

MODIFICATION OF A POLYETHYLENE AND POLYPROPYLENE BLEND WITH UREA-FUNCTIONALIZED PHENOL-FORMALDEHYDE CO-OLIGOMER

T.T. Shirinov, T.M. Naibova

Azerbaijan State Oil and Industry University

E-mail: tshirinov61@gmail.com, n.tamilla51@gmail.com

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Abstract: This research presents a novel approach to addressing the challenges in recycling polyethylene and polypropylene (PE/PP) waste. Since PE and PP-based waste generally originates from the same household and industrial sources, they are often encountered as a mixture. Due to their differing physicochemical properties, separating these polymers becomes necessary prior to recycling. However, the separation and sorting of waste is a complex process, which limits the implementation of recycling.

This study offers a more efficient recycling method that enables the processing of waste together without the need for separation. To improve the chemical compatibility and blending of PE/PP mixtures, a urea-functionalized phenol-formaldehyde co-oligomer (UFFCO) was synthesized and added to the system as a modifier. This modifier enhanced the overall physicochemical properties of the blend by facilitating better interaction between the two polymer phases. The key characteristics of the modified blends were investigated using physicochemical analysis methods.

Keywords: polyethylene, polypropylene, recycling, modification, co-oligomer, extrusion, urea

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Introduction

Over the past few decades, the sharp increase in the production of plastic-based products has led to serious environmental issues. By 2023, annual plastic production had surged to over 390 million tons, compared to just 1.5 million tons in the 1950s [1]. As a result, a large volume of plastic waste has accumulated in the environment, disrupting ecological balance. The growing demand for plastics in packaging, automotive, and electronics sectors, driven by population growth, is a key factor behind this problem [2-3].

Another factor exacerbating the ecological crisis is the global greenhouse gas emissions generated during plastic production and their disposal after use [4]. While traditional recycling methods (such as waste incineration and mechanical recycling) address this issue to some extent, they still have many limitations. For example, incineration reduces waste volume but releases harmful chemicals and greenhouse gases, damaging the atmosphere [5-8]. Mechanical recycling, although more widely used, also faces challenges due to the separation

of mixed plastics and the deterioration of properties after recycling, limiting its effectiveness [9].

Among plastic wastes, the most common are discarded polyethylene (PE) and polypropylene (PP). Due to their similar physicochemical properties, separating PE and PP during recycling is technically complex and costly, often resulting in lower-quality recycled materials [10-11].

This research aims to offer a solution to this problem by recycling mixed PE and PP waste through chemical modification, without separation. In this study, a urea-functionalized phenol-formaldehyde co-oligomer (UFFCO) was added as a modifier to the system to reduce interfacial tension and enhance compatibility between PE and PP. This approach significantly improved the physicochemical and mechanical properties of the composite.

The objective of this research is to substantially enhance the key properties of discarded PE and PP blends using UFFCO and to explore new recycling methods for discarded

thermoplastics in this context.

