Received: 27 August 2020 | Revised: 24 October 2020 | Accepted: 29 October 2020
DOI: 10.22034/ecc.2020.249574.1076
Eurasian Chemical Communications
SAMI

FULL PAPER

Applying ultrasonic treatment to melts of polymer compositions under laboratory and experimental industrial conditions

Kirsh Irina Anatolyevna |Beznaeva Olga Vladimirovna* |Bannikova Olga Anatolyevna |Gubanova Marina Ivanovna |Tveritnikova Isabella Sergeevna |Romanova Valentina Alexandrovna |Novikov Maxim Nikolaevich

Moscow State University of Food Production, 125080 Moscow, Russia

***Corresponding Author:**
Beznaeva Olga Vladimirovna
Email: esfehani.mohamad3@gmail.com
Tel.: +7(926)5912059

Nowadays, environmental protection has become a global issue due to the sharp increase of waste as a result of the rapid and almost uncontrollable growth in the consumption of synthetic plastics in many sectors of the economy. The issue of the disposal of the products is therefore becoming increasingly important. The creation of biodegradable materials is one of the most acceptable ways to solve the issue, along with the development and research of new biodegradable polymer materials. This study approached the physicochemical properties and the decomposition time of biodegradable polymer compositions obtained by the impact of the ultrasonic treatment on their melts under the laboratory and experimental industrial conditions. The results indicated that The ultrasonic treatment of polymer composite materials (PCMs), based on starch and polyethylene, could lead to the increase in their physicomechanical properties by 1.5-2 times, compared with the control samples, which is associated with the uniform distribution of the filler in the polymer matrix.

KEYWORDS

Polymer composite materials; ultrasonic treatment; physico-chemical properties; biodegradation.

Introduction

In recent years, intensive work has been carried out to create a new class of biodegradable, compostable plastics, based on natural materials, not harmful for the environment and human health [1-11]. A very effective and widespread method of imparting biological degradability to synthetic polymers is the introduction of various natural materials and additives into the polymer structure, which accelerates the process of destruction of the polymer matrix [1,2,5-9, 12].

The creation of biodegradable polymers is one of the promising areas for the creation of mixtures, made from polyolefins filled with starches, which are the source of nutrition for microorganisms [5,6,8,13]. Significant attention is paid to the study of corn starch as a filler in the wide range of content in compositions with polyethylene (PE). However, when using a large amount of filler, there is a tendency for uneven distribution of the filler in the polymer matrix. Therefore, for the uniform distribution of the filler, it is advisable to use the ultrasonic treatment of melts of polymer composite materials (PCM),

since the preliminary results of the work performed have shown positive results on the dispersion of fillers in polymer systems [14-16]. However, reseach on the effect of the ultrasonic treatment of polymer melts on the properties of polymer compositions is not adequate; therefore, the purpose of this work was to study the physicochemical properties of polymer compositions, based on polyethylene and starch, obtained with the ultrasonic treatment of the melt. In this case, it is advisable to conduct a study using samples, obtained both under the laboratory and industrial conditions.

Objects and research methods

To improve the quality of the samples, obtained from the polyethylene (PE)-starch composition and to improve the technological characteristics, it is important to remove moisture from the starch before its introduction into the composition. It was found that with the increase of the temperature and moisture content of the starch, the thermal stability of the composite material decreased. In this regard, as the preparatory process for the production of starch-filled polymers, the composition should be dried at the temperature of 105 °C. The control was carried out by determining the fluctuation of the mass with an accuracy of 0.01%. The boundary conditions for processing the composite material are 160 °C and 190 °C.

High-pressure polyethylene grade 15813-020 (GOST 16337-77) (hereinafter PE) was selected as the object of the research. Table 1 shows the characteristics of the studied polymers.

