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Effect of ultrasound exposure on melts of polyolefin compositions

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Abstract

This study aimed at investigating the dependence of the ultrasonic (US) effects on the structure and properties of the polymer mixtures with different viscosity values. It should be noted that in the current study, polypropylene and high-pressure polyethylene of different brands were selected. The polymer composite materials (PCM) of various compositions treated with and without ultrasound were used. The formation dependence of the phase structures of polyolefin compositions on composition and viscosity of polymer systems was established. The regularity "structure-properties" of modified mixtures of polyolefins was determined. The influence of ultrasonic on the restoration process of the structure and the formation of new chemical bonds in polyolefin mixtures was discussed. The structure of the compositions of the polymer and technological conditions for their processing, which providing high physical and mechanical characteristics of PCM, were also proposed. The results indicated that to create compositions with high physical and mechanical characteristics, it is recommended to use a mixture of polyolefins containing 70% PE, modified by ultrasonic treatment.

Keywords: Polyethylene; polyolefin mixtures; ultrasound; structure of composition; recycling.

Introduction

Currently, development of polymer composite materials is relevant. Such materials have high technological characteristics, meeting all the necessary operational requirements. However, a significant drawback is the complexity of the disposal of waste generated during production and after the use of such materials [1,2].

Recycling of polymeric materials is the most promising method of disposal. Despite the fact that mixed waste consists predominantly of polyolefins, the components of this system are thermodynamically incompatible with each other, leading to deterioration in the physicomechanical properties of products from mixtures in comparison with pure polymers [2-7].

At the same time, polymer mixtures have the characteristic features of colloidal systems. With the correct selection of the structure of such combinations, it is possible to obtain the necessary properties of the compositions [3, 5, 6]. The structure of such systems is influenced by the following factors: the nature of the polymers, the ratio of the components in the mixture, the size

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and shape of the particles in the dispersed phase, molecular weight, viscosity, the interaction of particles in the interfacial layer, and processing conditions.

In turn, the viscosity and size of the particles that make up the polymer mixture can be controlled using the technological methods [8-10]. One of such techniques is the effect of ultrasonic vibrations (hereinafter referred to as ultrasound) on polymer melts. It is known that the use of ultrasound in the processing of polymers is accompanied by the breaking of chemical bonds of macromolecules (mechanochemical destruction), which in turn leads to a decrease in the molecular weight of polymers. Similar processes have been also observed with other types of damage, including in the process of multiple polymer processing (mechanical destruction) [11-16, 5].

Nowadays, recycling of polymeric materials to create compositions with high-performance characteristics is an important issue. It is obtained by modifying their structural properties using ultrasonic treatment [17-19]. As a novel strategy, in the current study, the dependence of the structural features and properties of polyolefin mixtures with different viscosity values were assessed. The tasks were set:

- To establish the dependence of the formation of phase structures of polyolefin compositions on the composition and viscosity of the system.
- To establish the pattern of "structure-properties" of mixtures of polyolefins modified by ultrasonic action.
- To determine the role of ultrasound in the process of restoring the structure and formation of new chemical bonds in polyolefin mixtures.
- To determine the optimal values of the composition and conditions for processing mixtures of polyolefins to create compositions with high physicomechanical characteristics.

Materials and methods

Polypropylene of the Balen-01020 brand (GOST 26996-86) (hereinafter PP), high-pressure polyethylene of the brand 15813-020 (GOST 16337-77) (hereinafter PE-158), high-pressure polyethylene of the brand 11503-070 (GOST 16337-77) (PE - 115) were utilized in this study. Experimental samples were made in the process of processing polymer blends based on PP and PE-158, PP, and PE-115 to obtain strands by extrusion. In the process of the work, an extrusion line with an ultrasonic vibrating attachment mounted on a forming tool was used. During the polymeric work compositions of PE, PP at the ratio of 80:20 (wt.%), 70:30 (wt.%), 50:50 (wt.%), 30:70 (wt.%), 20:80 (wt.%), respectively, treated with ultrasound. Samples were obtained using a double processing method of the studied compositions with and without ultrasound exposure.