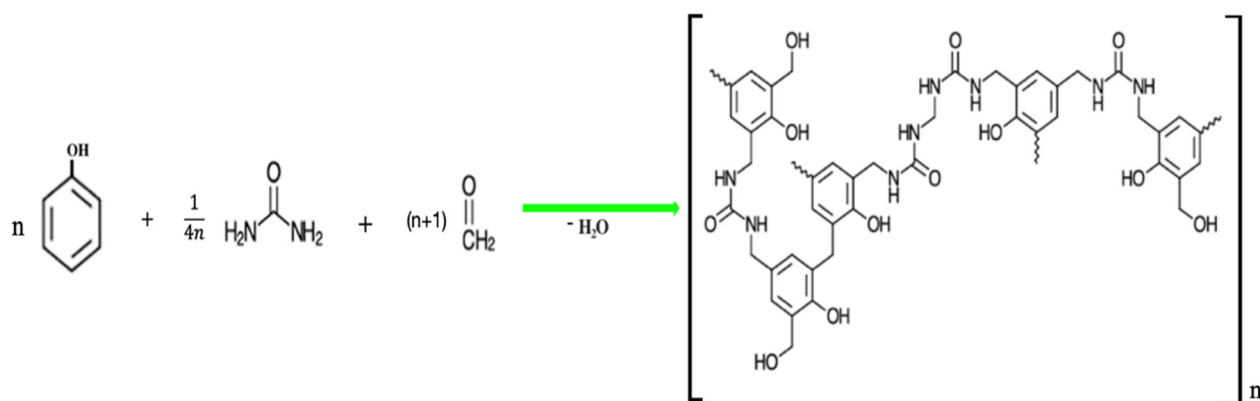
Experimental part

The materials used in this research are industrial waste from discarded polyethylene (PE) and polypropylene (PP). The polymer blends were initially prepared using the "HAAKE MiniLab microcompounder extruder" at the Charles Sadron Institute in Strasbourg, France. Infrared (IR) spectral analyses of the prepared samples were then conducted using a "Thermo Scientific Nicolet" device at the Institute of Catalysis and Inorganic Chemistry (Baku). The melt flow index, thermal properties, and density measurements were conducted using "Ceast MFR," "SCITEQ DSC," and a density measurement device at the "STP Polymer LLC"

laboratory in Sumgait. The synthesis and characterization of urea-functionalized phenol-formaldehyde co-oligomer were conducted in the laboratory of the "Department of Organic Substances and High Molecular Compounds Technology" at the Azerbaijan State Oil and Industry University.

During the synthesis process, a calculated amount of urea was gradually added to the reaction medium to functionalize the phenol-formaldehyde oligomer (PFO).

The synthesis of UFFCO proceeded according to the reaction shown below:



The waste PE and PP were first chopped into small particles (approximately 3-5 mm) and dried in an oven at 100°C until a constant weight was achieved to remove moisture. The dried polymer waste was then fed into a co-rotating twin-screw extruder and blended in various

ratios. The extrusion process was carried out within a temperature range of 180-190°C, with a screw speed set at 10 RPM to ensure thorough mixing. During extrusion, urea-functionalized phenol-formaldehyde co-oligomer was added to the mixing zone at a mass ratio of 5-10%.

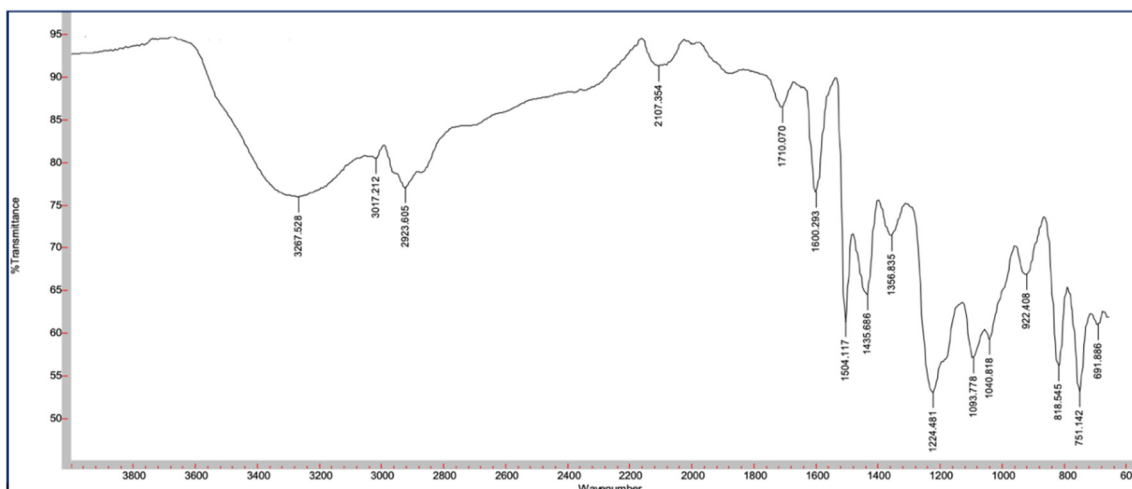


Fig. 1. IR Spectrum of Urea-Functionalized Phenol-Formaldehyde Co-Oligomer

The extruded material was then cooled, and its main properties were investigated. For comparison, the IR spectra of both UFFCO and UFFCO-modified PE/PP blends were examined. The spectra were analyzed in the 400-4000 cm⁻¹

range using Fourier spectrophotometry to identify characteristic absorption bands related to the functional groups present in the samples (Fig. 1 and 2).

