MECHANICAL BEHAVIOUR OF PLANT-FILLED COMPOSITES BASED ON POLYVINYL CHLORIDE/ POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYHEXANOATE) MATRICES

Samuilova E.O., Podshivalov A.V., Fokina M.I., Chursina V.S., Uspenskaya M.V.
ITMO University, Russia, Saint Petersburg

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.

Materials and Methods

Materials. As a macrocomponent of the polymer matrix we used suspension polyvinyl chloride (PVC) by Klekner Pentaplast Rus has a Fikentscher constant value of 57–58. Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) had an average molecular weight of Mw = 500 000–600 000 g/mol and a ratio of 3HB/3HH = 95/5. To fill the polymer matrix, solid natural fillers based on plant materials, such as wood flour without lignin (WLF), spruce flour (SF), rice husk (RH) were used. 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.%. 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.

Light microscopy. 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). Then, the calculated AR values were distributed according to their frequency and their statistics were determined.

Mechanical tensile testing. Mechanical tests of the samples were carried out at a tensile strain rate of 180 mm/min 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.

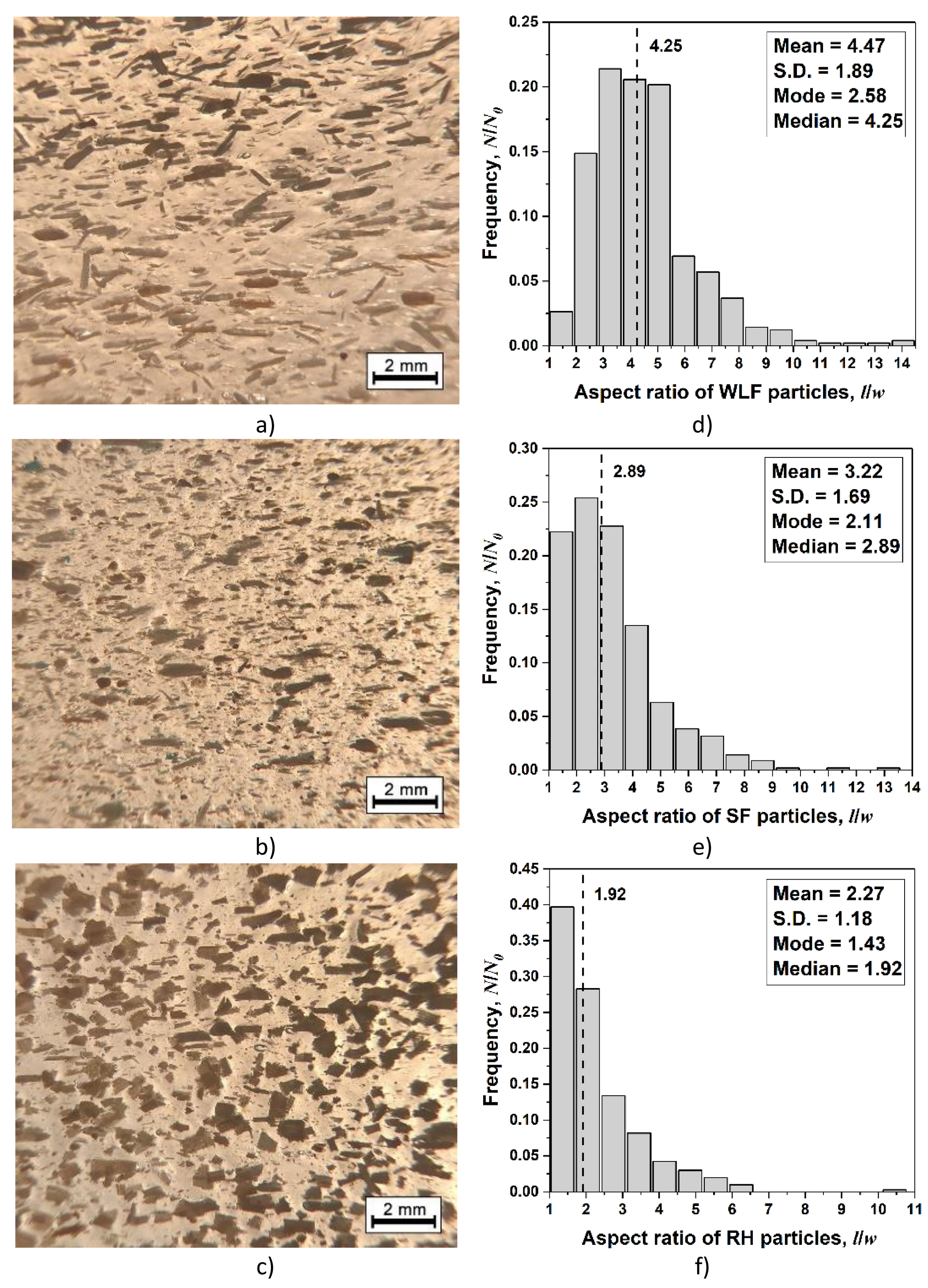

