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Tensile properties of wood plastic composites based on plant-filled polyvinyl chloride/poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) matrices

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Abstract. The article considers the obtaining and studying of microcomposites based on polyvinyl chloride (PVC)/poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) polymer matrix, filled with a various faction of different natural plant fillers. In work, such plant fillers as wood flour without lignin, spruce flour and rice husk were used. Microcomposites were obtained by melt rolling processing method with subsequent analysis of their morphology and mechanical tensile properties. It is shown that the filler particles were strongly oriented in the direction of the melt rolling process and have a different aspect ratio depending on the filler type. The tensile strength of materials strongly depends on the particle's aspect ratio. When the aspect ratio of the particles is 4.25, the material has a strength value comparable to a pure PVC/PHBHHx matrix.

Key words: polyvinyl chloride, polyhydroxyalkanoate, wood-polymer composites, composites morphology, mechanical properties.

INTRODUCTION

Polyvinyl chloride (PVC) is one of the main applicable polymers produced and consumed worldwide after polyethylene and polypropylene. It is widely used to produce packaging and household goods consumed around the world, due to high mechanical properties, thermal stability and low cost (Clough et al., 1996). Life cycle studies of PVC have shown that PVC-based products have high energy uptake and low thermal transfer value, as well as high rigidity. The impact of vinyl products on health and the environment is usually comparable or less than that of alternatives. Despite this, PVC has some lacks that limit its current use. These include a relatively low ability to plastic deformations and non-biodegradability of disposable packaging waste (Amass et al., 1998). The first of these disadvantages of PVC is expressed in the excessive fragility of materials based on it, which can be compensated by the addition of a significant number of additives including heat stabilizers, plasticizers, and shock modifiers. Such additives and fillers, as a rule, have less rigid and mobile chains, which, when they are embedded in between the PVC molecules, leads to an increase in its ductility and processability. Unfortunately, the solution of the problem for non-biodegradability of PVC is not possible, but a partial solution may be to apply the approach of obtaining semi-biodegradable compositions/blends such as PVC/biodegradable materials (Kann & Padwa, 2014).

Currently, the use of biodegradable polyesters from the family of polyhydroxyalkanoates and their derivatives is relevant as a biodegradable thermoplastic filler. One such polymer is a polyoxy acids copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx) with the linear polyester isotactic structure (Kushwah et al., 2016). It is synthesized by different types of bacteria (de Carvalho et al., 2016) as an intracellular stock of carbon and energy in response to physical stress conditions (Kushwah et al., 2016), e.g., nutrient deficiencies (nitrogen, sulfates, etc.). Moreover, an increase in the faction of 3-hydroxyhexanoate (HHx) in the copolymer composition leads to a decrease in the glass transition and melting temperatures and reduces the rigidity and brittleness of the material (Chang et al., 2014). PHBHHx filling of PVC leads to a decrease in the glass transition temperature of the blend and allows you to get the material with a homogeneous structure and high miscibility of the components (Kann & Padwa, 2014; Sitnikova et al., 2018; Samuilova et al., 2019b).

At the same time, one of the relevant approaches to creating cheap and green semi-biodegradable materials is the creation of wood-based plastic composites (WPCs) (Marcovich et al., 2001; Nunez et al., 2002; Marcovich et al., 2005). To create them, wood and other plants are used as a filler which containing lignocellulose or other plant polysaccharides most often in the form of fibers. One of the disadvantages of such fillers is that they make the material more combustible (Ashori, 2017). In one work (Müller M. et al., 2012), the introduction of wood flour obtained from *Picea abies* into the PVC matrix did not significantly affect the thermal degradation of a material with a similar of destruction temperature of 272 °C for WPC and pure polymer. Probably, this effect is due to the increase in heat resistance of the wood filler when it is inside the polymer matrix. Despite this, this result is not typical for this type of composites (Klyosov, 2010). In this connection, PVC is not the most widespread basis for composites with plant fillers, inferior to polyethylene and polypropylene (Marcovich et al., 2005; Alao et al., 2019). In one of our works (Samuilova et al., 2019a), it was found that the introduction of various amounts of fillers such as wood flour without lignin, spruce flour, and rice husk into a polymer matrix based on a PVC/PHBHHx blend in some cases led to a decrease in the temperature of the degradation of the composite from 251.6 to 232.6 °C (for WPC with pine flour). However, the preparation of the PVC/PHBHHx polymer blend can decrease the processing temperature of composite and can act as actual matrix for the polymer/plant filler composite.