TABLE 1 Main technological characteristics of the studied polymers

Technical Data	PE-158
Density, kg/m^3	0,917-0,920
Melt Flow Index, g/10 min	2,0-2,2
Melting temperature, °C	105-108
Tensile yield strength, MPa	11 -12
Elongation at break, %	600-650

Corn starch with a particle size of up to 20 microns with the proportion of fractions up to 15 microns of at least 50% was selected as the filler of the composite materials, depending on the recipe.

The amount of starch in the PE compositions varied from 10 to 60% with the step of 10% (Table 2).

TABLE 2 Content of PCM based on LDPE and starch

№	PCM content, %		Weight of laboratory samples, kg	Weight of pilot-industrial batch, kg
	PE	Starch		
1	40	60	5	25
2	50	50	5	25
3	60	40	5	25
4	70	30	5	25
5	80	20	5	25
6	90	10	5	25
7	100	0	5	25

The PCM samples were obtained according to the following scheme:

1. Obtaining thermoplastic starch in a rotary mixer at the temperature of 23 ± 2 °C: Corn starch was loaded into the mixer, then the aqueous solution of sorbitol was added, mixed for 15 minutes and glycerin was added. The subsequent mixing was 45 minutes.
2. Loading the prepared mixture and polyethylene into the laboratory extruder with the ultrasonic processing of the melt for the subsequent obtaining of the samples: The ratio of the mixture components was as starch by 70%, the aqueous solution of sorbitol by 10%, glycerol by 20%. The resulting mixture appeared as a pasty form, which was mixed with PE, thermal stabilizers Irganox 1010, Irgafos 168, additives Dinamar 5911 and zinc stearate and then it was loaded into the

extruder to obtain PCM. Thermostabilizer Irganox 1010 was introduced in the amount of 0.1%, Irgafos 168-0.4%, Dinamar 5911-0.1%, and zinc stearate-0.4%.

3. Loading the prepared mixture and polyethylene into the laboratory extruder with the ultrasonic treatment of the melt for the subsequent obtaining of the samples (Figure 1). To obtain industrial samples, a pilot plant was used, designed as a laboratory one at the Rusplast LLC enterprise (Russia) with the capacity of at least 20 kg per hour.

The technological process for obtaining samples of polymer compositions includes the following stages:

1. Obtaining thermoplastic starch in a rotary mixer at the temperature of 23±2 °C.
2. Mixing with additives and heat stabilizers.
3. Loading the prepared mixture and polyethylene into the laboratory extruder with the ultrasonic treatment of the melt for the subsequent preparation of samples in the form of granules (Figure 1). Similar equipment with the capacity of more than 20 kg per hour was installed at the enterprise LLC "Rusplast".
4. The production of flat films was carried out on the extrusion line (Figure 2). When obtaining film materials under industrial conditions, the industrial partner used the extruder from Metakley LLC (Russia).

FIGURE 1 Laboratory extruder with the ultrasonic treatment of the melt (know-how of the technology is registered in the FSBEI VO "MGUPP")

PCMs obtained without the ultrasonic treatment of the melt were used as control samples. Control PCMs were obtained on the same laboratory extruder with the ultrasonic treatment of the melt, which was not included in the sample preparation process.

The main technical characteristics of the laboratory extrusion plant and the temperature conditions for processing polymer samples are presented in Tables 3 and 4.

TABLE 3 The main technological characteristics of the laboratory extrusion plant

Technological characteristics	Value
Ultrasonic vibrating attachment	
Oscillation frequency	22, 4 kHz
Ultrasonic generator power	300 W
Screw rotation frequency	90 revolutions per minute

TABLE 4 Temperature conditions for the of polymers and compositions based on them

PCM	Processing Temperature, ºC			
	1 зона	2 зона	3 зона	4 зона
PE+starch (<20%)	130	150	170	190
PE+starch (>20%)	120	130	140	150
PE	180	210	220	230

FIGURE 2 Laboratory flat film extrusion machine

The following research methods were used in the present inquiry:

1. To assess the rheological properties of polymeric materials, the method of capillary viscometry (GOST 11645-86) was used. The experiment was carried out on the IIRT-type device, due to the fact that it was necessary to compare the change in the rheological characteristics of various polymers.

