

TECHNOLOGY FOR THE PRODUCTION OF COMPOSITE POLYMER MATERIALS BASED ON RECYCLED POLYPROPYLENE AND POLYETHYLENE TEREPHTHALATE WITH THE ADDITION OF MODIFIED SODIUM MONTMORILLONITE

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ABSTRACT

The article presents data on the task of recycling polyester polymers based on recycled polypropylene (PP) and polyethylene terephthalate (PET), which accumulate in the form of polymer containers, bottles, carpets, and fabrics in nature and do not decompose and clog not only landfills but also reservoirs. In this regard, this paper discusses the issues of recycling polyethylene terephthalate waste in order to obtain polymer compositions with the addition of modified montmorillonite, which is used in the manufacture of press materials and cast products.

Keywords: Montmorillonite, Bentonite, Composite Material, Polyethylene Terephthalate, Bleached Clays, Polypropylene, Recycling.

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INTRODUCTION

The secondary processing of polymers can be carried out by chemical depolymerization of the polymer or by mechanical processing.¹ Mechanical processing is the most promising method of processing from a production and economic point of view. However, thermomechanical oxidation of polymer chains, including polymer chain rupture and molar mass reduction, occurs during processing. Typically, secondary polymers exhibit lower mechanical and barrier properties compared to the properties of the source material. On the other hand, the presence of undesirable impurities, including chemicals or other polymers, may increase the drop in polymer characteristics.² For this reason, the industry is currently considering the processing of plastics by mixing recycled and primary polymers to obtain balanced properties, sometimes with the addition of additives as chain extensions, compatibility agents, and stabilizers.³⁻⁴ Almost all types of polymers, such as thermosets, thermoplastics, and elastomers, have been used as polymer matrices for the development of polymer nanocomposites.⁵⁻⁶ In recent years, hybrid composites for food packaging have also been developed, for example, including natural fibers and nanoglins.⁷ Nevertheless, the need for the processing of post-consuming polymers has largely directed the research of nano-reinforced secondary polymers. On the territory of the Republic of Kazakhstan, there are huge reserves of clay minerals, one of which is Darbazin bentonite, which is located in the Saryagash district of the Turkestan region.⁸⁻¹⁰ The purpose of this work was to study and develop effective methods for modifying polymer waste for recycling them in the production of polymer composite materials for various functional purposes.

EXPERIMENTAL

Morphological studies of the studied samples were carried out on a scanning low-vacuum electron microscope of JEOLJSM - 6490 LV with energy dispersive microanalysis systems INCAEntry 350 (Oxford Instruments). On the Shimadzu IRPrestige-21 infrared Fourier spectrometer with the prefix of the frustrated total internal reflection (ATIR) Miracle of PikeTechnologies, studies of the absorption spectra

of minerals of the studied clays of the Darbazinsk deposit were performed. The chemical composition of the samples was determined by complexometric titration. The filler (carrier for polymerization filling) was natural clay (Bentonite of the Darbazinsk deposit) Na-montmorillonite (Na-MMT) with a cation exchange capacity of 78 mg-eq/100 g, as well as the selected clay for the production of motor oils. To improve thermodynamic compatibility with the polymer, DB was treated with various surfactants: hydrochloric acid, octadecyl amine, and amino alcohol. The cation exchange capacity of modified montmorillonite is 95 mg-eq/100 g with an average diameter of silicate plates ~ 77 nm. The cation exchange capacity of modified montmorillonite is 95 mg-eq/100 g with an average diameter of silicate plates ~ 77 nm.¹¹⁻¹² To improve the thermodynamic compatibility of Darbaza montmorillonite with polymer (Secondary polyethylene terephthalate), various surfactants were treated: 12-aminolauric acid, dioctadecyl-dimethylammonium bromide (99%, Acro Organics), amino alcohol, block copolymer polyethylene oxide polyethylene (molecular weight 573). To determine the functional composition of secondary PET and PP by IR spectroscopy, a Shimadzu IR Prestige-21 infrared Fourier spectrometer was used. To obtain a polymer composition, it is prepared in a twin-screw extruder. The temperature in the extruder Hopper 2000C, I –III zones 275°C, output 280°C. The components are taken in the following ratio, wt.%: secondary polyethylene terephthalate (polypropylene) 95-99 and montmorillonite 1-5. First, the secondary polyethylene terephthalate - crushed waste of polyethylene terephthalate and montmorillonite is pre-dried at 130°C in a thermal cabinet for 6 hours. Then, 198 g of secondary polyethylene terephthalate is loaded into a twin-screw extruder, with the stirring-crushed waste of polyethylene terephthalate and 10 g of modified Darbaza montmorillonite. The resulting composite is cooled in a water bath and granulated.