Basically, the WPCs it is necessary to try to keep operational properties of polymeric material on its basis. Especially it concerns the physical and mechanical properties of such materials. As a rule, in such materials, tensile strength and elastic modulus deteriorate significantly with the introduction and increase in the content of plant filler, due to the weak interaction of these fillers with the polymers of the matrix (Ismail H. et al., 1999; Danyadi L. et al., 2007; AlMaadeed M. A. et al., 2013). Moreover, the size of the fraction, the form factor and the processing method of the filler also have a strong influence on the properties of the composite. Currently, there is a lot of research on this topic (Bessa et al., 2017; Alao et al., 2019; Kalalia et al., 2019), but mainly wood polymer composites based on polyethylene or polypropylene were studied. PVC-based composites with plant fillers are not as widely distributed.

This article presents the results of the obtaining and studying of PVC/PHBHHx/plant filler microcomposites filled with various factions of wood flour without lignin, spruce flour, and rice husk. Composites were obtained by melt rolling processing method with subsequent analysis of their morphology and mechanical tensile properties.

MATERIALS AND METHODS

Materials

As a macrocomponent of the polymer matrix we used the industrial suspension polyvinyl chloride (PVC) in the form of granules provided by Klekner Pentaplast Rus with containing thermostabilizer mercaptodioctyl 0.2–1.5 wt.%, melt flow modifier 2.0–4.0 wt.% and external lubricant (paraffin) 0.1–0.5 wt.%. PVC contains up to 0.04 wt.% of volatile compounds and has a Fikentscher constant value of 57–58, which is provided by the manufacturer.

Poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHHx) Aonilex X131A in the form of granules manufactured by Kaneka was used as a biodegradable filler to lower the glass transition temperature and softening of PVC. PHBHHx had an average molecular weight of Mw = 500,000–600,000 g mol^{-1} and a ratio of3HB/3HH = 95/5. The main thermal properties of the used PVC and PHBHHx were established by us earlier (Sitnikova et al., 2018; Samuilova et al., 2019b)and are presented in Table 1.

To fill the polymer matrix, solid natural fillers based on plant materials, such as wood flour without lignin (WLF) produced by MS Ltd., spruce flour (SF) produced by KFH Agrodom Ltd. and rice husk (RH) produced by Southern Rice Company Ltd were used.

Table 1. Thermal properties of the using polymer materials (Sitnikova et al., 2018; Samuilova et al., 2019b)

Material	T_g, °C	T_f, °C
PVC	80.0	141.4
PHBHHx	01.8	< 126.9
PVC/PHBHHx (80/20 wt.%/wt.%)	33.5	113.2

T_g – glass transition temperature; T_f – flowing temperature.

Preparation of composites

Composite materials were obtained at different ratios of the mass fractions of the components PVC/PHBHHx/plant filler: 80/20/0, 70/20/10, 60/20/20 and 50/20/30 wt.%/wt.%/wt.%.

Before preparing the polymer composites, the plant fillers were milled for 5 min using a roller mill Brabender (Germany) at a roller speed of 140 rpm to obtain a powder with a narrow particle size distribution relative to the original.

First, PVC and PHBHHx solid granules were premixed with plant filler powder for 5 min using a high-speed mixer Henschel (Germany) until a homogeneous mixture was obtained. To prepare microcomposites, the resulting mixtures of solid components were fed to a laboratory two-roll mill Schwabenthan Polymix 150U and heated to 175 °C to obtain a melt. The heating temperature of the mixtures was chosen between the melting temperature of PVC (Table 1) and the degradation temperature (close to 195 °C) of the PVC/PHBHHx blend. Then the melt was rolled between the rollers at a rotation speed of 24 rpm for 2 min to obtain the material in the form of films. The resulting composites were cooled to room temperature and subjected to thickness measurement using a standard digital micrometer MCD-25 manufactured by Tehrim (Russia) with a measurement step of 0.001 mm and an error of ± 0.004 mm. The thickness value (d) of the obtained microcomposites was determined as the average value of ten different points in the film area. The average thickness of the films is presented in Table 2.

Table 2. Thickness of the obtained composites at varying composition filled with different plant filler

PVC/PHBHHx/ plant filler, wt.%/wt.%/wt.%.	Thickness with various plant filler d, mm		
	WLF	SF	RH
80/20/0	0.255		
70/20/10	0.368	0.308	0.371
60/20/20	0.416	0.365	0.435
50/20/30	0.411	0.402	0.432

Light microscopy

Visual analysis of the obtained composites with a plant filler content of 10 wt.% showed that the polymer matrix based on the PVC/PHBHHx blend transmits visible light well and has transparency. To study the materials structure, macrographs were obtained in transmission mode using an optical microscope MBS-9 (Russia) equipped with digital camera.