2. The method for determining the water absorption of compositions followed GOST 4650-2014 "Plastics. Methods for Determining Water Absorption" was used here. The method was used to determine the change in the water absorption of polymers and mixtures based on PP and PE under the impact of the ultrasound treatment on their melts. This method was also used here to determine the biodegradability of polyethylene compositions filled with agro-industrial complex waste. The samples with dimensions of 1 cm x 1 cm placed in 50 ml of water were used in work.

3. The determination of physicomechanical properties of polymers and compositions was carried out in accordance with GOST 14236-81 “Polymer films. Tensile test methods ". The tests were carried out on the PM-50 tensile testing machine equipped with the computer interface. The limit of the permissible value of the load measurement error during the forward stroke did not exceed ± 1% of the measured load. The deformation rate of the sample was 100 mm/min.

4. Determination of the biodegradation period was carried out by composting, using the forecasting method, according to GOST R57225-2016 "Plastics. Determination of the degree of decomposition of plastics under simulated composting conditions in laboratory tests was based on the following conditions: Temperature 23 °C, humidity 78-80%, exposure six months with a step of measurements at control points every two weeks. The change in the relative elongation upon rupture of PCM samples before and after composting was used as the assessment criterion.

5. Determination of the biodegradation time was also used by the Sturm method in accordance with GOST 32433-2013 “Methods for testing chemical products posing a threat to the environment. Evaluation of the biodegradability of organic compounds by the method of determining carbon dioxide in a closed vessel". The Sturm method is based on the measurement of the assimilation rate of the test material in the aqueous solution in the presence of bacterial microflora, recorded by the rate of carbon dioxide released as a result of the vital activity of microorganisms. The exposure time was 28 days. To evaluate polymer film materials, the biodegradation rate criterion was used, defined as the first derivative of the biodegradability index.

6. The experimental results were processed using the Microsoft Office software, STATISTICA.

Results and their discussion

When receiving experimental samples and pilot industrial batches of PCM, we assessed their rheological properties.

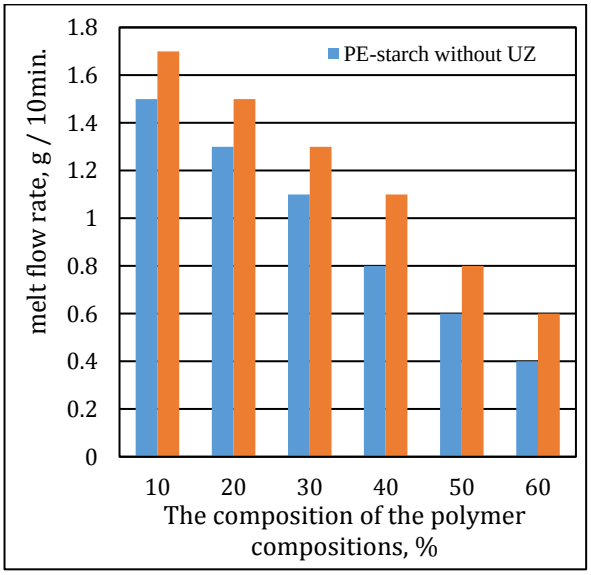

FIGURE 3 the average values of the melt flow index of PCM (experimental samples obtained on the laboratory extruder).

Figure 3 shows the values of the melt flow index depending on the amount of the filler in PCM. It is clearly seen from the results obtained that the introduction of thermoplastic starch decreases the Melt Flow Index (MFI) of PCM, which is typical for such systems. However, it should be noted that the ultrasonic treatment leads to an increase in the MFI of PCM at the same filler concentration. When comparing the MFI of industrial batches with experimental samples, we found that the values of the indicator differ from the laboratory ones by about 10-15% from batch to batch, which indicates that it is advisable to use mixers for averaging the compositions and MFI values of PCM.