The following research methods were used in work. Rheological properties of the polymeric materials were studied using the capillary viscometry (GOST 11645-86 Plastics, which is a method for determining the melt flow index of thermoplastics) on an IIRT-type instrument. The apparent density (hereinafter referred to as density) of the materials were measured using the flotation method with a pycnometer, working fluid - aqueous solutions of ethyl alcohol of various densities.

Phase transitions in polymer mixtures were studied by constructing the thermomechanical curves on a TPM251 instrument. Physicomechanical properties of polymer samples and polymer mixtures were determined according to the GOST 14236-81 Polymer films. Tensile test methods

were implemented on a tensile testing machine RM-50. To determine changes in the chemical structure and the structure of polymer mixtures, Fourier transform infrared spectroscopy was used. Tests were performed using a Varian 660-IR Fourier spectrometer.

Phase morphology of the polymer mixtures was investigated using the scanning electron microscope (SEM, model JSM U3)

Results and discussion

At the first stage of the work, samples from PE, PP compositions were obtained using the ultrasonic treatment of polymer melts. Next, we studied the physicomechanical properties of the obtained PCM samples. The results are presented in Figure 1.

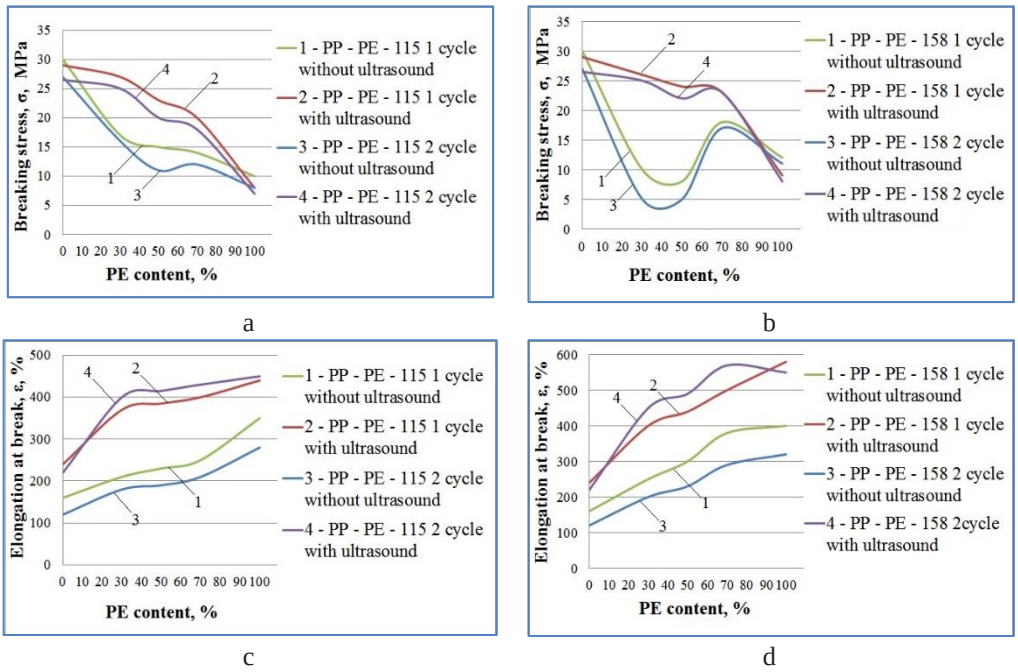


Figure 1. Dependence of breaking stress and elongation at the break on the content of PE-115 (a, b) and PE-158 (c, d) in compositions

In the case of Figure 1, it is necessary to mention that:

Breaking stress = Load / sample cross-sectional Area, MPa.

Elongation at break = (relative change in sample size during elongation under load / Initial sample length) * 100%.