Statistical analysis

The morphology of the composites was analyzed using statistical analysis of the obtained macrographs. For this purpose, in the images, particles of plant fillers that do not transmit visible light were segmented relatively to a transparent polymer matrix using ImageJ software v. 1.8.0 112 (USA) with a rotated rectangle tool. The form factor of the filler particles was calculated as the ratio of the length to the width of the rectangle ($AR = l\ w^{-1}$). Then, the calculated AR values were distributed according to their frequency and their statistics were determined.

Mechanical tensile testing

For mechanical tensile testing of the composites, ten samples of each composition were prepared in the form of strips with 10 mm wide and a measuring base length of 50 mm. Mechanical tests of the samples were carried out at a tensile strain rate of 180 mm min^{-1} using an electromechanical testing machine Instron 5966 (USA) equipped with the load cell (10 kN capacity) and pneumatic grip system. Signal processing was performed using Bluehill 3 software.

RESULTS AND DISCUSSION

Fig. 1, a–c shows the results of optical microscopy of PVC/PHBHHx/plant filler microcomposites with a content of 10 wt.% of plant fillers used.

A visual analysis of the morphology of the material with the addition of the WLF filler (Fig. 1, a) shows that most of its particles, obtained by pretreatment, are large in size and have elongated form, close to rectangular. It is also seen in the macrograph that the filler particles are strongly oriented in the direction of the melt rolling process. In the case of the PVC/PHBHHx/SF composite (Fig. 1, b), on average, there is a smaller planar size and a larger number of filler particles compared to using WLF, and the particle shape resembles short fibers. Moreover, the particles are also strongly oriented in the direction of the melt rolling process. In one of the works (Danyadi et al., 2007) according to SEM, it was noted that when a plant filler is introduced into polymer sheets up to 1 mm thick, the degree of orientation of the filler particles is greater than when filling with a larger thickness. Fig. 1, c shows that the RH filler particles in the PVC/PHBHHx polymer matrix have a relatively large planar size and a shape close to the square. In this case, the direction of the orientation of the particles is difficult to determine. In a general sense, the use of various kinds of plant fillers with the same pretreatment leads to the formation of rectangular particles with different planar size and form factor (aspect ratio). Moreover, the use of the melt rolling method of composite preparation allows the filler particles to be oriented in one direction in the structure of the resulting material.