Further, film materials were obtained from the granules, which were investigated by their physicomechanical properties (Figures 4 and 5).

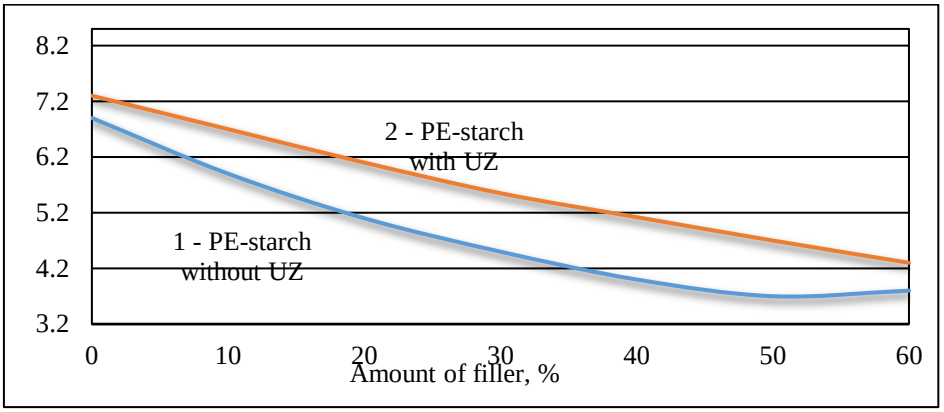

FIGURE 4 Dependence of the breaking stress of the experimental samples on the amount of starch in PCM

With the equal starch content in the samples obtained with and without the ultrasound treatment, it can be noted that the ultrasonic treatment of PCM melts leads to the increase of tensile stress in comparison with the materials obtained without the ultrasound treatment. At the same time, a similar pattern is also observed for the dependence of the relative elongation at the break on the amount of starch in the PCM obtained with and without the ultrasonic treatment (Figure 5)

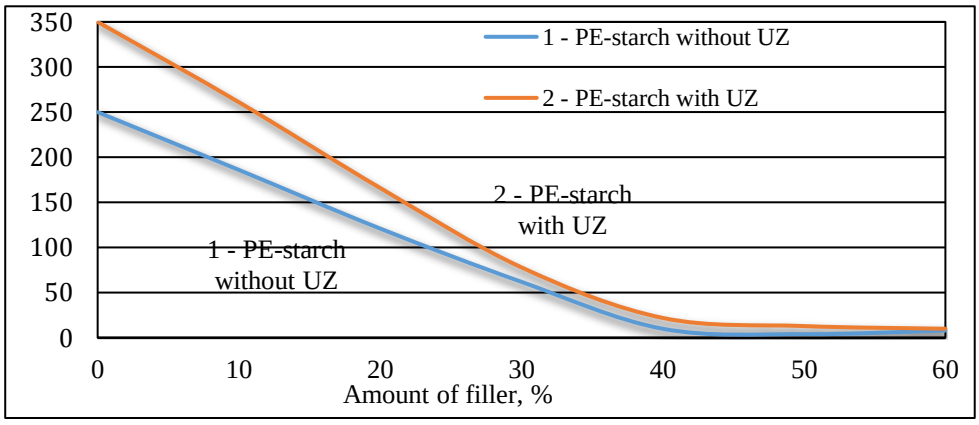

FIGURE 5 Dependence of the elongation at the break on the starch content in the PCM

Comparing the results of the study of experimental samples, obtained on the laboratory extruder with the results, obtained after testing samples of pilot industrial batches of films, reveals that the regularity of the effect of the ultrasound treatment remains the same. The ultrasonic treatment of PCMs, based on starch and polyethylene, leads to the

increase in their physicomechanical properties by 1.5-2 times compared to the control samples, associated with the uniform distribution of the filler in the polymer matrix, which is a good indicator in terms of operational characteristics. This can be attributed to the fact that the ultrasonic treatment of PCM melts operates effectively on two types of equipment and contributes to the dispersion of mixture components. Next, the biodegradability of PCM was assessed.