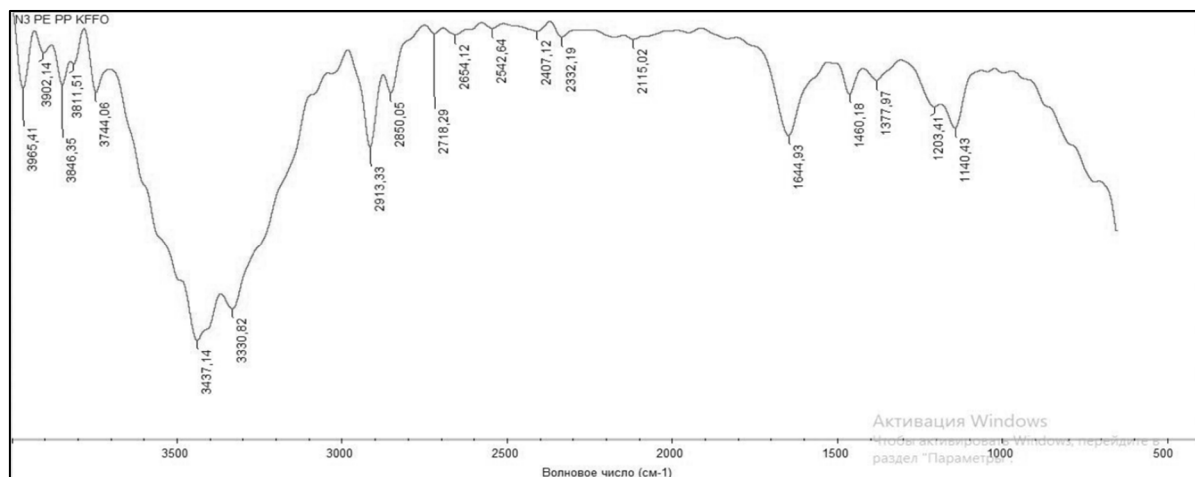


Fig. 2. IR Spectrum of PE/PP Blend Modified with Urea-Functionalized Phenol-Formaldehyde Co-Oligomer (UFFCO)

The IR spectrum shown in Fig. 1 displays a stretching vibration at 1710.07 cm⁻¹, confirming the chemical modification of phenol-formaldehyde oligomer with urea through the sopolycondensation method. Fig. 2 presents the IR spectrum of the PE/PP blend with urea-functionalized phenol-formaldehyde co-oligomer. Peaks corresponding to both the non-polar polymers and the modified co-oligomer are observed.

Thus, the IR spectra confirm the functionalization of phenol-formaldehyde with

urea, as well as the modification of the PE/PP blend with UFFCO. The smooth transitions between peaks indicate reduced phase separation and interfacial tension, demonstrating that the compatibilizer (UFFCO) improves blending between PE and PP.

The densities of the discarded PE/PP blend and the modified PE/PP blend were determined using the Archimedes principle-based method. The density of the samples was then calculated using the following formula:

$$\rho = \frac{\text{Mass in air}}{\text{Mass} - \text{Mass in ethanol}} \times \rho_{\text{ethanol}} \quad (1)$$

Fig. 3 presents a comparative display of the densities of unmodified and modified PE/PP blends.

The results indicate that the modified blend has higher density values. The average density of the discarded PE/PP blend was found to be 862 kg/m³, while the average density of the modified blend was determined to be 925 kg/m³.

The melt index of the samples was determined at 190°C under a 2.16 kg load. The

analysis was based on the mass of the material flowing in molten form over 10 minutes (g/10 min). Both the discarded and modified PE/PP blends were tested for comparison, and the average values were calculated. This decrease indicates that the modified blend has higher rigidity and strength, making it more suitable for applications requiring high mechanical strength and durability.

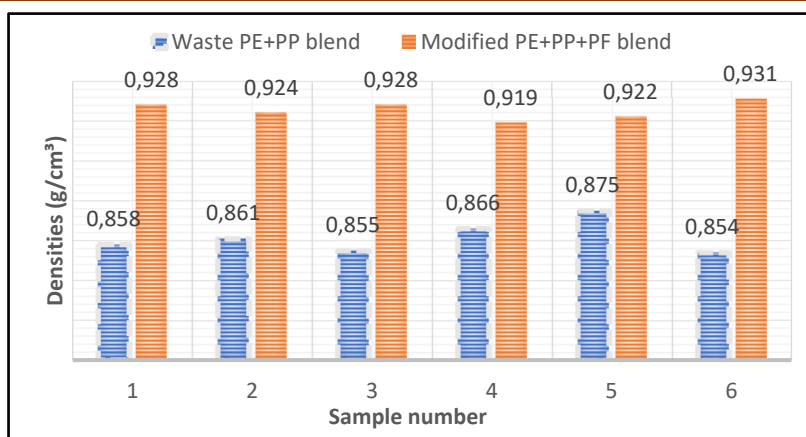


Fig. 3. Comparison of the densities of unmodified and modified PE/PP blends

As shown in Fig. 4, a significant decrease in the melt flow rate of the modified blend was observed, indicating an increase in the material's viscosity.

