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Use of Cellulose-Containing Fillers in Composites with Polypropylene

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The composites, containing recycled polypropylene and fillers, obtained from different lignocellulosics by the thermocatalytic destruction method, were investigated. Birch sawdust, newsprint wastes, cotton residues and wood bleached sulphate pulp were used as raw materials for obtaining fillers. The indices of mechanical properties (tensile strength, modulus of elasticity, deformation at break, shear modulus, toughness, twisting moment) of the composites' samples were determined. It has been found that the obtained composites have relatively good mechanical properties. Better results were obtained, using fillers from sawdust and wood pulp. After treating the fillers with rapeseed oil, their water vapour sorption and water retention value (WRV) decreased. In this case, the strength of the composites was higher.

Keywords: sawdust, newsprint wastes, cotton residues, wood pulp, thermocatalytic destruction method, tensile strength, modulus of elasticity.

INTRODUCTION

Recently, cellulose fibres and lignocellulosic materials such as paper and textile industry wastes, wood processing wastes, technical lignins etc. have aroused considerable interest for their use as fillers with a thermoplastic matrix [1 – 5]. They are highly filled composites, which contain up to 60 % organic fillers. Compared to classic mineral-inorganic fillers, they have a lot of advantages. Lignocellulosic fillers are biodegradable, renewable, exhibit a low density, and usually have a low cost. Compared to neat polymers, they have a greater stiffness. The rational use of wastes is the basis for the development of wasteless production, enhances its economic efficiency, increases the output, and favours the environment protection. At present, one of the most important avenues of investigations is the development of a resource-saving technology for obtaining moulded strips and sheetings such as boards of floor, skins, plinths, cover plates and handrails on the basis of recycled polyolefins, filled with lignocellulosic materials. However, these composites not always have high mechanical indices [6]. The application of these materials is limited owing to the lack of the compatibility between the polar, hydrophilic cellulose-containing fillers and the hydrophobic thermoplastic matrix. The poor interfacial adhesion reduces the mechanical properties and favours the degradation caused by the moisture and biological attack. Therefore, several methods have been developed to achieve chemical modifications of the cellulose surface in order to obtain better interfacial adhesion. These methods include corona or plasma discharges, laser or UV irradiations and the use of coupling or compatibilizing agents [7]. As coupling agents, silanes [8], isocyanates [9], maleic anhydrides [10] and others were used. One of the ways of modification may be the treatment of lignocellulosics by the thermocatalytic destruction method [11] and grinding of the destructed material in a ball mill.

The task of the present work was to investigate the composites that contain recycled polypropylene and cellulose-containing fillers, obtained by the thermocatalytic destruction method from lignocelulosics.

EXPERIMENTAL DETAILS

Birch sawdust, newsprint wastes, cotton residues and pine sulphate bleached pulp were used as raw materials for obtaining fillers. These materials were destructed by the thermocatalytic destruction method. In compliance with this method and the developed treatment regimes, the raw materials were impregnated with a weak hydrochloric acid solution (modulus 1 : 20) with the concentration 0.02 % – 0.05 % (0.2 % in the case of cotton residues), and thermally treated at the temperature 110 °C – 140 °C. The treatment regimes depended on the material. During this treatment, the polymerisation degree of cellulose fell to the so-called levelling-off degree of polimerisation, which was ~250. The treated material was ground in a ball mill. To remove the remaining acid, the obtained powder was washed with distilled water, filtered and dried at 105 °C. The dried powder was rubbed through a sieve. To decrease the hydrophility, some powder samples were treated with refined rapeseed oil, holding in it for 48 h (modulus 1 : 10) and then dried.

The structural parameters of the powder samples were determined using an optical microscope BIOLAM and an scanning electron microscope TESCAN 5136. Water vapour sorption was determined, holding the samples at the relative air moisture 95 % and temperature 20 °C till the equilibrium state occurred. The physico-chemical indices were determined by the methods indicated in the work

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[12], and the water retention value (WRV) by the centrifugation method, developed by Jayme [13].

As the thermoplastic polymer material in the composite, polypropylene (PP) powder-like residues were used.

The samples were prepared by the extrusion method at the temperature 170 °C – 180 °C as well as by moulding under pressure in a laboratory moulding machine at the mould temperature 180 °C and holding time 10 – 15 sec.

The mechanical tests were carried out, using the universal device "Instron".