It should be noted that the values of water absorption of PCMs, obtained on the laboratory extruder and the pilot plant, fall within the confidence interval; therefore, they are depicted by general curves. The ultrasonic treatment is of great importance for the process of water absorption of PCM. It is clearly seen that the ultrasonic treatment of PCM melts increases water absorption. It should be noted that for 180 days, the water absorption of PCM based on PE and starch was approximately 10-20%.

As a result of the studies carried out, it can be concluded that the water absorption of PCMs obtained with the ultrasonic treatment of the melt is higher than without the ultrasonic treatment, which is a good indicator from the point of view of biodegradability.

Further, PCM studies were carried out for the biodegradability of samples by Sturm's method (Figure 6).

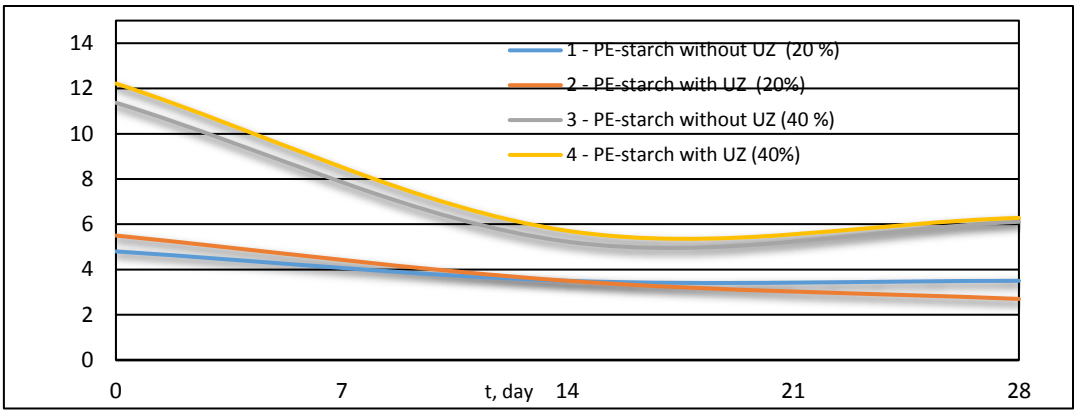

FIGURE 6 Dependence of the rate of PCM biodegradation on the time of the experiment

The results obtained show the dependence of the increase in the rate of biodegradation on the amount of starch in the PCM. It should also be noted that after 14 days of exposure, the rate of biodegradation decreased compared to the initial rate, but then the final rate of biodegradation increased in 28 days, which is a positive criterion from the point of view of creating a PCM with the accelerated decomposition time in the environment. To confirm the hypothesis obtained, studies of samples of composting methods were carried out (Table 5).

TABLE 5 Change in elongation at break of polymer compositions after six months composting

Value starch, % / PCM method of obtaining without/with UZ	Change in elongation at break of polymer compositions after composting, %	
	Laboratory sample	Experimental industrial sample
PE, (without UZ/40)	57±2	49±5
PE, (with UZ/40)	45±3	36±4
PE, (without UZ/50)	62±5	52±6
PE, (with UZ/50)	59±3	41±4
PE, (without UZ/60)	73±5	69±6
PE, (with UZ/60)	63±3	52±4
PE, without УЗ	4±1	3±1
PE, with УЗ	7±1	5±1

In the process of composting for six months, polymer compositions, based on starch, lost their performance characteristics by 50-70%, depending on the amount of starch in the compositions, and this figure is higher for samples obtained with the ultrasonic treatment of the melt, by about 10%. It should be noted that for the samples, obtained with the ultrasonic treatment of the melt, the change in elongation at the break during composting is 10-12% higher than for samples, obtained using the same technology, but in industrial conditions. This can be attributed to the fact that with increased productivity, the effect of reducing the uniform distribution of the filler in the polymer matrix is observed, which is contributed to the location of the larger amount of polymer on the sample surface.

