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Studying of Viscoelastic Properties of Secondary Polymeric Materials in the Presence of Natural Plant Based Fillers

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Abstract

The purpose of this study was to investigate the rheological characteristics of a polymer composition based on secondary polypropylene and natural plant based fillers.

A sample of secondary polypropylene corresponding to the primary polypropylene of brand FF/3350 was used in this study. It is a crushed material from non-standard products produced by injection moulding in the technological production LLC "ZPI Alternative" (Russia, the Republic of Bashkortostan, Oktyabrsky). Industrial waste products, buckwheat husk, wheat chaff, rice husk and wood flour, were considered as fillers. The modelling of the processing of polymer materials was carried out in melt at the laboratory station (plastograph) "PlastographEC" (Brabender, Germany). The physical-mechanical properties of the polymer composites at break were determined by the tensile testing machine "ShimadzuAGS-X" (Shimadzu, Japan). Rheological measurements of the polymer composition melts was performed using a Haake Mars III rheometer.

The increase in the viscosity of the polypropylene melt occurring upon addition of fillers to the composition was revealed. The increase in filler content in the system increased not only the viscous properties, but also the elastic characteristics. It was established that as the polymer was filled with natural excipients, an increase in the storage modulus occurred, typical for systems showing elastic properties. Composites, characterized by high values of the storage modulus and correspondingly increased the values of Young's modulus were formed, when rice husk and wood flour were used as fillers. It has been proven that the optimum filler content was a value corresponding to 10 mass.h.

Keywords: polymeric composition, rheology, secondary polypropylene, natural plant based fillers, viscoelastic properties.

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1. Introduction

The development and creation of polymer composite materials based on secondary polymer raw materials is a serious scientific task, especially important when it comes to the use of large-capacity polymers such as polyethylene or polypropylene [1–6]. Among the widest range of fillers used for creating composites, natural fillers, obtained on the basis of plant materials are of particular interest [7–13]. The introduction of natural fillers into the polymer matrix allows not only to reduce the cost of production by replacing part of the polymer with cheap raw materials, but also partially solve the biodegradability issue of the material, as well as to create a material with new properties [14–23].

Taking into consideration that the shear rate values realized in the processes of polymer processing by extrusion and injection moulding reach 1000 s^{-1}, the probability of occurrence of normal stresses caused by the manifestation of

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elastic properties by the polymer melt is very high. The introduction of a filler to an even higher degree can complicate processing, due to an increase in the viscosity of the polymer melt [24]. Moreover, not only an increase in the viscosity, but also the elastic component of the viscous flow can take place. The fundamental importance of determining the elastic component is due to the fact that the elasticity that can become a factor determining flow anomalies, such as jet separation, the Weissenberg effect, etc., which limit productivity and can lead to spoilage [25–27].

The aim of this work was a comprehensive study of the rheological characteristics of the polymer composition based on secondary polypropylene (SPP) and plant based fillers. When choosing a filler, the following requirements were taken into account:

– low cost and availability;

– environmental safety of biodegradable products;

– the possibility of grinding with standard grinding equipment;

– high temperature of thermal decomposition;

– rapid biodegradation under environmental conditions.

2. Experimental

In the study, we used a SPP sample corresponding to the primary polypropylene (PP) of brand FF/3350, which is crushed material from non-standard products produced by injection moulding in the technological production LLC "ZPI Alternative" (Russia, the Republic of Bashkortostan, Oktyabrsky).

We considered industrial wastes: buckwheat husk, wheat chaff, rice husk, and wood flour as a filler. The characteristics of the used fillers are presented in Table 1. Before mixing, the filler was dried in an oven at 100 °C for 5 h.

The modelling of the processing of polymer materials was carried out in the melt at the laboratory station (plastograph) "PlastographEC" (Brabender, Germany) for 15 min at a load of 200 N at a temperature of 180 °C. The amount of loaded polymer composite was 25 g. The deformation-strength properties of the material were determined on pressed material samples with a thickness of 1 mm. The pressing was carried out on an automatic hydraulic press "AutoMH-NE" (Carver, USA) at 210 °C and pressure was held at 7000 kgf for 3 min. The physical-mechanical properties of polymer composites at break were determined according to GOST 11262-2017 using a "ShimadzuAGS-X" (Shimadzu, Japan) tensile testing machine at a temperature of 20 °C and a motion speed of the movable grip of the tensile testing machine of 1 mm/min. The melt flow rate (MFR) was determined at 190 °C with a load weight of 2.16 kg using a melt flow indexer. The composition was divided into segments every 30 s, the obtained samples were weighed and the average weight was calculated. Rheological measurements were carried out using a Haake Mars III modular dynamic rheometer at 220 °C in the oscillation mode in the oscillation frequency range from 0.01 to 100 Hz.