RESULTS AND DISCUSSION

IR spectroscopic examination of the absorption of a PET sample (Fig.-1) in the studied area, the spectra after primary processing undergoes noticeable changes and have intense absorption bands in the areas of 1712, 1238, 1091, 1018, and 721 cm^{-1} , and there are also narrow absorption bands of less low intensity at the interval: 1408-524 cm^{-1} . The absorption bands 1338 and 1408 cm^{-1} characterize the C-H and $-\text{CH}_2-$ bonds. Intense absorption bands of valence oscillations in the region of 1700-1720 cm^{-1} with a peak of 1712 cm^{-1} can be attributed to the carbonyl group, and absorption bands in the region of 844, 968 and 1018 cm^{-1} characterize the presence of pendulum groups $-\text{CH}_2-$ and C-O valence bonds. Deformation oscillations of the pendulum CH_2 groups in the region of 721 cm^{-1} are also observed. The increase in the intensity of the absorption band in the region of 1200-1300 cm^{-1} with a peak of 1238 cm^{-1} is apparently associated with PET conformational transitions with trans-gauche transformations in ester fragments during melting of marocains in crystalline regions, because usually in primary PET the trans conformations $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ predominate, and in Both trans- and gauche conformations are present in secondary PET samples.

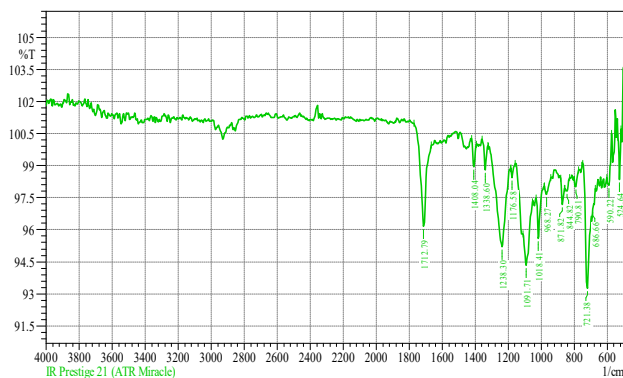


Fig.-1: IR Absorption Spectra of a Secondary PET Sample

IR spectroscopic examination of the absorption of the PP sample (Fig.-2) in the studied area, the spectra after primary processing undergoes noticeable changes, and a wide absorption band is observed in the region of 3000 - 2800 cm^{-1} , 1454, 1377 cm^{-1} and weak absorption bands at the interval of 1165- 600 cm^{-1} .

The wide absorption band in the region of 3000 - 2800 cm^{-1} with peaks of 2951, 2916, 2870, and 2839 cm^{-1} is caused by valence oscillations of C-H. The appearance is in the form of a complex band due to the overlap of intense absorption bands of CH_2 and CH_3 groups. These peaks in the region of 2951 and 2870 cm^{-1} can be attributed to fluctuations of the methyl group, and the peaks of 2916 and 2839 cm^{-1} belong to the valence fluctuations of the methylene group. Clear absorption bands in the region of 1454, 1377 cm^{-1} due to deformation vibrations of C-H bonds, that is, 1454 cm^{-1} asymmetric, and 1377 cm^{-1} - symmetric deformation vibration. In the IR spectra of the P samples, there are also absorption bands in the region of 1165 - 970 cm^{-1} with peaks of 1165, 1095, 1045, 999, and 972 cm^{-1} characterizing the presence of a C-O-C bond. Thus, the IR spectroscopic study of the absorption of PET and PP samples after primary processing undergoes noticeable changes that affect the physical and mechanical properties.

