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БИОРАЗЛАГАЕМЫЕ КОМПОЗИЦИОННЫЕ МАТЕРИАЛЫ НА ОСНОВЕ АЦЕТАТА ЦЕЛЛЮЛОЗЫ

Павел Сергеевич Захаров[1], Кристина Алексеевна Усова[2], Алексей Евгеньевич Шкуро[3]

[1–3] Уральский государственный лесотехнический университет, Екатеринбург, Россия
[1] zazaver@mail.ru, http://orcid.org/0000-0001-0027-3446
[2] usovaka@m.usfeu.ru, http://orcid.org/000-0002-6237-955X
[3] shkuroae@m.usfeu.ru, https://orcid.org/0000-0003-4016-2269

Аннотация. В данной статье обсуждается динамика биоразложения, а также физико-механические свойства ацетатов целлюлозы, наполненной древесиной. Ацетат целлюлозы со степенью замещения 2,65 использовали в качестве полимерной фазы для приготовления композиционных материалов. В качестве пластификаторов применяли триацетат глицерина (триацетин) и трифениловый эфир фосфорной кислоты (трифенилфосфат); в качестве наполнителя – древесную муку марки 180. Пластификацию ацетата целлюлозы и дальнейшее смешивание с наполнителем осуществляли прокаткой. Определены следующие свойства ацетатов древеснонаполненной целлюлозы: плотность, прочность на изгиб, твердость по Бринеллю, модуль сжатия, пластичность, прочность на разрыв, ударная вязкость, водопоглощение в течение семи суток, потеря массы после воздействия активного грунта в течение 75 сут. Таким образом, с увеличением содержания древесной муки в составе образца наблюдается увеличение твердости, плотности, модуля упругости при сжатии и водопоглощения. При этом наблюдается снижение показателя пластичности материала. Кроме того, зависимость ударной вязкости от содержания древесной муки чрезвычайно велика. Максимальное значение ударной вязкости имеет пластифицированный ацетат целлюлозы, содержащий 30 мас. % древесной муки. Образцы ацетатов целлюлозы с древесным наполнителем также демонстрируют значительно более высокую скорость биоразложения в незаполненных образцах активной почвы. Зависимость индекса потери массы после выдержки в активной почве в течение 75 сут от содержания древесной муки описывается уравнением $y = 3{,}19e^{0{,}01x}$ ($R^2 = 0{,}76$).

Ключевые слова: композит, ацетат целлюлозы, древесная мука, физико-механические свойства, биодеградация

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Original article

BIODEGRADABLE COMPOSITE MATERIALS BASED ON PLASTICIZED CELLULOSE ACETATE

Pavel S. Zakharov[1], Kristina A. Usova[2], Alexey E. Shkuro[3]

[1–3] Ural State Forest Engineering University, Yekaterinburg, Russia

[1] zazaver@mail.ru, http://orcid.org/0000-0001-0027-3446

[2] usovaka@m.usfeu.ru, http://orcid.org/000-0002-6237-955X

[3] shkuroae@m.usfeu.ru, https://orcid.org/0000-0003-4016-2269

Abstract. This paper discusses wood-filled cellulose acetates' biodegradation dynamics and physical and mechanical properties. Cellulose acetate with a degree of substitution of 2,65 was used as a polymeric phase to prepare composite materials. Glycerol triacetate (triacetin) and triphenyl ester of phosphoric acid (triphenyl phosphate) were used as plasticizers; wood flour grade 180 was used as a filler. Cellulose acetate plasticization and further mixing with filler were carried out by rolling. Following properties of wood-filled cellulose acetates were determined: density, flexural strength, Brinell hardness, compressive modulus, plasticity, tensile strength, impact strength, water absorption for seven days weight loss after exposure to active soil for 75 days. Thus, with an increase in wood flour content in the sample's composition, an increase in hardness, density, modulus of elasticity in compression, and water absorption is observed. At the same time, a decrease in the plasticity index of the material is observed. Furthermore, the dependence of the impact strength on the wood flour content is extreme. The maximum impact strength value has plasticized cellulose acetate containing 30 wt. % wood flour Samples of wood-filled cellulose acetates also offer a significantly higher rate of biodegradation in active soil unfilled samples. The dependence of the weight loss index after exposure in the active soil for 75 days on wood flour content is described by the equation $y = 3{,}19e^{0{,}01x}$ ($R^2 = 0{,}76$).

