RHEOLOGICAL PROPERTIES OF POLYMER-POLYMER MIXTURES ON CORN STARCH BASE

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The prospects for the use of polymer-polymer mixtures based on corn starch as alternative thermoplastic materials to polyolefins are considered. Rheological curves have been obtained, which confirm the possibility of processing such mixtures on standard equipment into products. It is shown that the starch content in polymer-polymer mixtures can reach 90 mass percent. Compared to existing biodegradable polymers, plasticized starch-based material is in no way inferior to them in terms of processability. Studies of the mechanical properties of polymer-polymer mixtures based on corn starch have been carried out. The data obtained indicate the possibility of using the developed composites as packaging materials, as well as alternative materials to known bioplastics and synthetic polymers.

KEYWORDS

Polymer, corn-starch, biodegradable polymer

1 INTRODUCTION

The prospects for creating polymer-polymer mixtures of polysaccharides with synthetic polymers have a great interest as they are biodegradable materials. Polysaccharides, in particular corn starch, decompose under the influence of natural factors, but most synthetic polymers, due to the nature of their origin, are not initially biodegradable. The high content of starch in polymer-polymer mixtures, provided that the starch is not an inert filler, but exhibits the properties of a polymer, gives grounds to assert that such compositions are biodegradable, particularly when the starch content reaches 90 %. Biodegradable materials are becoming more and more necessary in the production of short-term polymer products (packaging films and products, products of the cosmetic industry and household chemicals, films for agriculture, etc.) [Albertsson 1995, Suvorova 2006, Vinidiktova 2006, Leroy 2012]. They must have a set of properties inherent in synthetic polymers, but be capable of biodegradation in natural conditions after operation, i.e., when buried in the soil, when composting, etc. [Sherieva 2007, Popov 2007, Ermolovich 2007].

Efforts aimed at developing and improvements of advanced materials with tailored properties for various applications is closely connected with multifactorial analysis of their preparation, processing and properties characterization during lifetime [Man 2011, Modrak 2013, Anisimov 2019]. That means, in particular, that- biodegradable materials require an integrated approach involving precise composition preparation, appropriate product design with set of mechanical properties and biocompatibility, and a suitable manufacturing technique [Mascenik 2014 and 2022, Sukhodub 2018]. Recently, biodegradable materials have gained growing interest and are intensively investigated [Todic 2011]. As an example, Table 1 presents selected starch-based materials that are produced in the world.

Table 1. Representatives of starch-based materials

Trademark	Producer	Composition	Application and properties
Novon	Warner-Lambert & Co	Starch (43 %), plasticized with water; synthetic polymer (50 %)	Disposable dishes, boxes, films
Greensack	Convex Plastics	Corn starch	Packaging, bags
Biopac	Biologische Verpackungs-Systeme	Plasticized starch (87-94 %)	Packaging
Solanyl	Rodenburg Biopolymers	Biopolymer from starch waste	The packaging is obtained by the method of injection moulding
Bioflex	Biotec GmbH	Starch and plasticizers (alcohols, fats, sugar, wax, aliphatic polyesters)	Film material that decomposes in compost at a temperature of 30 °C in 56 days with the formation of products that promote plant growth.
Mater-Bi	Novamont S.p.A.	Mixture of starch (60-90 %) with polycaprolactone, glycerine and impurities of natural origin	Packages, flexible and rigid packaging
Ecofol	Fatra	Mixture of starch with polyolefin	Agricultural films for composting; decompose in 3-4 months
BAK	Bayer AG	Polyolefins with fillers (cellulose, tar flour, starch)	Moisture-proof packaging, agricultural bags for compost. Decomposes in 10 days into biomass, CO_2 and water
Ecoflex	BASF	Polystyrene mixed with starch and cellulose	Packaging and agricultural films; biodegradable by 60 % in 50 days, by 90 % in 80 days

The possibility of processing and moulding products from polymeric materials requires knowledge of their rheological properties [Sukhyy 2021a], that is, knowledge of the patterns of change in the fluidity of polymer systems in real conditions under the action of external stress, shear rates, and temperature. Mentioned mixed compositions based on natural polysaccharides and synthetic polymers can be used for the production of various polymeric environmentally friendly materials [Berladir 2016, Sukhyy 2021b]. However, a large number of monographs and articles are devoted to the study of the rheological properties of synthetic polymers, and the rheological properties of natural polysaccharides and mixtures containing these polysaccharides have been little studied. In this regard, it is necessary to consider the available data on the rheological behaviour of systems based on natural polysaccharides and their mixtures with synthetic polymers [Lamberty 2004].

2 MATERIALS AND METHODS

To obtain thermoplastic polymer-polymer mixtures, starch was preliminarily plasticized with glycerol. The process of plasticization of starch and mixing with a synthetic polymer was carried out in a worm press at a temperature of 140 °C. Ethylene-vinyl acetate (EVA) copolymer was used as the synthetic polymer. Biodegradation of a composite material obtained by this technology begins with the surface of the film enriched with starch. In the future, after decomposition, fine particles of a synthetic polymer may remain. The amount of non-degradable residue depends on the concentration of EVA in the polymer-polymer mixture.