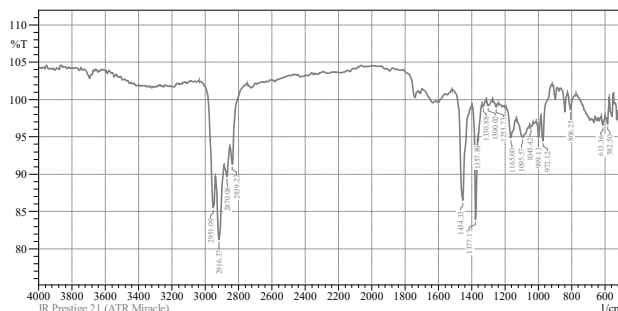


Fig.-2: IR Absorption Spectra of a Secondary PP Sample

In this regard, we further propose activated and organo-modified derivatives of Darbaza montmorillonite to improve these characteristics. Figures-3 to 6 show thermal studies of bentonite, secondary polypropylene, and compositions of Pv+5%bentonite, and PPwt+10%bentonite.



Fig.-3: DTG MMT

It follows from Fig.-3 that the differential thermal image of bentonite during the study showed that the mass loss at 200°C- 45mg is 8.2%, and at 890°C- 78mg is 13.9%. 1 peak area $S = 1.5 \text{ cm}^2$, 2 peak area $S = 0.413 \text{ cm}^2$, while the total area is 1.913 cm^2 . Figure-4 shows the data of the secondary polypropylene differential scanning calorimetry 1 peak area $S = 0.089 \text{ cm}^2$, 2 peak area $S = 0.798 \text{ cm}^2$. Mass loss in the range 2300C- 440°C - 8 mg, in the range 440°C- 485°C - 23.1 mg, total mass loss is 31.1 mg.

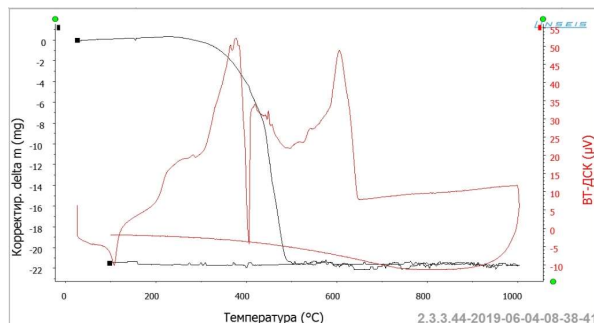


Fig.-4: Differential Scanning Calorimetry of Secondary Polypropylene

In Fig.-4, the changes in the secondary PP during heating are reflected. The maximum peak of the TG curve – 77.70% corresponds to the destruction of the main component of the mixture –PP. The destruction temperature of the secondary PP is 404.4°C. The residual mass of the sample upon reaching a temperature of 599.7°C – 0.09% corresponds to the content of minor mineral additives in PP.

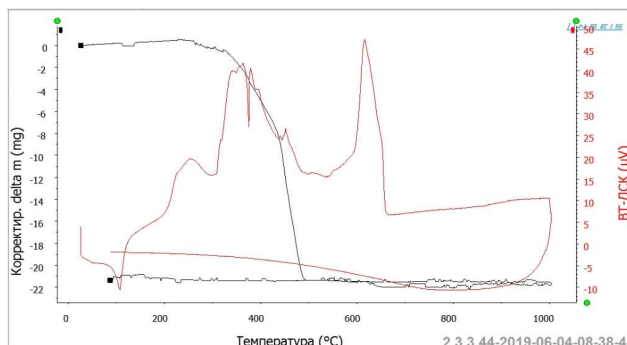


Fig.-5: Differential Scanning Calorimetry PP_{recycl.} + 5% MMT

Figure-5 shows that 1 peak area $S = 0.089 \text{ cm}^2$, 2 peak area $S = 0.19 \text{ cm}^2$, 3 peak area $S = 0.31 \text{ cm}^2$, and 4 peak area $S = 0.55 \text{ cm}^2$. Weight loss in the range of 257°C- 446°C - 8 mg, in the range of 446°C- 485°C - 12.5mg.