Keywords: composite, cellulose acetate, wood flour, physical and mechanical properties, biodegradation

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Introduction

Currently, biodegradable polymeric and composite materials are one of the most priority areas of scientific activity. In the future, biodegradable materials will solve a significant part of the problems associated with the collection and processing of municipal solid waste arising from the disposal of plastic containers and packaging (Glukhikh et al., 2020). Today's search for new biodegradable materials mainly focuses on compounds of polyesters of hydroxy acids and natural polymers, which have a broad raw material base (Long, 2013). Much attention is drawn to the search for ways to make synthetic polymers biodegradable: polyethylene, polypropylene, polyethylene terephthalate, etc.

One of the main advantages of using natural polymers to create biodegradable materials is the renewable nature of their sources (Nawrath, Poirier, 1995). However, polymers of natural origin do not always have good physical and mechanical properties, and their processing into products is often associated with several difficulties. For example, with numerous advantages, cellulose cannot pass into a viscous state, which does not allow obtaining a product from it using such high-performance polymer processing methods as injection molding or extrusion. Substances of different nature are added in natural polymers to improve the technological properties (Rogovin, 1979). Polymers of the same hydroxycarboxylic acids, polyhydric alcohols, polymers containing ester and carboxyl

functional groups, polyolefins, etc., can serve as such additives (Cong, 2015). In this case, the main problem is the selection of compositions that provide compositions based on natural polymers with properties that bring them closer to synthetic analogs (Long, 2013).

The most common natural polymers used to produce biodegradable materials are proteins, cellulose, and its esters, starch, and chitosan. A promising direction is the study of composite materials based on cellulose acetate since, unlike cellulose, its esters can pass into a viscous flow state and can be processed using the most known methods. Cellulose acetates with a degree of substitution from 2.2 to 2.5 are commonly used in industry (Roberta et al., 2017). Thermoplastic compositions consisting of cellulose acetate plasticizer, stabilizer, dye, filler, and other additives are obtained by extrusion and rolling.

As plasticizers for cellulose acetates, aliphatic esters of phthalic, sebacic, orthophosphoric, adipic, citric, and some other acids, as well as their mixtures, are used. As a rule, plasticizers give cellulose acetate products elastic properties but reduce heat resistance, hardness and strength (Zakharov et al., 2020). The specific type of plasticizer is selected depending on the properties required for the product. Some plasticizers can give the product unique properties: triphenyl phosphate – increases water resistance; trichloromethyl phosphate – reduces flammability; dibutyl sebacate – improves frost resistance. Today, plasticizers based on esters of phthalic and phosphoric acids are the most common (Wypych, 2017; Erceg et al., 2023). To date, there is a tendency to abandon the use of these plasticizers, associated with their negative impact on the environment and human health. The possibility of partial or complete replacement of phthalate-type plasticizers with citric acid esters – citrates (Schiller et al., 2015) and esters of glycerol and carboxylic acids (triacetin) is considered.

Plasticized cellulose acetate seems to be a promising raw material for producing biodegradable polymer composite materials (Ach, 1993; Preparation of biocomposites…, 2023). The most common type of lignocellulosic filler in polymer composite materials is traditionally wood flour. Its use provides composites with high mechanical properties (Problems…, et al., 2014). Furthermore, as fillers for plasticized cellulose acetates, various wastes of the timber industry complex can be considered (Levi, Gurkovskaya,1967).

Preliminary studies have shown the ability of unfilled samples of plasticized cellulose acetate to biodegrade in soil (Sam et al., 2014; Tatarinova, 2020). Therefore, this work aimed to study biodegradation dynamics in the active soil of samples of wood-filled cellulose acetates. The study included the assessment of the composites' mechanical properties and the establishment of the influence of the filler content.

Experimental

Cellulose acetate (technical specifications 6-05-943–75) was used as a polymer phase to prepare composite materials. Glycerol triacetate (triacetin, technical specifications 2435-070-00203521–2001) and orthophosphoric acid triphenyl ester (TPF, technical specifications 6-09-08-1679–84) were used as plasticizers. Stearic acid of technical grade T-32 (State Standard 6484–96) was used as a lubricant. Wood flour grade 180 was used as a filler in work.

Plastification of cellulose acetate and further mixing with the filler was carried out on laboratory rollers of the PD-320-160/160 brand at 160–170 °C. Standard samples for testing the physical and mechanical properties of the obtained composites were made by hot pressing. The formulations of the studied compositions are presented in table 1.