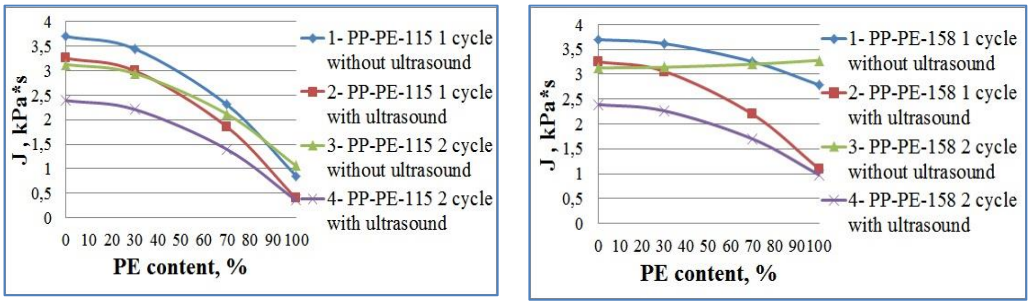
Calculations were carried out according to GOST 14236-81 polymer Films. Tensile test method.

The content of more than 20% PE in the polyolefin mixture leads to a noticeable decrease in the breaking stress of the polymer composition. The effect of ultrasound on the melts of polymer mixtures based on PE-115 and PP increased the breaking stress by about 1.5 times in comparison with that of the untreated samples, and for compositions based on PE-158 and PP, by almost 2-2.5 times.

The values of the relative elongation at break of the polymer compositions PP + PE-158 and PP + PE-115 obtained using ultrasonic treatment, are approximately 1.5 - 2 times higher compared to the control samples. At the next stage of the study, the rheological and structural-morphological properties of polyolefin mixtures were studied.

The processing temperature of the PE, PP mixture corresponds to the processing temperature of the polymer

with a higher melting point (i.e., PP at 230 ºC). Such a temperature regime is not typical for PE. With increasing temperature, the viscosity of PE decreases, and for samples obtained using ultrasonic treatment, the decrease in this indicator is more intense. For the samples obtained without the use of ultrasound, the viscosity values in the second processing cycle were found to be higher than in the first. This correlates with the results of the study of the rheological properties of individual polymers at T = 190 ° C. Regarding the recycling compositions, there is a clear tendency toward a decrease in the viscosity index, which, as for individual polymers, decreases more intensively with ultrasonic treatment. Mixtures containing 70% of PP are more susceptible to the multiplicity of processing due to a more intensive decrease in the viscosity of PP. When studying the viscosity-composition curves (Figure 2), we can conclude the following: as the amount of PE in the composition increases, the overall viscosity of the system decreases, and the ultrasonic effect enhances this process.



a b

Figure 2. The dependence of the viscosity of the melt on the percentage of PE-115 (a) and PE-158 (b) in the composition

An exception is a composition without ultrasonic treatment of the second processing cycle, containing 70% PE-158, the viscosity of which is higher than that of PP. Thus, the ultrasonic effect leads to a decrease in the viscosity of the polyolefin mixtures.

As it can be seen in Figure 2, the increase in the PE content slightly decreased the particle sizes. However, their anisometric shape remained unchanged. Ultrasound-treated compositions containing 70% PP in the mixture also had a layered structure, but the particle size of the dispersed phase was much smaller, led to a better distribution of one polymer in another. When 70% PE is contained in the mixtures treated with ultrasound, a fibrous type of phase structure is observed with the uniform distribution of dispersed phase particles in the matrix volume.

The electron microscopy method was used to study the resulting phase structures of mixed compositions. Figure 3 illustrates the photographs of samples obtained after the first processing cycle. The analysis of micrographs of the samples showed the presence of various types of phase structures, the formation of which is directly related to various values of the viscosity of the constituent components, as well as their ratio in the mixture.