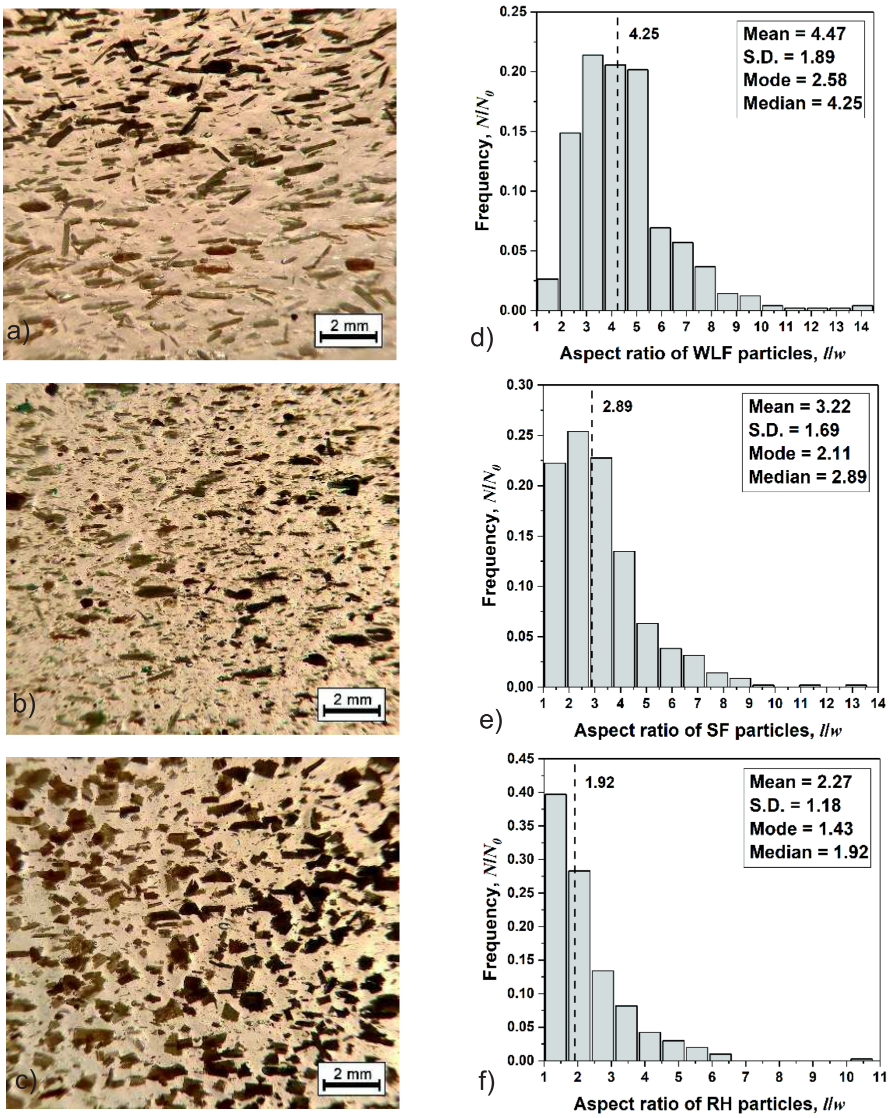

Figure 1. Light macrographs of a) PVC/PHBHHx/WLF; b) PVC/PHBHHx/SF and c) PVC/PHBHHx/RH microcomposites at a filler content of 10 wt.% and the corresponding statistical distributions of AR values.

The corresponding results of the statistical analysis of the considered macrographs in the form of statistical distributions of the calculated aspect ratio values (AR) of the filler particles are presented in Figs 1, d – f. The values of central trend measures for distributions are indicated in boxes. The diagrams show that the AR values of the filler particles are not distributed according to the normal law. This feature of the distributions is due to the physical property of the particle form factor, where AR ≥ 1. Moreover, under real conditions, the normality of the AR distribution will decrease when AR → 1. Given these distribution features, the median seems to be the most adequate measure of the central distribution trend. The median values of the distributions of AR values well reflect the results of the visual analysis of macrographs.

Fig. 2 shows the results of mechanical testing of the composites depending on their composition at the addition of the different types of plant fillers. The dependence shows that the introduction of all the considered types of plant fillers into the PVC/PHBHHx polymer matrix leads to a decrease in the tensile strength (σ) of the material. An increase in the filler fraction in the composition enhances this effect. Similar effects were observed by other authors (Ismail et al., 1999) for WPC from natural rubber/oil palm wood flour where, upon introduction and an increase in the proportion of flour from 0 to 50 wt.%, the tensile strength decreases in the range from 25 to 7 MPa. Also, in another work (Danyadi et al., 2007), when filling a matrix based on polypropylene with wood flour filler, σ value decreases from 25 to 5 MPa. Other authors (AlMaadeed et al., 2013) have shown, that filling the LDPE matrix with such a filler as date palm wood powder in a fraction of 20% led to a reduction in σ value to 9.2 MPa compared to 18.5 MPa for pure LDPE.

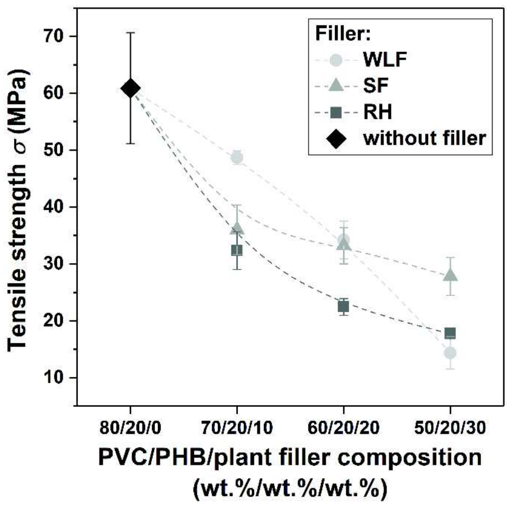

Figure 2. Dependence of the tensile strength of PVC/PHBHHx/plant filler microcomposites on the composition at adding of various filler type.

The observed behavior of σ value indicates a weak interfacial interaction of the matrix–filler. Using the analysis of SEM and mechanical fatigue of the WPC samples, the (Ismail et al., 1999) showed that with an increase in the content of the plant filler in the composition, its particles aggregate with the formation of stress centers.

It can be seen that the strength of this effect depends on the type of plant filler. In one of the works (Jiang et al., 2017), the authors also observed a different effect of fillers from different raw materials, such as straw fibers, on the mechanical strength of the PVC/straw fiber WPCs. However, the reasons for this behavior are not completely clear. An analysis of the microcomposites morphology showed that the type of filler used is significantly different in terms of the AR value. In this regard, we believe that the σ value of the considered microcomposites is controlled not only by the fraction of the filler in the material composition but also by the AR index of the filler particles.