In oscillation mode, an alternating shear stress with a small amplitude was applied to the sample $\tau(t) = \tau_0 e^{iwt}$ and its deformation $\gamma(t) = \gamma_0 e^{(iwt+\delta)}$ with a phase shift δ relatively to the voltage was registered. Angular velocity ω related to the oscillation frequency was as follows:

$$\omega = 2\pi f,$$

where the frequency *f* in Hz (1 Hz = cycle/s); ω – 1/s or rad/s.

The total resistance of the sample to the applied deformation, called the complex modulus *G** was defined as:

$$G^* = G' + iG'' = \frac{\tau_0(t)}{Y_E(t)}.$$

In this equation, the quantities *G*′ and *G*″:

$$G' = G^* \cos\delta = \frac{\tau_0}{\gamma_0}\cos\delta \text{ – storage modulus;}$$

Table 1. Characteristics of the used fillers

Filler	Chemical composition, % [28–31]		Average diameter, mm
	cellulose	lignin	
wood flour	42.0	31.0	0.17
rice husk	48.9	19.1	0.20
buckwheat husk	29.4	34.7	0.24
wheat chaff	51.0	19.5	0.19

$G'' = G^* \sin\delta = \frac{\tau_0}{\gamma_0}\sin\delta$ – loss modulus.

The term “storage modulus” indicates that the voltage energy was temporarily stored during the test, but can be returned later. The term “loss modulus” indicates that the energy used to initiate the flow is irreversibly converted into heat (“lost”).

3. Results and discussion

It is well known that according to Newton’s law, viscosity is a constant that should not depend on the shear rate $\dot{\gamma}$ nor on the frequency of exposure f (during test in the oscillation mode), i.e. $\eta \sim f^n$, where $n = 0$. Index n is easily defined as the slope of the logarithmic dependence of viscosity on the oscillation frequency. However, often the fluid flow disobeys Newton’s law. For example, during the flow of pseudoplastic liquids, which include both solutions and polymer melts, a decrease in viscosity with an increase in shear rate (oscillation frequency) is characteristic, and the n value in the power dependence of viscosity on shear rate or oscillation frequency is $n < 1$.

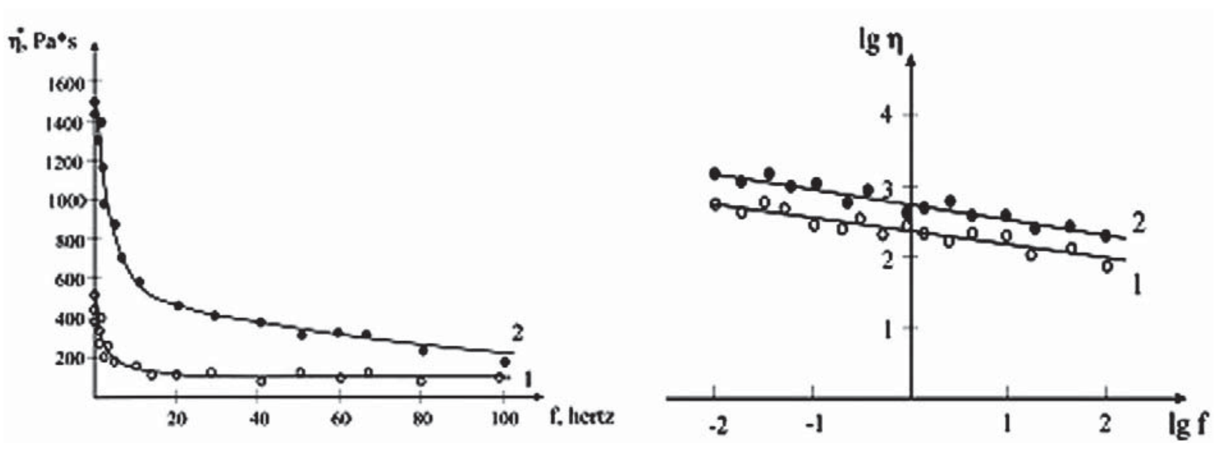
The complex viscosity frequency of the oscillatory action curves in direct and logarithmic coordinates for a SPP white masterbatch melt filled with 2 and 10 % mass. wood flour are shown in Fig. 1. For the rest of the fillers, the curves were similar.