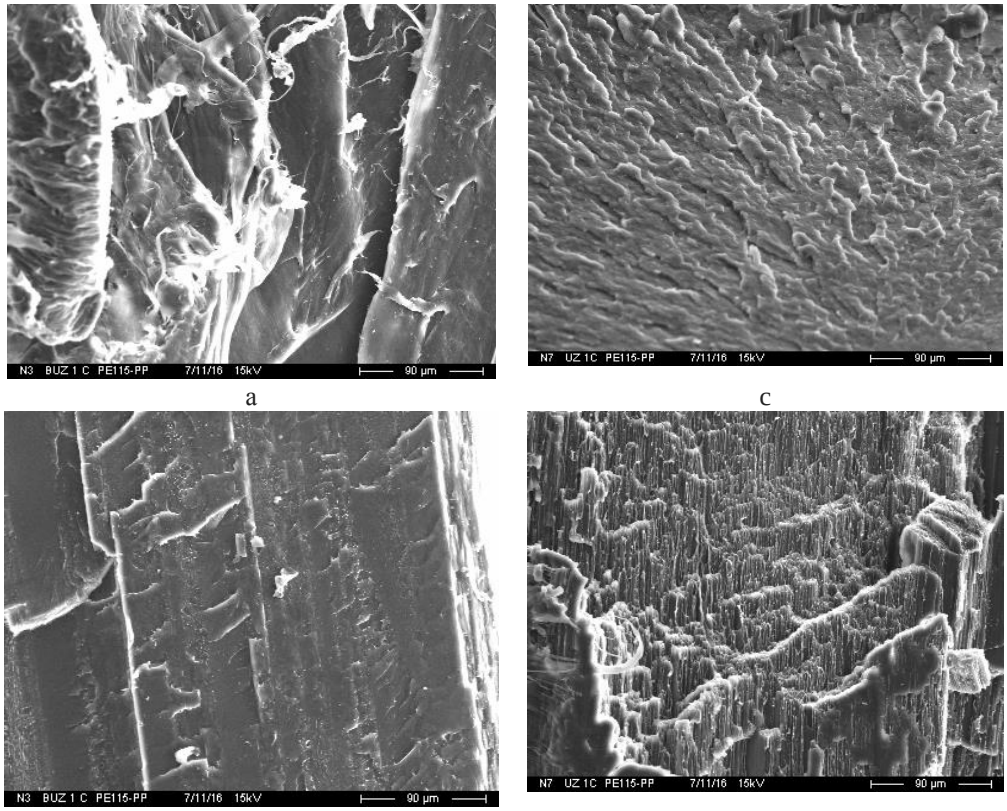


Figure 3. Microphotographs of the surface of the cleaved strands of compositions after the first processing cycle: 70% PP + 30% PE-115 (a), 70% PP + 30% PE-115 with ultrasound (b), 30% PP + 70% PE-115 (c), 30% PP + 70% PE-115 with ultrasound (d)

After the first processing cycle, a fibrous structure of dispersed phase particles was observed in the compositions obtained using the ultrasonic treatment, the size of which was smaller than that of samples without ultrasound. In the control samples, a predominantly layered phase structure was observed. The use of ultrasound leads to a decrease in the particle size of the dispersed phase, which contributes to a better distribution of them in the matrix volume. In the samples obtained using ultrasound, formation of the phase structure of the transition type was observed with the liquid cylinder stabilization effect when the fibrous structure changed with the formation of particles of a spherical (in this case, "drop-shaped") shape.

After the second processing cycle (Figure 4), in the samples with high PP content that were not sonicated, the particles of the dispersed phase were large and unevenly distributed in the matrix. In this regard, the surface area of the interface is reduced, which leads to a decrease in the segmental interaction of polymers in the transition layer. With the increase in the PE content in the mixture to 70%, the particles of the dispersed phase are distributed more uniformly in the medium. The influence of ultrasonic vibrations is the determining factor in the formation of the fibrous phase structure of the mixture. In the compositions obtained using ultrasonic treatment, the minimum fiber size, and their uniform distribution throughout the matrix were observed. A decrease in particle size increased the interaction area between the dispersed phase and the dispersion medium, which may favorably affect their mutual solubility, increasing the deformation-strength characteristics.