Fig. 3 demonstrates the dependence of the tensile strength of PVC/PHBHHx/ plant filler microcomposites at a content of 10 wt.% of plant filler on the median value of the AR index distribution.

The dependence shows that at linear tensile deformations in the direction of melt rolling and, accordingly, the direction of the filler particles orientation (see Fig. 1, a – c) the strength of the material significantly increases with an increase in the AR value. Thus, at AR = 4.25 the energy of the strain deformations is efficiently transferred from the PVC/PHBHHx polymer matrix to the more rigid filler phase, compensating for the weak matrix-filler interfacial interaction. This behavior of the material under tensile strain leads to its reinforcing to $\sigma = 48.7$ MPa, which is comparable with the range of σ values for a pure polymer matrix PVC/PHBHHx.

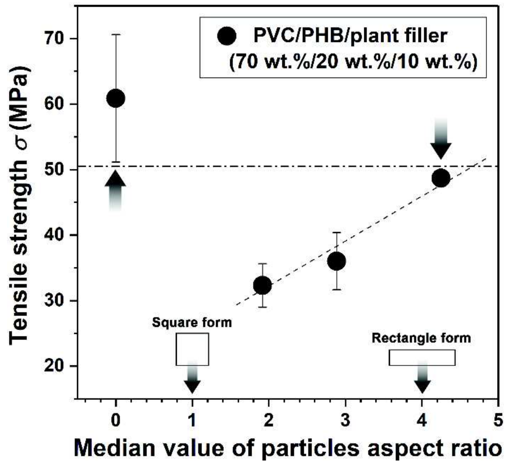

Figure 3. Dependence of the tensile strength of PVC/PHBHHx/plant filler microcomposites at a filler content of 10 wt.% on the median of AR value.

An analysis of the elastic deformations of microcomposites under tension depending on their composition with the introduction of various types of plant fillers is presented in Fig. 4.

The graph shows that the introduction of 10 and 20 wt.% of filler in the polymer matrix PVC/PHBHHx leads to an increase in its rigidity. However, the use of RH as a filler has a weak effect on the elastic properties of the polymer matrix, and the use of rigid wood fillers WLF and SF, on the contrary, leads to a significant increase in the stiffness of the material. This behavior of Young's modulus value of microcomposites is caused not only by the form factor of the filler particles but mainly by its type and the value of its own rigidity (Jiang et al., 2017). Comparing the E values with the σ values, the concept of the rigidity of microcomposites can be considered as fragility. Similar effects have also been observed for other WPCs (Ismail et al., 1999; Danyadi et al., 2007; AlMaadeed et al., 2013).

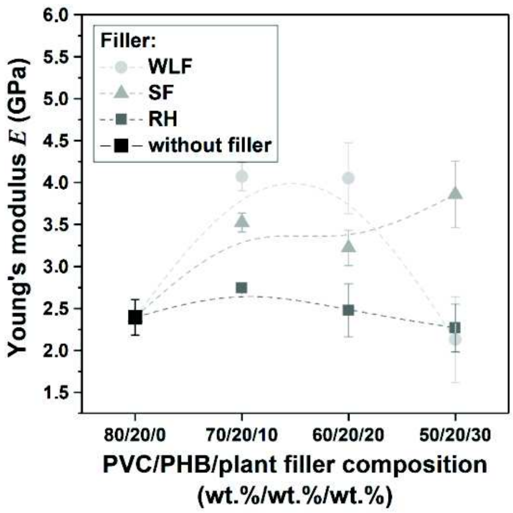

Figure 4. Dependence of the Young's modulus of PVC/PHBHHx/plant filler microcomposites on the composition at adding of various filler type.

CONCLUSIONS

In the course of work, the melt rolling method was used to prepare PVC/PHBHHx/plant filler polymer microcomposites with a ratio of mass fractions of components: 80/20/0, 70/20/10, 60/20/20 and 50/20/30 wt.%/wt.%/wt.%. Materials such as wood flour without lignin, spruce flour, and rice husk were used as plant fillers. It was found that preliminary mechanical processing of the fillers leads to the formation of particles with predominantly of rectangular shape and different aspect ratio. It is shown that the filler particles were strongly oriented in the direction of the melt rolling process. The mechanical analysis of the composites showed that the tensile strength of the PVC/PHBHHx polymer matrix decreases with the introduction and increase in the faction of filler. However, the strength of materials strongly depends on the aspect ratio of the particles of the filler phase. When the aspect ratio of the particles is 4.25, the material has a strength value comparable to a pure PVC/PHBHHx matrix. The rigidity of the microcomposites depends not only on the composition and aspect ratio of the filler phase particles but also on its type.

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