On the basis of the studies carried out by the Sturm and composting methods, using the direct extrapolation method of forecasting, studies of the decomposition times of experimental samples and pilot industrial batches of PCM, with the starch content of 60% (Figure 7) were carried out.

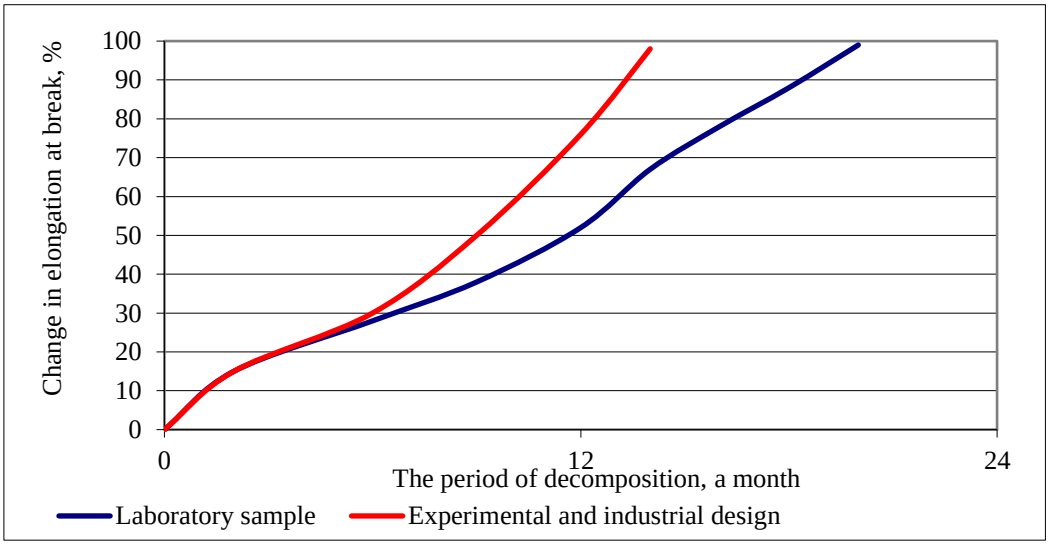

FIGURE 7 Dependence of the change in the relative elongation at the break on the composting period of the PCM

As a result, it was found out that the experimental samples, obtained at the laboratory facility, will have a decomposition period of about 4.5 years, and at the experimental industrial facility about five years. Based on the results obtained, scientific and technical documentation for PCM of the Biostar PE-F 4060 brand (Rusplast LLC) was

developed; a pilot batch of the biodegradable polymer composition was produced.

Based on the above remarks, the following conclusions can be drawn:

When comparing the MFR of pilot batches with experimental samples, we found that that the value of this indicator differed from the laboratory values by about 10-15% from batch to batch, which indicates that it is advisable to use mixers for averaging the compositions and MFR values of PCM.

When comparing the results obtained in the study of experimental samples obtained on the laboratory extruder, with the results, obtained after testing samples of pilot industrial batches of films, we found that the regularity of the effect of the ultrasonic treatment remained the same. The ultrasonic treatment of PCMs, based on starch and polyethylene, leads to the increase in their physicomechanical properties by 1.5-2 times, compared to the control samples, which is associated with the uniform distribution of the filler in the polymer matrix.

As a result of the complex studies of PCM biodegradation by the composting, Sturm and water absorption methods, the terms of decomposition by composting were established. Thus, it can be claimed that the experimental samples, obtained in the laboratory facility, will have the decomposition period of about 4.5 years, and for the experimental industrial samples - about five years. The laboratory samples, obtained with the ultrasonic treatment of the melt as the change in elongation at break after composting, have values of this indicator by 10-12% higher, higher than the samples obtained using the same technology. However, in the industrial conditions, which can be related to the fact that with the increased performance in polymer matrices, the effect of reducing the uniform distribution of the filler in the polymer matrix on the sample surface is observed.