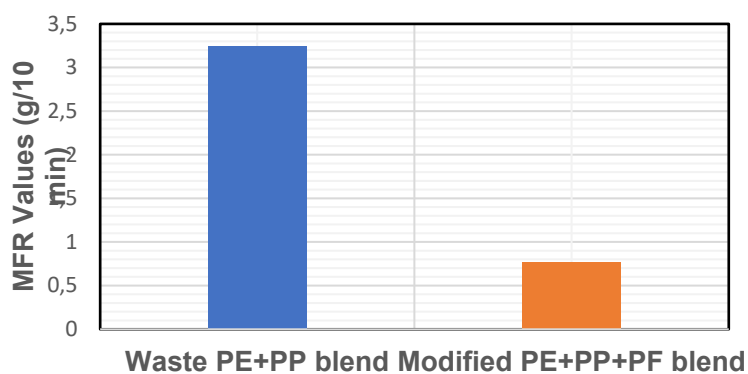


Fig. 4. Comparison of melt flow rate between discarded PE/PP blend and modified blend

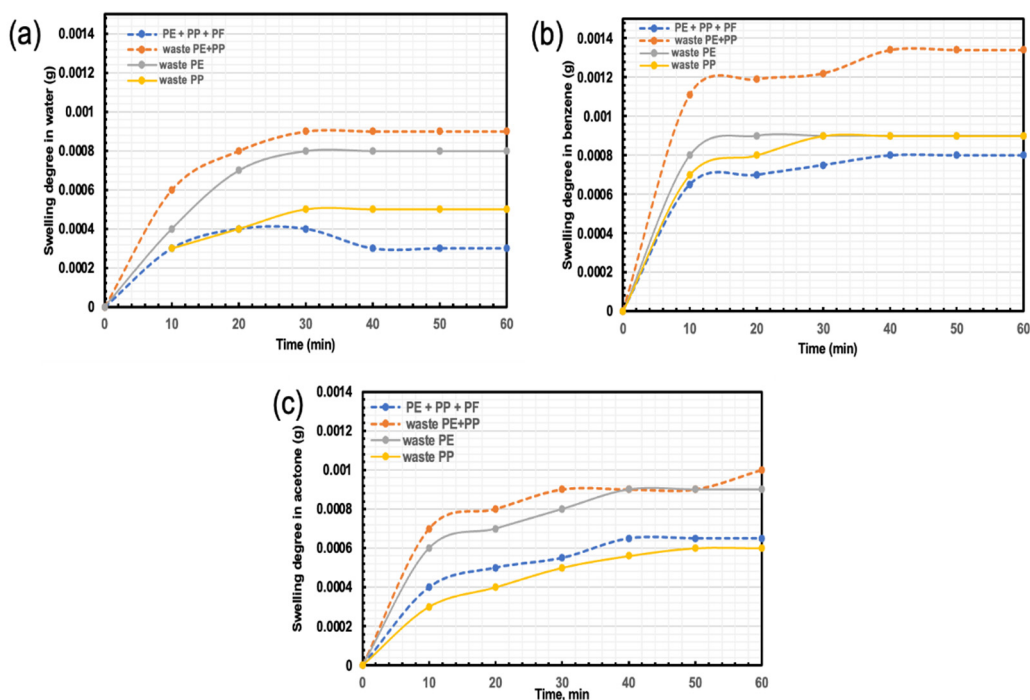


Fig. 5. Curves characterizing the swelling degree of discarded PE, discarded PP, discarded PE/PP blend, and modified PE/PP blend at different time intervals in (a) water, (b) benzene, and (c) acetone

The swelling degree of discarded PE, PP, PE/PP blends, and PE+PP blends modified with UFFCO was determined in solvents such as water, benzene, and acetone. The samples were cut into small pieces and immersed in the respective solvents for predetermined time intervals (20, 30, 40, 50, and 60 minutes). The swelling degree was calculated gravimetrically by measuring the change in mass before and after the analysis, expressed as the percentage increase

in mass relative to the initial dry mass of the sample (Fig. 5).

According to the results, the modified blend exhibited a lower swelling degree, indicating improved resistance to water, acetone, and benzene.

Differential scanning calorimetry (DSC) analysis confirmed the significance of the chemical modification between the PE/PP blend (Fig. 6) and the UFFCO-modified blend (Fig. 7).