Figure 1. Light macrographs of a) PVC/PHBHHx/WLF; b) PVC/PHBHHx/SF and c) PVC/PHBHHx/RH microcomposites at a filler content of 10 wt.% and the corresponding statistical distributions of AR values

Results

A visual analysis of the morphology of the material with the addition of the WLF filler (Fig. 1a) 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. 1b), 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. Figure 1c 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.

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 Figures 1d–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.

Figure 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.

The observed behavior of σ value indicates a weak interfacial interaction of the matrix–filler. 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. Figure 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. 1a–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 σ = 48.7 MPa, which is comparable with the range of σ values for a pure polymer matrix PVC/PHBHHx.

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 Figure 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. Comparing the E values with the σ values, the concept of the rigidity of microcomposites can be considered as fragility.

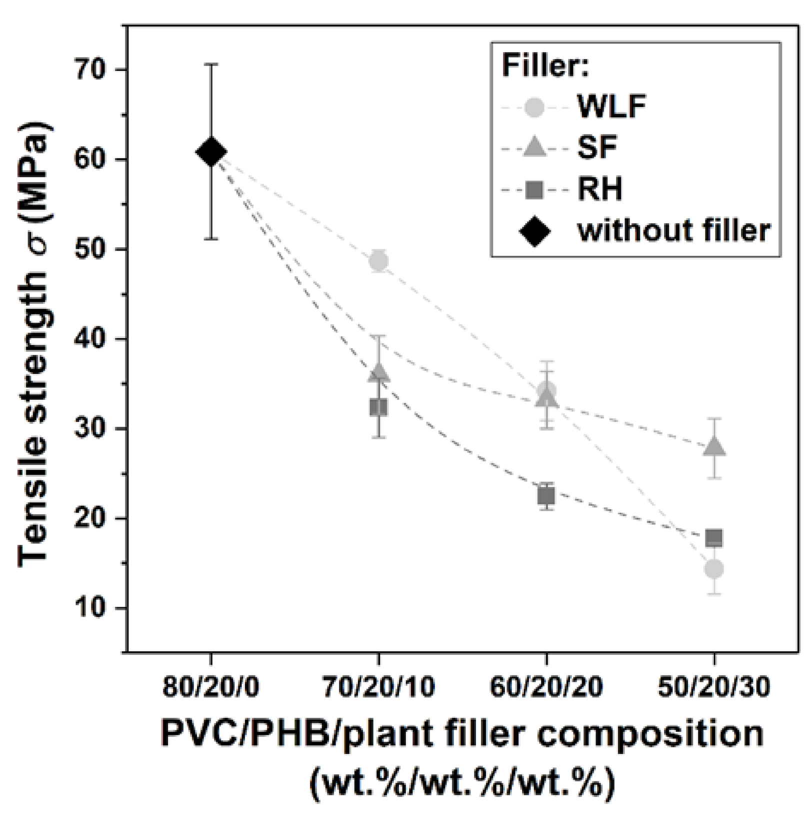

Figure 2. Dependence of the tensile strength of PVC/PHBHHx/plant filler microcomposites on the composition at adding of various filler type