Acknowledgements

The authors acknowledge that the research was supported by the Ministry of Education and Science of the Russian Federation; the unique identifier of the project is RFMEFI57418X0191.

Orcid:

Kirsh Irina Anatolyevna: https://orcid.org/0000-0003-4569-7035

References

[1] I.A. Kirsh, T.I. Chalykh, D.A. Pomogova, *J. Charact. Dev. Nov. Mate,* **2016,** *8*, 119.

[2] I.A. Kirsh, Yu.V. Babin, V.V. Ananiev, I.S. Tveriynikova, V.A.Romanova, O.A. Bannikov, O.V. Beznaeva, *Promyshlennosti,* **2019**, *2*, 85-90.

[3] A. Jimenez, J.N. Aneli, S. Kubica, *CRC Press,* **2013**, 235–251.

[4] I.A. Kirsh, V.V. Ananiev, T.I. Chalykh, D.A. Sogrina, D.A. Pomogova, *Plast. Massy,* **2014**, *1112*, 45-48.

[5] I.A. Kirsh, O.V. Beznaeva, O.A. Bannikova, V.A. Romanova, I.V. Barulya, *International Journal of Advanced Biotechnology and Research (IJABR),* **2019**, *10*, 15-23.

[6] I.A. Kirsh, O.V. Beznaeva, O.A. Bannikova, V.A. Romanova, I.V. Barulya, *Bioscience Biotechnology Research Communications,* **2019**, *12*, 196-202.

[7] I.A. Kirsh, O.V. Beznaeva, O.A. Bannikova, V.A. Romanova, D.M. Zagrebina, I.S. Tveritnikova, *Jour of Adv Research in Dynamical & Control Systems*, **2019**, *11*, 1944-1949.

[8] I.A. Kirsh, D.A. Pomogova, I.S. Tveritnikova, O.V. Beznaeva, O.A. Bannikova, V.A. Romanova, D.M. Zagrebina, *Iranian Chemical Communication,* **2019**, 604-612.

[9] I.A. Kirsh, O.V. Beznaeva, O.A. Bannikova, D.M. Myalenko, V.A. Romanova, *Iranian Chemical Communication,* **2019**, 595-60.

[10] A. Farhadian, M.A. Varfolomeev, A. Kudbanov, S.R. Gallyamova, *Chemical Engineering Science*, **2019**, *206*, 507-517.
[11] R.D. Saini, *Asian Journal of Research in Chemistry*, **2018**, *11*, 179-188.
[12] I. Alig, T. Skipa, D. Lellinger, P. Pötschke, *Polymer*, **2008**, *49*, 3524-3532.
[13] S. Mangaraj, A. Yadav, L.M. Bal, S.K. Dash, N.K. Mahanti, *Journal of Packaging Technology and Research*, **2019**, *3*, 77-96.
[14] I. Krish, D.A. Pomogova, I.S. Tveritnikova, O.V. Beznaeva, O.A. Bannikova, V.A. Romanova, D.M. Zagrebina, *Eurasian Chemical Communications*, **2019**, *1*, 604-612.
[15] I. Kirsh, Y. Frolova, O. Beznaeva, O. Bannikova, M. Gubanova, I. Tveritnikova, Y. Filinskaya, *Polymers*, **2020**, *12*, 2412.
[16] I. Krish, O.V. Beznaeva, O.A. Bannikova, D. M. Myalenko, V.A. Romanova, *Eurasian Chemical Communication*, **2019,** *1*(6), 595-601.

How to cite this article: Kirsh Irina Anatolyevna, Beznaeva Olga Vladimirovna*, Bannikova Olga Anatolyevna, Gubanova Marina Ivanovna, Tveritnikova Isabella Sergeevna, Romanova Valentina Alexandrovna, Novikov Maxim Nikolaevich. Applying ultrasonic treatment to melts of polymer compositions under laboratory and experimental industrial conditions. *Eurasian Chemical Communications*, 2020, 2(11), 1101-1109. **Link:** http://www.echemcom.com/article_118647.html