The rheological characteristics of the samples were determined using a capillary viscometer, the scheme of which is shown in the Figure 1.

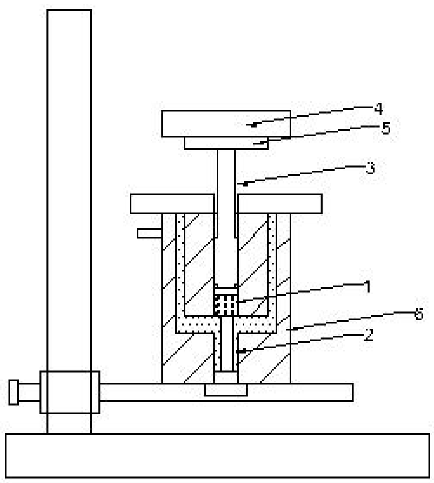

Figure 1. Capillary viscometer; 1 - chamber with a sample; 2 - capillary; 3 - piston; 4 - weight; 5 - control of the piston displacement speed; 6 - thermostatic jacket

The samples were placed in the working chamber, which was thermostated at a temperature of 140 to 180 °C (depending on the temperature of the experiment) for 30 minutes. A load was applied to the piston, under the action of which the melt left the chamber and filled the capillary. When the capillary was filled, the experiment was started. To do this, increasing weights from 200 to 8000 g were placed on the piston. The speed of the piston was fixed. Melt viscosity was measured in the stress range 10^2–10^3 Pa and shear rate 10^{-1}–10^1.

The rheological consideration of any systems is based on Newton's law, which relates the viscosity (η) to the stress (τ) applied to the system and the shear rate (γ):

$$\tau = \eta\gamma \qquad (1)$$

For this, the results of the experiment are presented in the form of flow curves in the form of dependence $\log\gamma = f(\lg\tau)$ or $\log\eta = f(\lg\tau)$.

The rheological characteristics of polymer-polymer mixtures are of interest for evaluating the possibility of their processing in a certain range of compositions, temperatures, and mechanical stresses, which is of great practical importance. Analysing the patterns obtained, it can be argued: is it possible to process such a polymeric material on a certain type of equipment into certain products.

In accordance with the task set in the work, the rheological characteristics of mixtures based on plasticized corn starch with EVA were evaluated.

3 RESULTS AND DISCUSSION

The rheological behaviour of polymer systems is influenced by the difference in the chemical structure of synthetic and natural polymers. The higher the content of polysaccharide polymer in the polymer mixture, the better from an environmental point of view. But the rheology will change depending on the concentration, and therefore, at certain ratios of natural and synthetic polymer, it can be difficult to process such a mixture into a product.

Figure 2 shows the concentration dependence of the viscosities of EVA-starch mixtures.

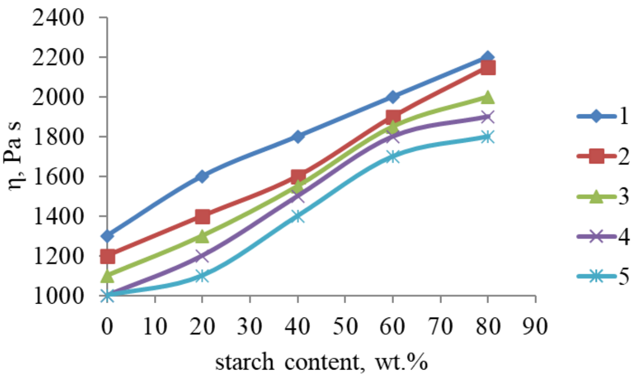

Figure 2. Concentration dependence of the viscosities of EVA-starch mixtures; 1 - temperature 140 °C, 2 – 150 °C, 3 – 160 °C, 4 – 170 °C, 5 – 180 °C

According to the Figure 2 data, it can be concluded that the operating temperature of the polymer-polymer mixture is in the range of 160-180 °C

Hanging the starch content increases the viscosity of the melt, however, at the operating temperature range (regarding dependencies 3-5) from a concentration of 60 %, the curves begin to reach a stable value of the melt viscosity. This is confirmed in the Figure 3.

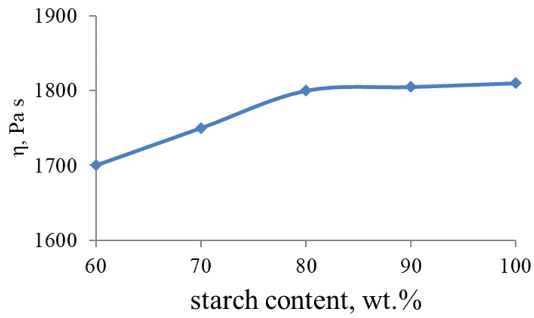

Figure 3. Starch content

Starting from 80 % starch in the polymer-polymer mixture, the melt viscosity practically does not change, or changes slightly. In this case, we can discuss about the optimal concentration for rheology in the range of 80-90 % of corn starch plasticized with glycerol.