The analysis of the obtained data suggests that SPP melts, both in the absence of filler and in their presence, behave like typical pseudoplastic fluids, the viscosity of which decreases with increasing oscillation frequency. For all studied fillers, their addition to the composition leads to a clear increase in viscosity. Moreover, the more filler the composition contains, the more significant is the viscosity anomaly. This is evidenced by deviations of the slope depending on the complex viscosity on the frequency determined in the logarithmic coordinates (Table 2). For all the studied systems, the slope is non-zero, and the more filler that was in the composition, the higher was the value of the slope (in absolute value). The slope characterizes the degree of manifestation of the viscosity anomaly. It can be seen that for all four studied fillers, wood flour, rice husk, wheat chaff and buckwheat husk, the values of the slope deviate from the zero value characterizing a Newtonian fluid.

The accumulated data are presented in Table 2.

Also, as the filler content in the system increased, not only the viscous properties of the system increased, as evidenced by the complex viscosity values (Fig. 2) and MFR (Fig. 3), but also the elastic characteristics. This conclusion can be made based on an analysis of the dependences of the storage and loss modules on the oscillation frequency.

It was established that as the polymer is filled with plant components, a natural increase in the storage modulus occurs (Fig. 4). This behaviour of the system is characteristic of systems



a b

Fig. 1. Dependence of complex viscosity of SPP determined in oscillatory mode in direct (a) and logarithmic (b) coordinates containing 2 (*1*) and 10 (*2*) mass.h. of wood flour

Table 2. Results of investigation of viscosity anomaly of secondary polymers filled with natural fillers

Polymer	Filler	Filler content, % mass.	Slope as a function of viscosity versus oscillation frequency
white master-batch	chaff	2	–0.15
		5	–0.16
		10	–0.18
		15	–0.21
		30	–0.26
	buckwheat husk	2	–0.15
		5	–0.16
		10	–0.17
		15	–0.18
		30	–0.19
	wood flour	2	–0.15
		5	–0.16
		10	–0.18
		15	–0.21
		30	–0.27
	rice husk	2	–0.12
		5	–0.15
		10	–0.16
		15	–0.18
		30	–0.24

exhibiting elastic properties. The highest values of the storage modulus were characteristic for composites filled with rice husk and wood flour. Buckwheat husk and chaff fillers increased the elastic properties of SPP melt to a lesser extent.

The value of the loss modulus from the filler content in the composite passes through a maximum (Fig. 5).

Moreover, it can be noted that when the filler content in the composition was higher than 10 mass.h. the general increase in the resistance of the system to the flow process was due to an increase in the elastic component of the viscous flow.

The study of the viscoelastic characteristics of secondary polymer raw materials in the presence of natural plant based fillers allowing to analyse the influence of the nature of the filler on the resistance of composites to mechanical stress.