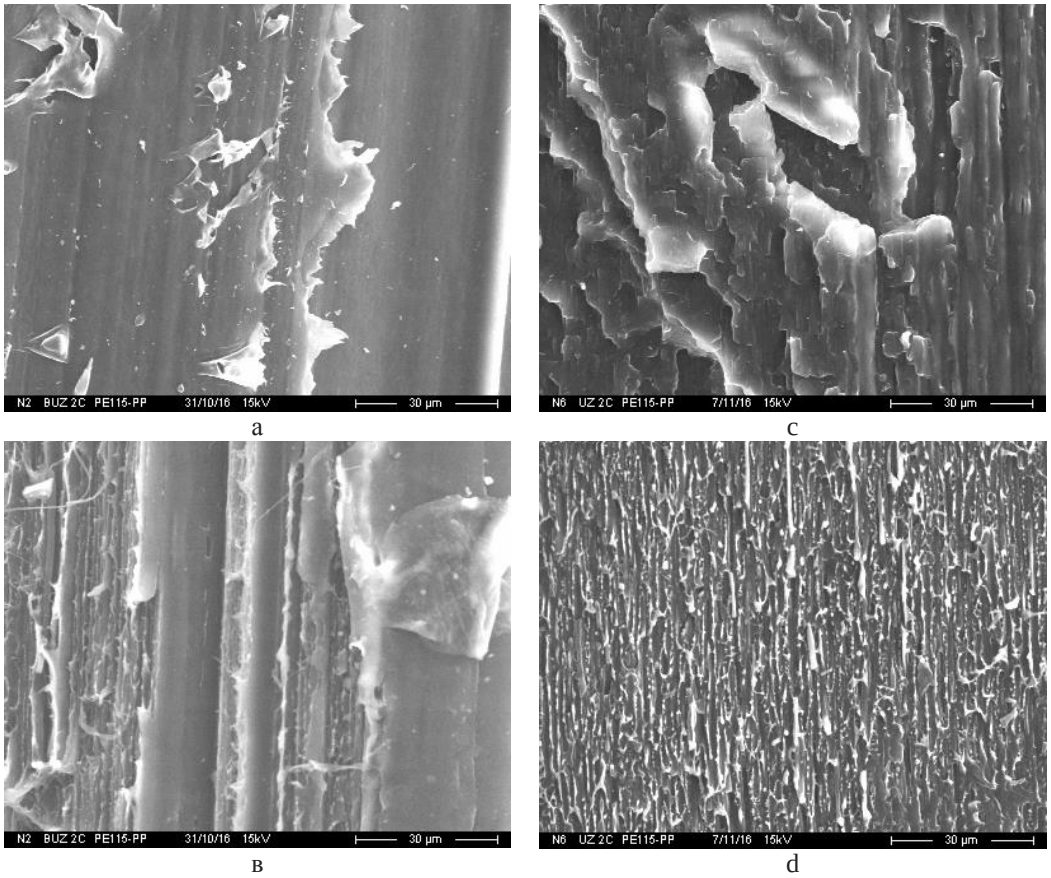


Figure 4 - Microphotographs of the surface of the cleaved strands of compositions after the second processing cycle: 70% PP + 30% PE-115 (a), 70% PP + 30% PE-115 with ultrasound (b), 30% PP + 70% PE-115 (c), 30% PP + 70% PE-115 with ultrasound (d)

Studies of apparent density showed that the ultrasonic-treated polymer compositions have lower density values regardless of the composition of the mixture, which can indirectly prove the presence of phenomena associated with a decrease in the degree of crystallinity in polyolefin mixtures. The data obtained are correlated with the results of a study of the thermomechanical properties of polymer compositions [20]. The melting points of the compositions of the corresponding processing cycles obtained using ultrasonic treatment were found to be 4-5 °C lower than that of the samples without ultrasound. Subsequent processing reduced the melting point by around 3 °C. It is also worth noting that the ultrasonic effect increased the deformation properties of the compositions by 60-80%, which confirms the assumption about the formation of phase structures with the uniform distribution of components in the polymer system.

The increase in the proportion of the amorphous phase can change the chemical structure of the polymers of the system as a result of oxidative processes in these areas. Further, the chemical structure of polymer mixtures was studied using the IR spectroscopy. The IR spectroscopy is a spectrum obtained by infrared spectroscopy. The results are presented in Table 1.