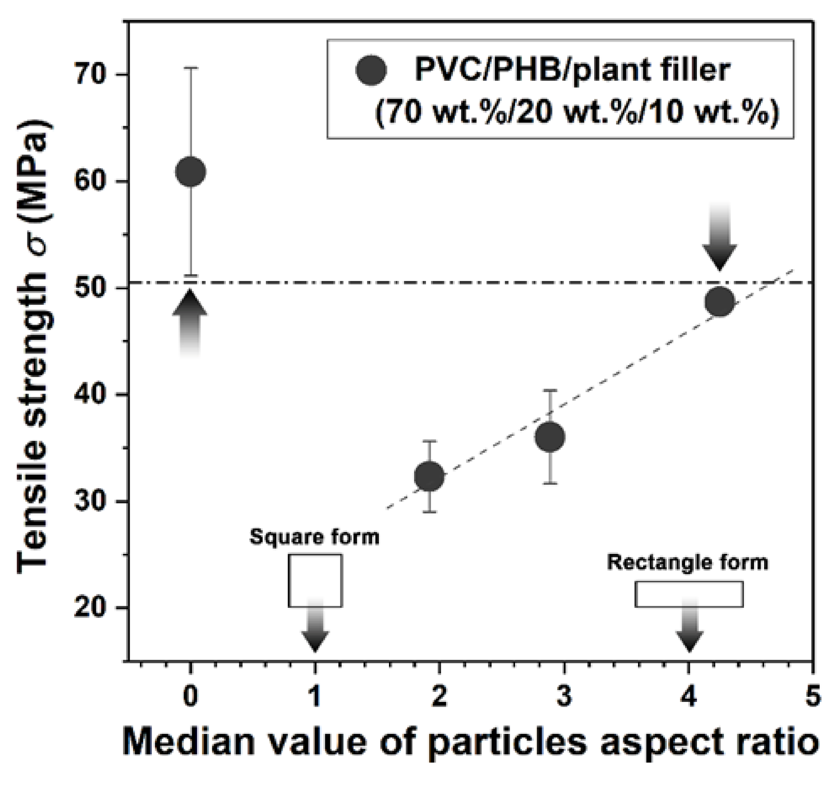

Figure 3. Dependence of the tensile strength of PVC/PHBHHx/plant filler microcomposites at a filler content of 10 wt.% on the median of AR value

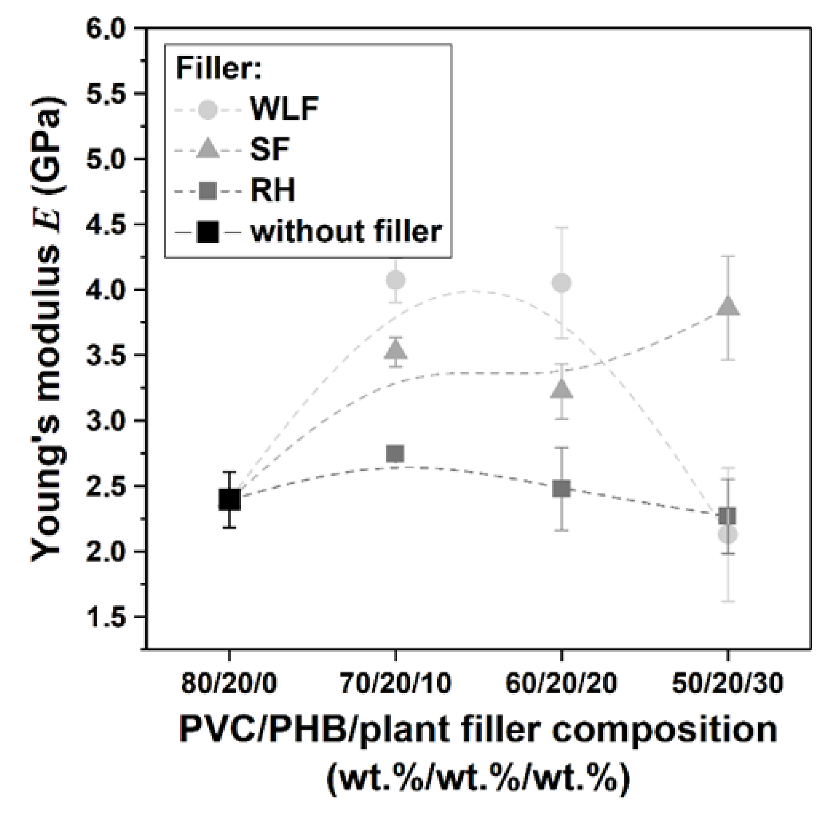

Figure 4. Dependence of the Young's modulus of PVC/PHBHHx/plant filler microcomposites on the composition at adding of various filler type

Conclusion

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.