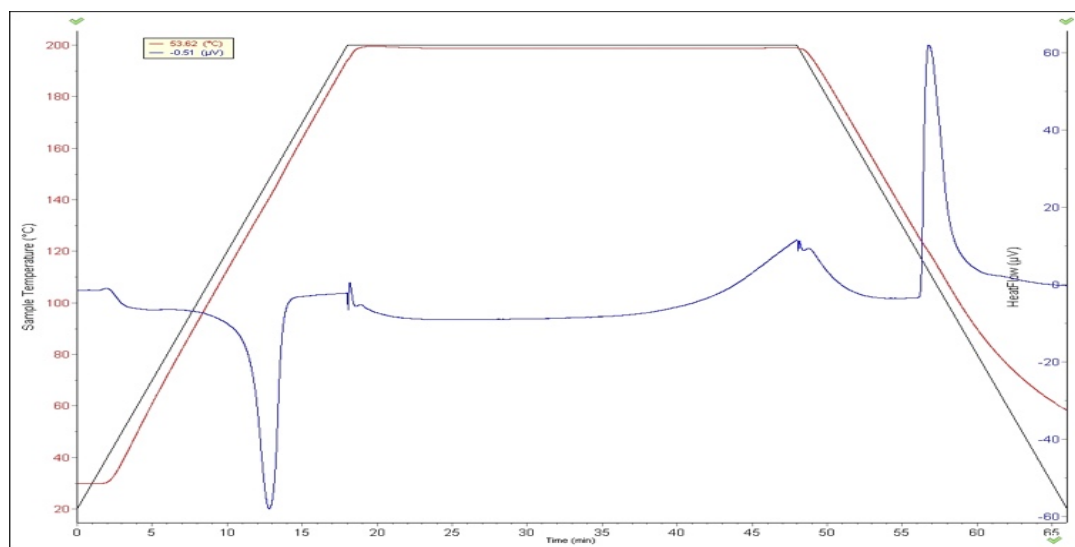


Fig. 6. DSC Analysis of the PE/PP blend

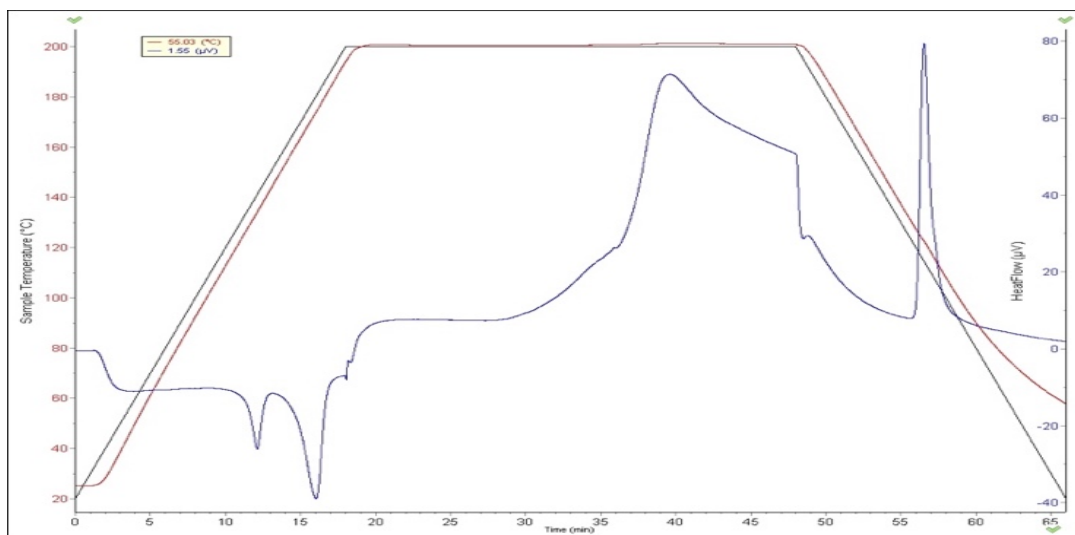


Fig. 7. DSC Analysis of the UFFCO-Modified PE/PP blend

The DSC curve shown in Fig. 6 reflects the typical thermal characteristics of a PE/PP blend. The curve displays a noticeable peak around 120°C, corresponding to the melting temperature of polyethylene. This peak indicates the transition of the polyethylene component in the blend from a crystalline to an amorphous state.

Additionally, the unmodified blend shows an exothermic peak related to the oxidation process and a broader endothermic peak at higher temperatures, which is associated with thermal degradation. Oxidation occurred within a 5-15 minute interval, while the endothermic process continued for about 45-60 minutes. The

crystallization observed during cooling suggests the semi-crystalline nature of polyethylene.