Table 1. The results of IR spectroscopy

Material	Processing cycle	D1650/D1460 + D1720/D1460		D720/D1460	
		without the US treated	with the US treated	without the US treated	with the US treated
70 %PP + 30 % PE-115	1	0.012	0.011	0.26	0.3
	2	0.028	0.01	0.05	0.35
70 % PP+ 30 % PE-158	1	0.011	0.01	0.227	0.29
	2	0.012	0.008	0.2	0.35
30 % PP + 70 % PE-115	1	0.005	0	0.3	0.368
	2	0.006	0	0.27	0.8
30 % PP + 70 % PE-158	1	0.005	0	0.45	0.5
	2	0.01	0	0.41	0.525

The samples were assessed using the IR spectroscopy. The obtained results were processed by the length of the peaks of oxygen-containing groups in relation to the internal standard (C-C bonds).

The obtained results of IR spectroscopy allow us to derive the following patters. The total index of oxygen-containing groups in the samples, obtained without ultrasonic treatment, increases from the multiplicity of processing, and the increase in the PP content in the compositions increased this indicator. These results indicated the more severe destruction of PP during double processing, which correlates with studies of the viscosity of these samples. The polymer compositions, obtained using ultrasonic treatment revealed inverse relationship, as the decrease in the total oxygen-containing group index from cycle to cycle for mixtures containing PE-158, and the absence of peaks in the IR spectra in the regions of stretching vibrations of 1640 cm^{-1} and 1720 cm^{-1} for the mixtures containing PE-115. Double processing of polymer mixtures not treated with ultrasound leads to the decrease in the peak in the regions of stretching vibrations corresponding to the bonds - (CH2) x-, regardless of the composition, whereas in the samples treated with ultrasound, the increase in this indicator is observed. Thus, the ultrasonic effect contributes to the several processes simultaneously: the oxidation of polymers and the formation of a certain amount of oxygen-containing products, as well as the recombination of macroradicals with subsequent changes in the structural and morphological properties of the compositions, which is confirmed by the results of electron microscopy. The effect of the ultrasonic vibrations on the melts of polyolefin compositions was accompanied by the decrease in the viscosity of the melt of the polymer mixture, the decrease in oxygen-containing groups and the increase in the groups - (CH2) x-, which, in turn mat affect the uniform distribution of one polymer in another and leads to the increase of the interval of technological compatibility. Based on the research results, the technology of ultrasonic processing of melts of polyolefin mixtures in industrial conditions was tested. An experimental batch of material based on industrial wastes of the polyethylene-polypropylene film processed by ultrasonic treatment was obtained. Physico-mechanical properties of the obtained material correspond to the normative indicators for film packaging materials. The resulting composition is recommended to be used as a middle layer in multilayer films for food usage. It is also recommended to use the technology of ultrasonic processing of polyolefin

melts to obtain the products with high physical and mechanical characteristics.

Conclusion

Based on the results of the study, the following conclusions were made:

- Dependence of the formation of phase structures of mixtures of polyolefins on the composition and viscosity of the system was established. Compositions not treated with ultrasound, with the predominance of PP in the composition, have layered structure with particles of the phase medium of the anisometric shape of large sizes. As the PE content enhances, the particle size slightly decreases, but their anisometric shape would remain unchanged. A layered structure has been also seen in the ultrasound-treated compositions consisting of 70% PP in the mix; however, the particle in the dispersed phase has a very small size, causing more reasonable distribution of one polymer in another. In fact, as the mixes treated with ultrasound contain 70% PE, a fibrous sort of the phase structure would be seen, which has smooth distribution of the dispersed phase particles in the matrix volume. The size and distribution of the particles of the dispersed phase depends on the viscosity values of the dispersed medium, therefore, in compositions with PE-115 content, PP phase particles are easier to disperse in the less viscous medium, which leads to the general increase in the area of interaction between the phase and the medium;
- The role of ultrasonic action in the process of restoring the structure and the formation of new chemical bonds in polyolefin mixtures is determined. Formation of oxygen-containing products and an increase in the proportion of the amorphous phase in the samples, obtained from pure polymers treated with ultrasound, are favorable conditions for the occurrence of recombination reactions of macroradicals in the process of their joint processing, which helps to restore the structure and increase the number of - (CH2) x- groups in mixtures;
- Therefore, for creating compositions with higher physical and mechanical properties, we suggest the utilization of a mix of polyolefins consisting of 70% PE, which has been modified by the ultrasonic treatments.

Acknowledgements

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