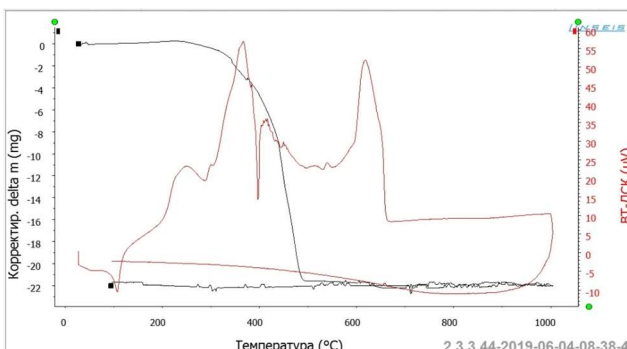


Fig.-6: Differential Scanning Calorimetry PP_{recycl.} +10% Bentonite

It follows from Fig.-6 that 1 peak area $S = 0.532 \text{ cm}^2$, 2 peak area $S = 0.707 \text{ cm}^2$, and 3 peak area $S = 0.919 \text{ cm}^2$. Weight loss in the range of 2360C- 436°C - 8 mg, in the range of 436°C- 490°C - 12.3 mg.

Table-1: Thermal Characteristics of Polymers and Composites Based on them Containing Bentonite (test atmosphere - air).

Name of samples and the ratio of components (in wt.%)		Mass loss temperature, °C		
		5%	10%	50%
PP _{recycl.}	100	322	354	445
PP _{recycl.} / MMT	95/5	334	360	448
PP _{recycl.} / MMT	95/10	336	363	449

It follows from Table-1 that with an increase in the content of modified montmorillonite (5-10%), the temperature of mass loss increases at 5% by 12-16°C, at 10% mass loss by 6-9°C, at 50% mass loss by 3-4°C. The properties of polyethylene terephthalate and polypropylene composites filled with modified montmorillonite are presented in Table-2.

Table-2: Properties of Polyethylene Terephthalate and Polypropylene Composites Filled with Modified Montmorillonite

№ p/l	Composition	Features			
		PTR	Elongation at break, %	Destructive tensile stress, MPa	Statistical bending strength, MPa
1	PET _{recycl.}	2,0	8	27	25

2	PET _{recycl.} +1% MMT	2,3	12	52	40
3	PET _{recycl.} +3% MMT	2,4	13	56	45
4	PET _{recycl.} +5% MMT	2,5	13,5	59	47
5	PP _{recycl.}	0,35	165	23	850
6	PP _{recycl.} +1% MMT	0,37	185	25,5	900
7	PP _{recycl.} +3% MMT	0,39	193	26,2	1010
8	PP _{recycl.} +5% MMT	0,4	210	27	1235
9	PP GOST 26996-86	0,2-0,5	200-1000	24,5-39	1220-1670

It follows from the data in Table-2 that the ratio of components and the technological parameters of synthesis can be varied within a sufficiently wide range in order to obtain the required properties of the composite.

CONCLUSION

The developed composite secondary polypropylene of 5% modified montmorillonite leads to an increase in mechanical characteristics and fully meets the requirements of GOST 26996-86 Polypropylene and copolymers of polypropylene and polyethylene terephthalate GOST RK 51695-2000. The developed technology makes it possible to obtain compositions for processing waste of polyethylene terephthalate and polypropylene, which expands the arsenal of technical means for processing waste of polyethylene terephthalate and polypropylene. According to the results of experimental studies, it was determined that in the composition of PET_{recycl.} + 5% of modified montmorillonite, PP_{recycl.} + 5% MMT increases mechanical characteristics. Thus, the use of modified montmorillonites makes it possible to expand the range of raw materials, dispose of household and industrial waste, reduce production costs, and improve the physicomaterial properties of polymers.¹³⁻¹⁴

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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