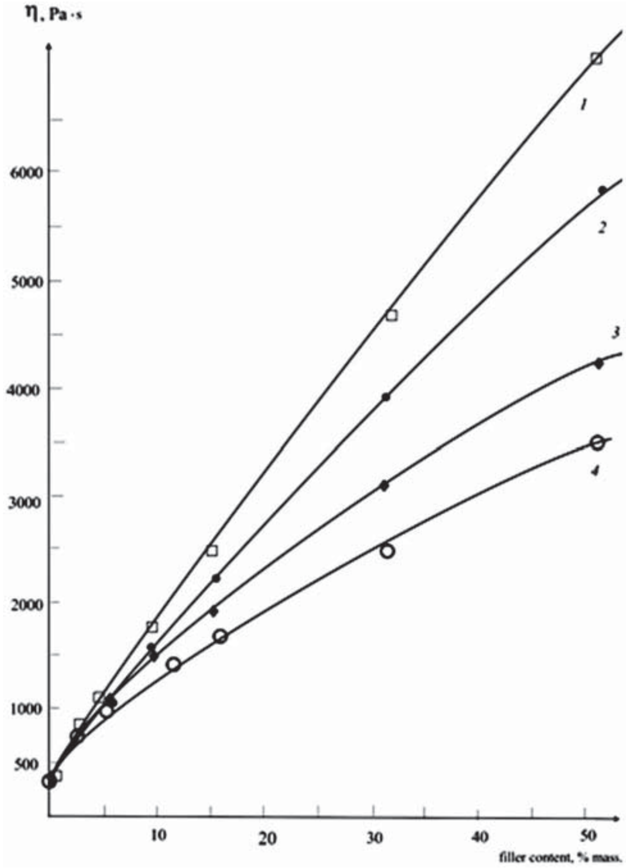


Fig. 2. Dependence of complex viscosity determined at oscillation frequency 0.01 Hz on content of rice husk (*1*), wood flour (*2*), buckwheat (*3*) and chaff (*4*) in the system

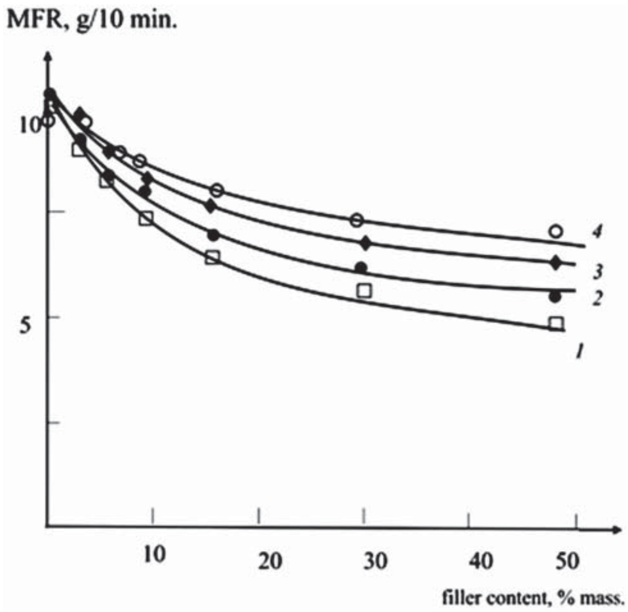


Fig. 3. Dependence of MFR of composition based on SPP at the content of rice husks (*1*), wood flour (*2*), buckwheat (*3*) and chaff (*4*) in the system

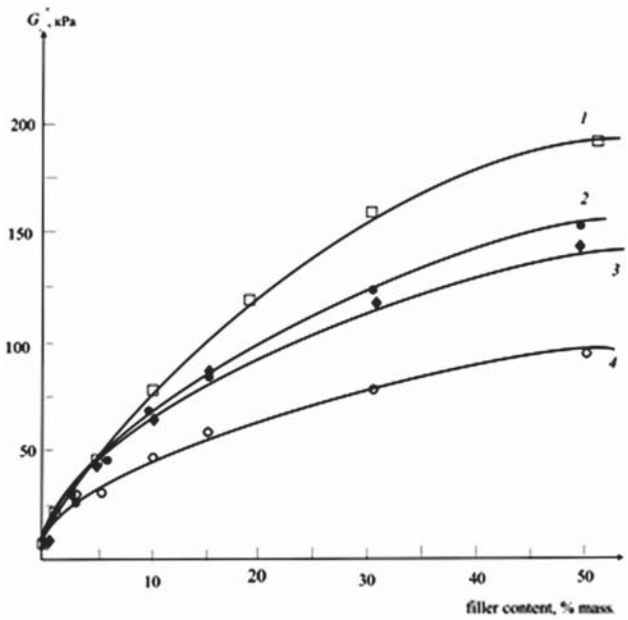


Fig. 4. Dependence of the storage modulus determined at an oscillation frequency of 100 Hz on the content of rice husks (*1*), wood flour (*2*), buckwheat (*3*) and chaff (*4*) in the system