RESULTS AND DISCUSSION

Grinding the materials, treated by the thermocatalytic destruction method, in ball mill, fine-disperse powders were obtained. Fig. 1 shows percentage distribution graphs of the number of particles in longitudinal and transversal sizes for the powder obtained from birch and pine wood sawdust, and birch and pine wood sulphate bleached pulp.

It can be seen that ~90 % of powder particles, obtained from sawdust and pulp, have the average sizes

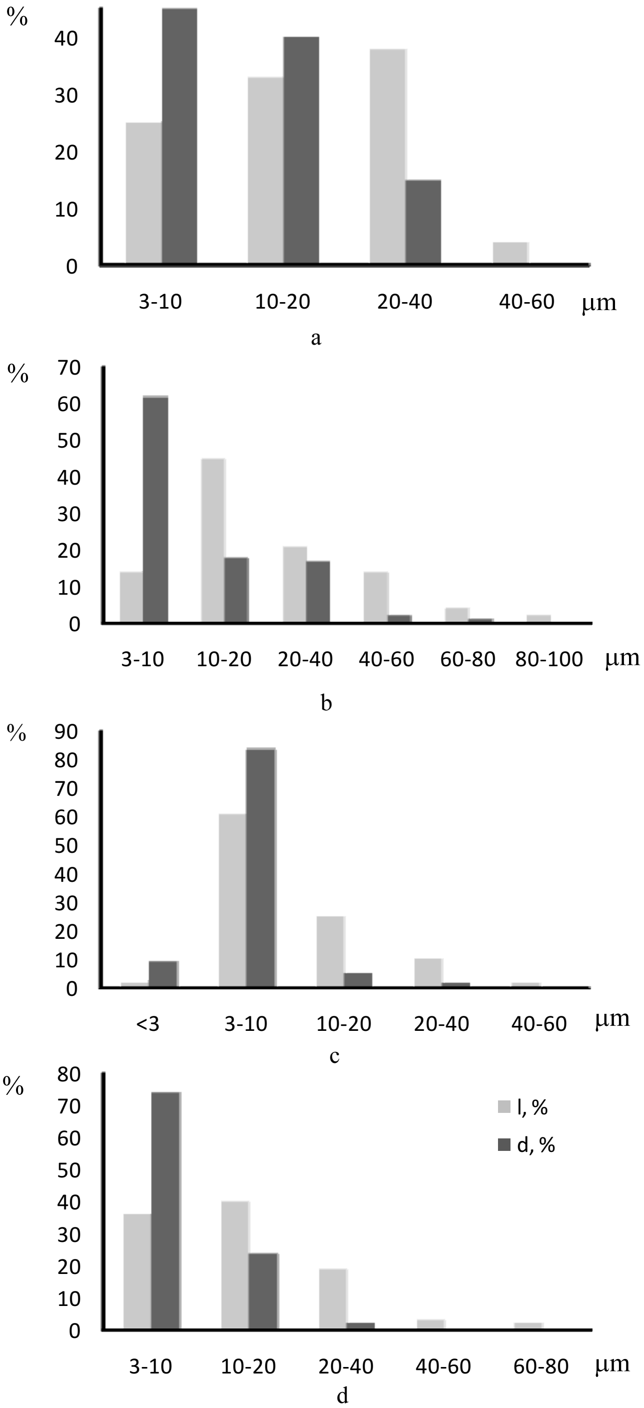

Fig. 1. Percentage distribution graphs of the particles in the longitudinal l and transversal d sizes for powder obtained from: a – birch and b – pine wood sulphate pulp, c – birch and d – pine sawdust