Density, flexural strength, Brinell hardness, compressive modulus, ductility, tensile strength, impact strength, and water absorption were determined for the resulting composite samples for seven days.

The value of weight loss assessed the ability of samples of wood-filled cellulose acetates to biodegrade after exposure to active soil. An active soil was prepared for the experiment with the following composition: garden soil (State Standard R 53381–2009) – 89 vol. %, distilled water – 10 vol. %, microbiological preparation "Tamir" (State Standard 9291-002-70213832–2007) – 1 vol. %. Before the experiment, the active soil was kept at room temperature for 21 days. During the experiment, soil moisture was maintained at 30 %.

For testing in the active soil, a composite sample was used in a rectangular plate with dimensions of 15 × ten × 5 mm. Before exposure in the soil, composite samples were dried in an oven at 105 °C

Table 1

Sample formulations of wood-filled cellulose acetates

Sample number	The proportion of components in the composite sample, wt. %			
	Wood flour	Cellulose acetate	Triacetin	Triphenyl phosphate
1	0,0	66,7	26,7	6,7
2	20,0	53,4	21,4	5,4
3	30,0	46,7	18,7	4,7
4	40,0	40,0	16,0	4,0
5	50,0	33,4	13,4	3,4

to constant weight. After that, they were immersed in the active soil to at least 2 cm depth. Next, the samples were removed from the soil, thoroughly cleaned, and washed with ethyl alcohol at fixed intervals. Then samples were dried to a constant weight, after which the change in weight (loss) relative to the initial values was determined.

Results and discussion

The results of testing the physical and mechanical properties of samples of the obtained composites are presented in Table 2. Trends in the dependence of COMPOSITE properties on the content of wood flour (x) in them in the studied range are shown in Figures 1–6.

With a change in the content of wood flour in COMPOSITE, a slight drop in the bending strength of the composite is observed (Table 2), and other measured properties are characterized by experimental-statistical dependences adequate for a confidence probability of 0,95 with high values of the coefficient of determination R^2 (Table 3).

The data obtained shows that the COMPOSITE samples density increases with an increase in the wood flour content in the composite (Fig. 1). It may be due to the strengthening of bonds between the cellulose acetate phase and COMPOSITE filler, increasing the proportion of wood flour in the composite.

A similar effect of the content of wood flour in COMPOSITE is also characteristic of the indicators of Brinell hardness (Fig. 2), modulus of elasticity in compression (Fig. 3), and water absorption for seven days (Fig. 4).

With an increase in the wood flour content, a decrease in the plasticity index of the material is observed (Fig. 5).

The dependence of the impact strength index on the content of wood flour is extreme (Fig. 6). The maximum impact strength values (10,5 kJ/m^2) are demonstrated by a composite sample containing 30 wt. % wood flour.

Table 2

Properties of composites samples

Indicator	Content of wood flour wt. %				
	0	20	30	40	50
Density, kg/m^3	1285,1	1308,8	1316,7	1324,7	1330,6
Hardness, MPa	36,5	70,1	109,5	135,1	141,8
Plasticity, %	37,6	24,2	21,1	16,0	16,0
Tensile strength, MPa	24,7	45,3	68,6	83,4	87,2
Compressive modulus, MPa	299,9	726,1	1001,3	1254,6	1338,2
Flexural strength, MPa	–	56,1	51,6	55,1	49,8
Impact strength, kJ/m^2	–	8,3	10,5	8,0	8,7
Water absorption for 7 days, %	2,1	4,9	5,6	6,8	7,6

Table 3

Dependences of WPC properties on the content of wood flour

Indicator	Dependence	R^2
Density (ρ), kg/m³	$\rho = 1285{,}2 + 1{,}31x - 0{,}0082x^2$	1,00
Brinell hardness (H_B), MPa	$H_B = 34{,}44 + 0{,}138x^2 - 0{,}0019x^3$	0,99
Plasticity (P), %	$P = 35{,}89 - 0{,}44x$	0,92
Tensile strength (σ_t), МПа	$\sigma_t = 23{,}96 + 1{,}35x$	0,97
Compressive modulus (E), MPa	$E = 313{,}1 + 21{,}8x$	0,98
Flexural strength (σ_f), MPa	$\Sigma_f = 156{,}3 - 9{,}73x + 0{,}292x^2 + 0{,}0028x^3$	1,00
Impact strength (a), kJ/m²	$a = -41{,}8 + 4{,}82x - 0{,}142x^2 + 0{,}0013x^3$	1,00
Water absorption for 7 days (WA_7), %	$WA_7 = 2{,}3 + 0{,}11x$	0,99

