comparative assessment of the manufacturability of composites, rheological studies of melts were carried out with HAAKE MARS III rheometer.

The tests were carried out in dynamic mode with an amplitude of rotor oscillations of 0.001 rad., in the range of angular velocities 0…800 s^{-1}, and melt temperatures 150…200 °C to avoid melt continuity in the gap of the measuring system "plane-to-plane" of the rheometer (with the diameters of the movable rotor and the fixed plane of 20 mm). The working gap between the corrugated planes of the measuring system was 1 mm.

3 RESULTS AND DISCUSSION

Today, WPC manufacturers are offered various mineral fillers that can reduce the cost of final products. This paper was aimed to evaluate the effect of shungite powder dosages on properties of the developed composites.

The mechanical characteristics of the obtained wood-polymer composites are presented in table 2.

Table 2. Mechanical properties of the developed composites.

	WPC 1	WPC 2	WPC 3	WPC 4	WPC 5	WPC 6
Tensile strength, MPa	24.9	27.6	27.7	27.8	27.8	27.9
Tensile modulus, MPa	1650	1710	1690	1680	1680	1710
Density, kg/m^3	1105	1122	1158	1156	1181	1202
Water absorption per day,%	1.76	1.65	1.43	1.17	1.14	0.86

Table 1 data tells that increase in shungite powder concentration leads to increase in tensile strength, and the elastic modulus remains almost at the same level. Thus, shungite does not affect the rigidity of composites. Tensile strength with the introduction of shungite increases by more than 10%. This is due to the uniform distribution of particles in the polymer matrix, as well as the formation of strong macromolecular bonds.

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Water absorption is one of the main indicators of WPC durability, since it allows to evaluate the resistance of the material to aggressive atmospheric factors. Water causes material swelling and accumulation of defects, especially at negative temperatures [18].

Water absorption of composites per day is shown in Table 2. The data obtained indicate a decrease in water absorption with an increase in shungite powder content. In composites with 20%s hungite concentration, there is a 2-fold decrease in water absorption compared to the original composition. The obtained values are due to the fact that the content of hydrophilic barley straw in the compositions is reduced.

Water absorption is closely related to another important parameter, namely the density of composites [25]. Table 2 shows that the greater the density, the lower the water absorption. It is obviously, the higher the density, the lower the porosity and the lower the water absorption.

High mechanical properties are also achieved due to the introduction of the Maleid F compatibilizer and the technological additive Hexol HPI. The results obtained correlate with previous studies [6,7].

An important indicator of thermoplastic wood-polymer composites is their ability to recycle. It can be assessed by conducting rheological tests.

Figure 1 and 2 shows the dependences of effective viscosity and dynamic modulus of elasticity of melts in the WPC1 and WPC6 compositions on the shear rate. Table 3 shows the rheological characteristics of composite melts.

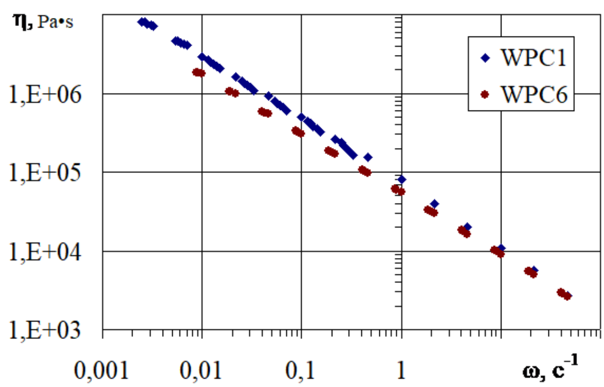

Fig. 1. Dependence of complex viscosity on shear rate at a temperature of 150 °C.

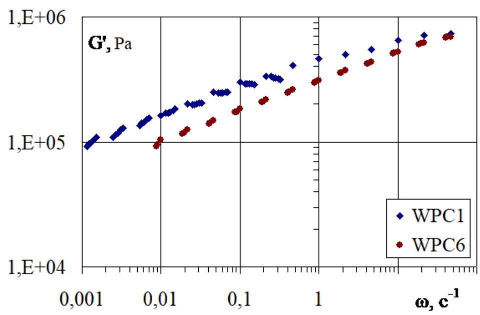

Fig. 2. Dependence of dynamic modulus of elasticity on shear rate at a temperature of 150 °C.

It can be seen from the graphs that a high content of shungite in the composite leads to a decrease in effective viscosity, thereby improving its manufacturability.

The given data show that composite melts viscosity decreases when shungite powder is added. As the mineral filler content in the composition increases, not only their viscous properties decrease, as evidenced by the effective viscosity values, but also their elastic characteristics. This effect reduces the load on the screws and increases extrusion equipment productivity.

Table 3. Rheological characteristics of the developed composites

	WPC 1	WPC 2	WPC 3	WPC 4	WPC 5	WPC 6
Consistency index, Pa•s	77215	93101	98444	89433	82086	52088
Exponent	-0,7697	-0.7912	-0.7999	-0.8129	-0.8008	-0.7622
Correlation coefficient	0.998	0.999	0.999	0.999	0.999	0.999

The values of the consistency index and exponent, determined from the dependence presented in double logarithmic coordinates, deviate from the classical values that the Maxwell model should correspond to. It indicates that the rheological behavior of the wood-polymer composite melt is more complex than its model representations.

4 Conclusion

As a result of the study, the following conclusions can be drawn:

- the possibility of using shungite powder with a dispersion of less than 20 microns as a mineral filler in WPC is shown;
- compositions were developed and WPC compositions with up to 20% shungite concentration were obtained with a laboratory two-rotor batch mixer;
- an increase in shungite powder content in WPC leads to an increase in tensile strength and does not greatly affect the modulus of elasticity;
- as a result of shungite powder introduction, the density of composites increases and their water absorption per day decreases;
- an increase in shungite concentration leads to a decrease in the effective viscosity of the WPC melts.

The conducted studies allow us to recommend the use of shungite powder in WPC formulation and to improve the manufacturability of extrusion processing.

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