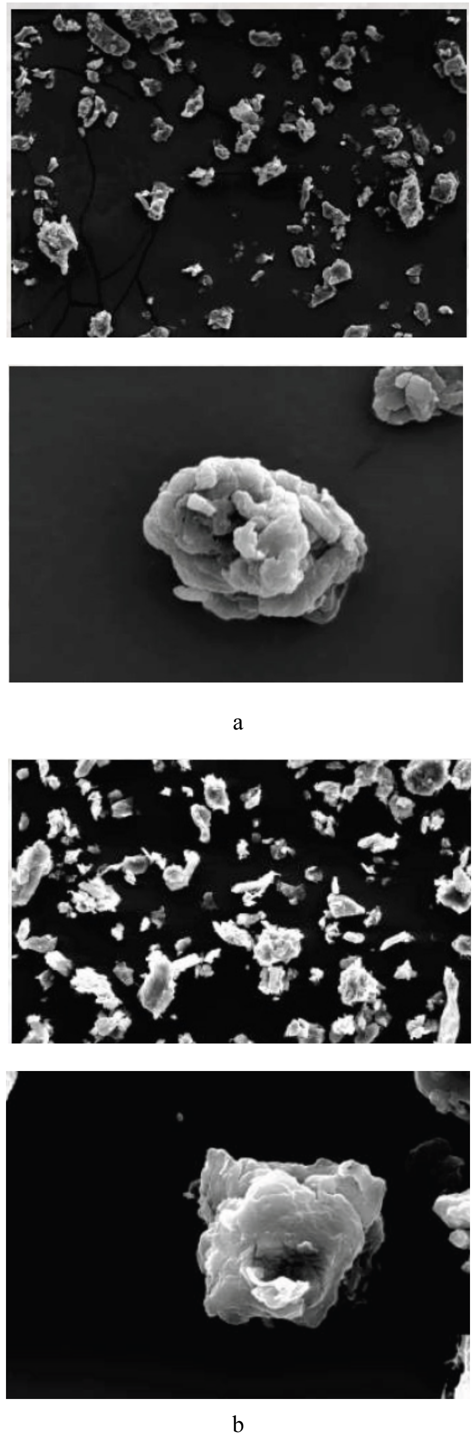

Fig. 2. Electron micrographs of powder particles obtained from: a – birch and b – pine sulphate pulp at two different magnifications: ×150 and ×1250

3 μm – 20 μm and 3 μm – 40 μm, respectively. Maximal sizes were 60 μm – 100 μm.

Fig. 2 shows electron micrographs of powder particles obtained from birch and pine wood sulphate pulp at two different magnifications.

Table 1 shows physico-chemical and quality parameters for powder samples, obtained by the thermo-catalytic method from different cellulose-containing raw materials. It can be seen that the chemical purity of the powders obtained from wood sulphate pulp is greater than that of the powders obtained from newsprint wastes, cotton residues and sawdust.

A study of the mechanical properties of the composites has shown that our method for modification of lignocellulose by thermocatalytic destruction improves the mechanical indices of the obtained composites in comparison with those of pure polypropylene, which does not contain fillers. Thus, for example, modified sawdust at its content 50 % increases tensile strength and modulus of elasticity 1.32 times and 1.21 times, respectively, and decreases relative elongation 33 times. This agrees with the results obtained in our earlier work [14], which were gained in the study of composites of low density polyethylene and pine wood sawdust treated by the thermocatalytic destruction method. It has been found that tensile strength, modulus of elasticity and bending modulus for composites, which contain 55 % of treated sawdust, are 1.2, 3 and 13 times, respectively, higher, but relative elongation at break 60 times lower than these indices in the case of pure polyethylene. The increase in the mechanical indices of the composites at a sufficiently high content of the cellulose-containing fillers, obtained by thermocatalytic treatment from lignocellulosics, can be connected with the formation of a lattice structure among the filler particles, which enhances the composites' strength [15].

Table 2 shows mechanical indices for the composites, which contain powders obtained from birch sawdust [16] and other cellulose-containing raw materials. In all cases, the content of cellulose-containing fillers in the composite was 50 %. At a lower content, the fillers practically did not enhance the composites' indices. If composite samples are compared, which contain 50 % of polypropylene, 25 % of fillers obtained by the thermocatalytic method from different raw materials and 25 % of wood flour, then the best results are in the case of sawdust and wood sulphate pulp and the lowest in the case of newsprint wastes. Thus, for example, for the samples that contain 50 % of polypropylene, 25 % of wood flour and 25 % of fillers, obtained from sawdust, wood pulp or newsprint wastes, tensile strength is 11.2, 12.4 and 8.9 MPa and modulus of elasticity 809.1, 806.1 and 631.7 MPa, respectively. However, higher tensile strength and modulus of elasticity are shown by the samples that do not contain the wood flour, but contain only 50 % of the fillers obtained by the thermocatalytic method. It is obviously connected with the

Table 1. Physico-chemical indices of cellulose-containing fillers from different raw materials