The DSC curve showed in Fig. 7 for the UFFCO-modified PE/PP blend exhibits more complex thermal characteristics. The modified blend shows broader melting peaks, indicating

significant changes in the crystalline structure of the polymer matrix. These changes are attributed to the functionality of UFFCO, which led to interactions that facilitated the formation of additional crystalline zones.

Conclusion

The research demonstrated that the modification of discarded PE and PP blends with UFFCO significantly affected their physicochemical properties. IR and differential scanning calorimetry analyses revealed that the co-oligomer used as a modifier enhanced compatibility between the two polymer phases, facilitating their co-processing and promoting a more stable crystalline structure. Additionally, the observed decrease in melt index indicated

increased viscosity and mechanical strength, making the modified blend suitable for applications requiring higher mechanical durability.

The results showed that this method of modifying PE and PP waste allows for the preparation of efficient and usable materials without the need for separation during recycling. The analysis confirmed that this approach is both environmentally and economically efficient.

References

1. Thiounn T., Smith R. Advances and approaches for chemical recycling of plastic waste. *Journal of Polymer Science*, 2020, **Vol. 58**, p. 1347–1364. DOI: 10.1002/pol.20190261
2. Akchurina T., Israfilova Z., Sadeghian N., Farzaliyev V., Sujayev A., Efendiyeva, K. Synthesis and study of some novel β -arylamino-2-oxy-5-methylpropiophenones as polyethylene stabilizers. *Chemical Problems*, 2024, **Vol. 22**, p. 187–196. DOI: 10.32737/2221-8688-2024-2-187-196
3. Borrelle S.B., Ringma J., Leonard G.H., Polidoro B., Tahir A., Lebreton L., Rochman C., Barnes M., Bernard M., De Frond H., Eriksen M., Monnahan C.C., Hilleary M.A., Mallos N., Law K. L., Gerber L.R., Mcgovern A., Jambeck J., Possingham H.P., Murphy E. Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science*, 2020, **Vol. 369(6510)**, p. 1515–1518. DOI: 10.1126/science.aba3656
4. Wang H., Li L., Sun J., Shen M. Carbon emissions abatement with duopoly generators and eco-conscious consumers: Carbon tax vs carbon allowance. *Economic Analysis and Policy*, 2023, **Vol. 80**, p. 786–804. DOI: 10.1016/j.eap.2023.09.022
5. Zheng J., Suh S. Strategies to reduce the global carbon footprint of plastics. *Nature Climate Change*, 2019, **Vol. 9(5)**, p. 374–378. DOI: 10.1038/s41558-019-0459-z
6. Reis F., Potyatynnyk K., Wu S. Life in Plastic, It's not Fantastic: The Economics of Plastic Pollution. *Science for Sustainability Journal*, 2019, **Vol. 3(1)**, p. 20–35. DOI: 10.53466/veri6053.s4srei
7. Jehanno C., Sardon H., Dove A. P., Roosen M., De Meester S., Leibfarth F.A., Chen E.Y.-X., Alty J.W. Critical advances and future opportunities in upcycling commodity polymers. *Nature*, 2022, **Vol. 603(7903)**, p. 803–814. DOI: 10.1038/s41586-021-04350-0
8. Balu R., Roy C.N., Dutta, N.K. Plastic Waste Upcycling: A Sustainable Solution for Waste Management, Product Development, and Circular Economy. *Polymers*, 2022, **Vol. 14(22)**, 4788. DOI: 10.3390/polym14224788
9. Mustafayeva F.A., Kahramanov N.T. Thermomechanical properties of composite materials based on mixtures of high and low density polyethylenes. *Chemical Problems*, 2023, **Vol. 21**, p. 41–47. DOI: 10.32737/2221-8688-2023-1-41-47
10. Chu M., Yang S., Zhang Q., Tu W., Chen J., Li Q., Zhang C. Sustainable chemical upcycling of waste polyolefins by heterogeneous catalysis. *SusMat*, 2022, **Vol. 2(2)**, p. 161–185. DOI: 10.1002/sus2.55

11. Roy P.S., Allais F., Saito K., Garnier G. Chemical Upcycling Possibilities. Strategic Approach Towards Plastic Waste Valorization: Challenges and Promising *ChemSusChem*, 2021, **Vol. 14(9)**, p. 4007-4027. DOI: 10/1002/.cssc.202100904