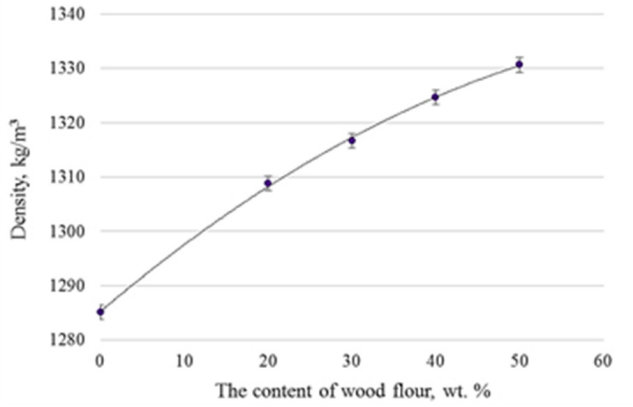

Fig. 1. Dependence of density on the content of wood flour

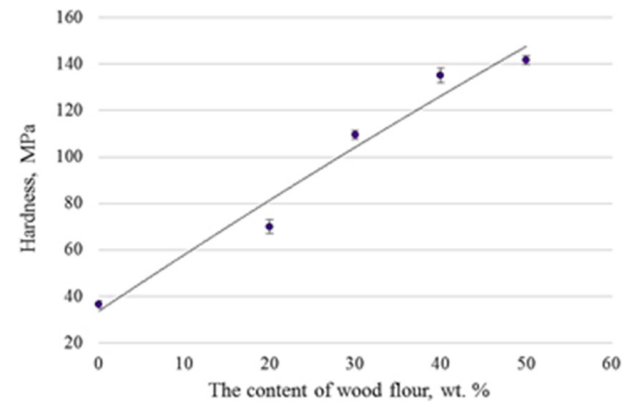

Fig. 2. Dependence of Brinell hardness on the content of wood flour

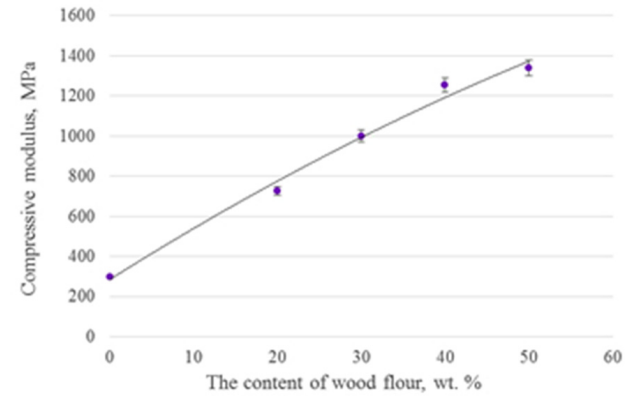

Fig. 3. Dependence of the modulus of elasticity on the content of wood flour

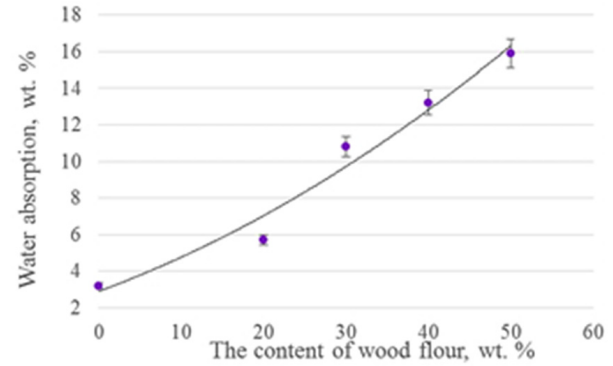

Fig. 4. Dependence of water absorption for seven days on the content of wood flour

Figure 7 shows the dependence of the index mass loss after its exposure in the active soil for 75 days (B_{75}) on the content of wood flour in the composite material.

With an increase in wood filler content in WPC, an increase in its degree of biodegradation in activated soil is observed. Therefore, the dependence on the wood flour content of the weight loss after exposure in the active soil for 75 days can be described with sufficient accuracy by the equation $B_{75} = 3{,}19e^{0{,}01x}$ ($R^2 = 0{,}76$).