Raw material	Solubility	Water extract pH	Ether-soluble substances, %	Water-soluble substances, %	Mass loss upon drying, %	Sulphate ash, %
Cotton residues	Practically insoluble in water, diluted acids, acetone, 95 % alcohol	4.5 – 4.7	0.50 – 0.88	0.36 – 0.80	2.0 – 6.0	1.4 – 1.9
Newsprint wastes	Practically insoluble in water, diluted acids, acetone, 95 % alcohol	5.2 – 5.6	0.22 – 0.30	0.27 – 0.50	4.3 – 6.0	0.43 – 0.70
Birch sawdust	Practically insoluble in water, diluted acids, acetone, 95 % alcohol	4.5 – 4.9	0.21 – 0.30	2.2 – 2.8	4.2 – 5.5	1.1 – 1.8
Wood sulphate pulp	Practically insoluble in water, diluted acids, acetone, 95 % alcohol	6.2 – 6.8	0.05 – 0.10	0.12 – 0.16	3.7 – 5.8	0.19 – 0.30

Table 2. Mechanical indices for composites, containing recycled polypropylene (PP) and cellulose-containing fillers obtained from different thermocatalytically treated raw materials

Indices	Filler from sawdust 50 %, PP 50 %	Filler from sawdust 25 %, wood flour 25 %, PP 50 %	Filler from waste paper 25 %, wood flour 25 %, PP 50 %	Filler from cotton residues 25 %, wood flour 25 %, PP 50 %	Filler from pine wood pulp 25 %, wood flour 25 %, PP 50 %
Tensile strength, MPa	13.47	11.24	8.9	9.57	12.42
Modulus of elasticity, MPa	1502.21	890.06	631.73	717.17	806.14
Deformation at break, %	4.44	3.32	3.38	3.36	4.75
Shear modulus, MPa	261.89	290.22	301.33	148.66	109.15
Toughness, kJ/m^2	7.5	8.0	7.5	7.5	7.0
Twisting moment, Nm	11.2	24.4	17.9	15.6	18.6

fact that the content of cellulose-containing fillers, obtained by mechanical way, impairs the results. Thus, for example, in the study [17] it is shown that, tensile strength for the composites, containing polypropylene and 60 % of wood flour, decreases 2.45 times in comparison with that for pure polypropylene. In the same way, if 50 % of eucalyptus kraft pulp is used in the composites, tensile strength decreases 1.23 times [7]. Upon adding polyethylenimine as a coupling agent in these composites, the drop of tensile strength is reduced. In this case, it is 1.07 times lower than that of pure polypropylene.

The composites, which contain cellulose-containing fillers, are water-unstable, and absorb water with time, which diminishes their mechanical indices. To prevent this, the powder obtained from sawdust by the thermocatalytic method was treated with rapeseed oil. As a result, the water vapour sorption and WRV of the powder samples decreased by 37 % (from 25.0 % to 15.8 %) and 30 % (from 73 % to 51 %), respectively. The particle size after the treatment did not change considerably. The particles' average and maximal sizes were ~13 μm and 100 μm.

Table 3 shows the mechanical indices of composites, which contain a filler from sawdust after its treatment with rapseed oil.

Table 3. Mechanical indices of composites, containing recycled polypropylene (PP) and the filler obtained by the thermocatalytic destruction method from sawdust after its treatment with rapeseed oil

Indices	Filler from sawdust after its treatment with rapseed oil 50 %, PP 50 %	Filler from sawdust after its treatment with rapseed oil 25 %, wood flour 25 %, PP 50 %
Tensile strength, MPa	20.45	15.75
Modulus of elasticity, MPa	1556.17	1548.95
Deformation at break, %	3.32	5.22
Shear modulus, MPa	116.21	414.58
Toughness, kJ/ m^2	7.75	5.25
Twisting moment, Nm	18.6	17.6

The mechanical indices of the composites, which contain the fillers treated with rapeseed oil, are better. At the filler content 50 %, tensile strength and twisting moment increase by 52 % and 66 %, respectively (see Tables 2 and 3). At the same time, shear modulus decreases by 57 %.

CONCLUSIONS

1. Using cellulose-containing fillers, obtained by the thermocatalytic destruction method, jointly with recycled polypropylene, composites with relatively good mechanical indices are obtained.
2. Better results are obtained, using fillers from sawdust and wood pulp.
3. The treatment of the fillers with rapeseed oil decreases their hydrophility and increases the composites' strength.

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