Figures 4 show the flow curves of the EVA-starch polymer-polymer mixture at 180 °C.

Analysis of the obtained rheological data shows that with an increase in the concentration of polysaccharide - starch, the viscosity of the melts of EVA-starch mixtures increases. In this case, the absolute values of the viscosity of the mixtures remain within the limits characteristic of the flow of melts of industrial thermoplastics during their moulding. Comparison of the rheological behaviour of the studied EVA-starch system with the few data on the rheology of biodegradable systems known from the literature, in particular, with the rheological characteristics of the melt of the Mater-Bi AF05H material (a mixture of polyvinyl alcohol with 60 % starch, industrially produced by Novamont), obtained at similar temperatures, allows us to conclude that the viscosity values of the EVA-starch and Mater-Bi systems are comparable. This testifies in favour of the conclusion about the possibility of using the mixtures obtained as a basis for creating biodegradable compositions.

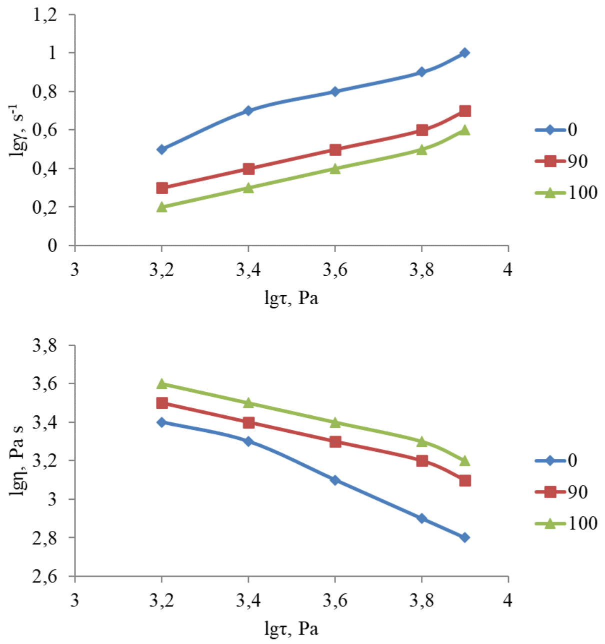

Figure 4. Flow curves of the EVA-starch polymer-polymer mixture at 180 °C; 0 is EVA without starch, 90 is 90 % plasticized starch, and 100 is plasticized starch without synthetic polymer

Further studies were carried out on compositions of EVA-starch with different starch content. It was interesting to follow the trend in mechanical properties with increasing starch content. In addition to rheological characteristics, indicating the possibility or impossibility of processing a starch-based polymer-polymer mixture by a standard method, mechanical properties are also important. The possibility of using the developed composition as a specific product depends on them. That is why during the research we were interested in the mechanical properties of the material with the highest possible content of corn starch and comparing them with existing biopolymers.

These changes in properties with hanging contents in the composition of starch are presented in Table 2.

Table 2. Properties of the different starch composition

Composition, %		Izod impact strength, kJ/m²	Tensile strength, MPa	Elongation at break, %
EVA	starch			
70	30	-	82	95
60	40	-	79	80
50	50	-	73	65
40	60	-	70	40
30	70	85	67	30
20	80	70	65	25
10	90	65	63	25

An increase in the content of corn starch in the polymer-polymer mixture leads to a decrease in the mechanical characteristics of the material. But it is impossible to say that the strength of products made from this material decreases disastrously with an increase in the starch content. Yes, indeed, there is a decrease in strength indicators, but they remain at a relatively high level. From an economic point of view, a high starch content in the composition is more beneficial, since it is an inexpensive component, the resources of which are renewed annually.

The following Table 3 presents comparison of the properties of corn starch-based polymer-polymer blend with well-known brands of biodegradable polymers. In this case, for comparison, test samples were obtained by injection moulding. Moreover, the procedure for obtaining samples and testing was the same for all materials. When receiving samples, the recommendations of manufacturers regarding processing modes were taken into account.

Table 3. Properties of the different starch composition

Material	Izod impact strength, kJ/m²	Tensile strength, MPa	Elongation at break, %
Mater-Bi DI01A	46	48	22
Novon	50	65	25
Bioflex	44	58	54
Polymer-polymer blend based on corn starch	65	63	25

4 CONCLUSIONS

The data obtained experimentally entirely correlate with the technical characteristics indicated by the manufacturers of biodegradable polymers.

The corn content increase of starch in the polymer-polymer mixture results in a deterioration of the mechanical properties of the material, in particular, considerable decrease in strength indicators. On the other side, taking into account the economic point of view, a high starch content as a renewable inexpensive component in the compositions may be rated as beneficial.

The resulting composite material, namely: a polymer-polymer mixture based on corn starch, is quite competitive with some known biodegradable polymers and can be processed by standard methods into various products, for example films, rigid packaging, or disposable tableware.

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