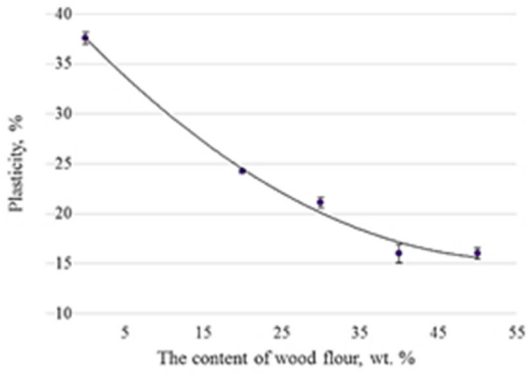

Fig. 5. Dependence of the plasticity index on the content of wood flour

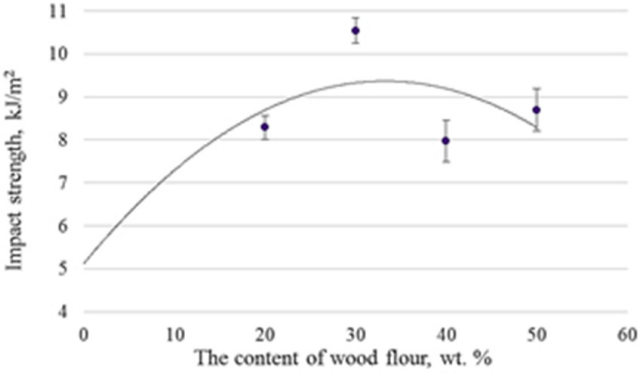

Fig. 6. The dependence of impact strength on the content of wood flour

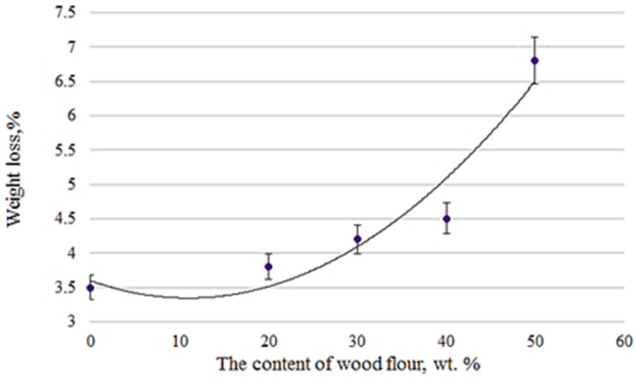

Fig. 7. Dependence of the weight loss index after exposure in the active soil for 75 days on the content of wood

The hardness and compressive modulus of the composite material samples increases with an increase in the content of wood flour, which indicates good phase compatibility and uniformity of the filler distribution in the polymer matrix. In addition, high values of the water absorption index of WPC samples are an indirect sign of a greater propensity for biodegradation of highly filled composite samples. In general, WPC with a polymeric phase of cellulose acetate are superior in their physical and mechanical properties to samples of wood-polymer composites based on polyolefins and are comparable to WPC based-on polyvinyl chloride.

The use of wood flour as a filler, the investigated plasticized cellulose acetate, leads to a significant increase in the biodegradation rate of the composite material while maintaining important physical and mechanical properties at a sufficiently high level. Also, the use of wood flour can significantly reduce the cost of the composite material compared to unfilled cellulose acetate.

Conclusion

As a result of the work carried out, several patterns of influence of the content of wood flour on the main physical and mechanical properties of composites with plasticized cellulose acetate were established. Thus, with an increase in the content of wood flour in the composition of a COMPOSITE sample, an increase in hardness, density, modulus of elasticity in compression and water absorption is observed. At the same time, a decrease in the plasticity index of the material is observed. The dependence of the impact strength index on the content of wood flour in WPC is extreme.

Samples of cellulose acetate composites filled with wood flour show a significantly higher biodegradation rate in active soil than unfilled cellulose acetate. The use of wood flour as a cellulose acetate filler can find a practical application for the production and use of demanded COMPOSITE products with the necessary physical and mechanical properties and biodegradation rate in the soil.

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Information about the authors

K. A. Usova – student;

P. S. Zakharov – postgraduate student;

A. E. Shkuro – Doctor of Technical Sciences, *Associate Professor.*

Информация об авторах

К. А. Усова – студент;

П. С. Захаров – аспирант;

А. Е. Шкуро – доктор технических наук, *доцент.*

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