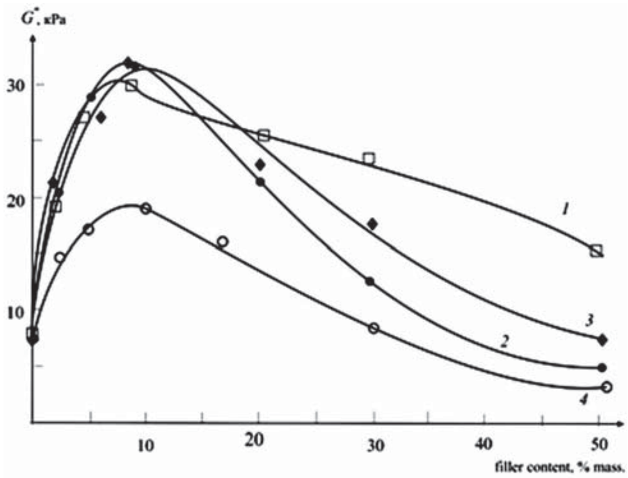


Fig. 5. Dependence of the loss modulus determined at an oscillation frequency of 100 Hz on the content of rice husks (*1*), wood flour (*2*), buckwheat (*3*) and chaff (*4*) in the system

For example, at a qualitative level there is a correlation of the rheological data determined in the oscillation mode and the elastic modulus values from the data of deformation-strength measurements. It can be noted that by the nature of the changes in Young's modulus *E* that all the analysed fillers unequivocally affected the polymer, they undergo an extreme change in the composition corresponding to 10% mass.h. of the filler (Fig. 6). The maximum values of Young's modulus were revealed for composites filled with rice husk and wood flour, e.g. for composites with maximum storage moduli.

Thus, based on an experiment conducted in the range of oscillation frequencies from 0.01 to 100 Hz, for the analysed SPP sample, the maximum viscosity values were realized when rice husk and wood flour were used as filler, and the minimum values were detected for chaff and buckwheat husks. Composites, characterized by high values of the storage modulus and correspondingly higher values of Young's modulus were formed when rice husks and wood flour were used as fillers. The optimal filler content had a value corresponding to 10 mass.h., which when exceeded, an increase in the elastic properties of the polymer melt was accompanied

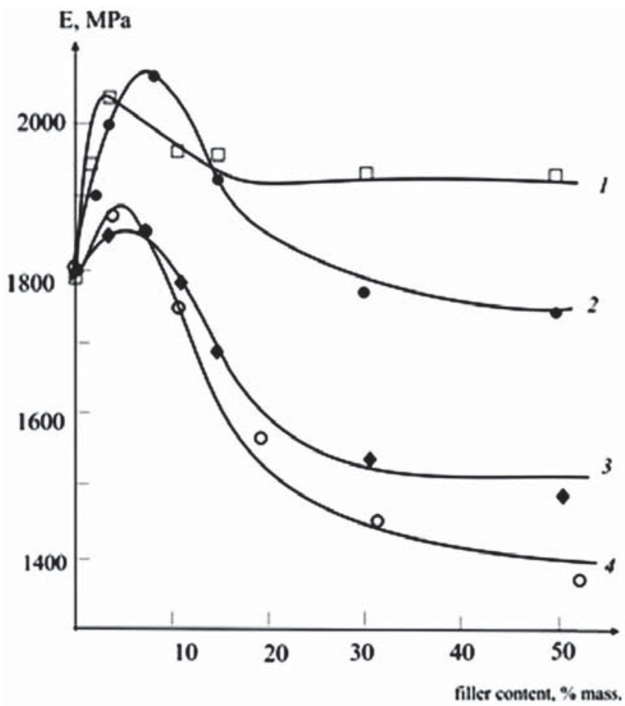


Fig. 6. Dependence of Young 's modulus of the composition based on SPP on the content of rice husks (*1*), wood flour (*2*), buckwheat (*3*) and chaff (*4*) in the system

by a deterioration of the processing properties of the composites and their deformation-strength properties.

4. Conclusions

1. The introduction of filler in all studied cases led to an increase in complex viscosity and a decrease in MFR. The more filler the composition

contained, the more significant was the viscosity anomaly, i.e., the dependence of viscosity on the oscillation frequency was stronger.

2. The increase in filler content in the system increased not only the viscous properties, but also the elastic characteristics. When the filler content in the composition was higher than 10 mass.h. the overall increase in the resistance of the system to the flow process was due to the increase in the elastic component of the viscous flow, since the storage modulus continued to increase, and the loss modulus started to decrease.

3. Based on the nature of the changes in Young's modulus, all analysed fillers possessed the same action on the polymer. They had maximum values in the composition region corresponding to a 10 mass.h. filler. Thus, the composition of a 10 mass.h. filler should be considered to be optimal.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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