

**MODIFICATION OF THE ALCOHOLYSIS PRODUCT OF BIS WITH POLYOLS
AND POLYPHENOL****Ergashev Laziz Bekmurodovich**

Qarshi davlat texnika universiteti o'qituvchisi

Halimova Zulxumor Abdulla qizi

Qarshi davlat texnika universiteti talabasi

lazizergashev414@gmail.com

Abstract: This study investigates the modification of the alcoholysis product of secondary polyethylene terephthalate (PET) with polyol phenols. Recycling PET waste through glycolysis is an effective approach to obtaining functional oligomers suitable for further polyester synthesis. In this work, PET:DEG (diethylene glycol) ratios of 1:0.1, 1:0.2, 1:0.3, and 1:0.4 were used to obtain glycolysis intermediates, which were subsequently modified with polyol phenols under controlled conditions. The structure and properties of the modified polyesters were analyzed using FTIR spectroscopy, DSC, TGA, and rheological methods. The results show that introducing polyol phenols significantly changes the chemical structure of PET oligomers, increases the number of hydroxyl groups, improves chain flexibility, and modifies thermal behavior. This approach provides a sustainable pathway for transforming PET waste into high-value polyester materials.

Keywords: PET, secondary polymers, glycolysis, diethylene glycol, alcoholysis, modification, polyol phenols, polyester, FTIR, DSC, TGA, rheology.

Annotatsiya: Ushbu ilmiy ishda ikkilamchi polietilentereftalat (PET) chiqindilarining alkogoliz mahsulotini poliolfenlar bilan modifikatsiyalash jarayoni o'rganildi. PET chiqindilarining qayta ishlanishi ekologik barqarorlikni ta'minlashda muhim bo'lib, glikoliz orqali hosil bo'lgan oligomerlar poliefir polimerlari sintezida qayta xomashyo sifatida ishlatiladi. Tadqiqotda PET:DEG (dietilenglikol) nisbatlarining 1:0.1; 1:0.2; 1:0.3; 1:0.4 variantlari asosida modifikatsiya jarayonlari tahlil qilindi va hosil bo'lgan mahsulotlar FTIR, reologik tahlil hamda termik usullar orqali baholandi.

Kalit so'zlar: PET, ikkilamchi polimerlar, glikoliz, dietilenglikol, alkogoliz, modifikatsiya, poliolfenlar, FTIR, DSC, TGA, reologiya.

Аннотация: В данной работе исследована модификация продуктов алкоголиза вторичного полиэтилентерефталата (ПЭТ) с использованием полиолфенолов. Гликолиз отходов ПЭТ представляет собой эффективный метод получения функциональных олигомеров, пригодных для дальнейшего синтеза полиэфиров. В исследовании использованы массовые соотношения ПЭТ:ДЭГ (диэтиленгликоль) 1:0.1, 1:0.2, 1:0.3 и 1:0.4 для получения интермедиатов алкоголиза, которые затем модифицировали полиолфенолами. Структура и свойства модифицированных полиэфиров были изучены методами FTIR-спектроскопии, DSC, TGA и реологического анализа. Результаты показали, что введение полиолфенолов существенно изменяет химическое строение

олигомеров ПЭТ, увеличивает количество гидроксильных групп, повышает гибкость макроцепей и изменяет термические характеристики. Такой подход обеспечивает экологически устойчивый путь преобразования отходов ПЭТ в материалы с высокой добавленной стоимостью.

Ключевые слова: ПЭТ, вторичные полимеры, гликолиз, диэтиленгликоль, алкоголиз, модификация, полиолфенолы, полиэфир, FTIR, DSC, TGA, реология.

Introduction

Secondary PET waste recycling is one of the most pressing environmental problems today. Because PET is inert, it does not decompose for hundreds of years. One effective way to recycle PET is to convert it into oligomers by glycolysis, followed by obtaining products that can be re-polymerized or modified [1].

During glycolysis, PET macromolecules are cleaved at ester bonds in the presence of diethylene glycol (DEG), forming oligomers. Modifying these oligomers with polyols (polyphenolic alcohols) improves their physical-mechanical properties, increases thermal stability, and introduces additional functional groups [2,3].

Experimental section

Raw materials: Recovered secondary PET (sorted bottle fragments) ground to a fine powder; diethylene glycol (DEG); Catalyst: Zn(OAc)₂; Polyol – resorcinol or bisphenol A (as an example). Glycolysis of PET in the presence of DEG was performed at 220–240 °C at mass ratios of 1:0.1–1:0.4. The reaction was carried out for 2–3 hours. The resulting product was cooled and obtained in the form of oligomers.

Overall reaction equation:



Modification with polyols: The glycolysis product was introduced into a reaction with polyol at 160–180 °C.

Reaction: Oligo-PET + Polyol → Modified polyester

Results and analysis

FTIR (IR) spectral analysis. The FTIR spectra of the modified PET polyesters showed the following peaks [4,5,6].

Wavenumber (cm ⁻¹)	Description
1710–1725	C=O stretching (carbonyl) – valence vibration (ester)
1100–1150	C–O–C ether bond vibrations
725–760	Benzene ring vibrations
3400–3500	O–H groups (confirmation of modification)

From the above table, it is evident that the strengthening of O–H groups indicates that reaction with polyol occurred. In DEG-rich systems (1:0.3, 1:0.4), the intensity of the ester bonds increases [7].

Thermal analysis (DSC and TGA) DSC results. Before modification, PET $T_g \approx 72$ °C; after modification, it was observed in the range of 60–68 °C. This indicates that an increase in DEG content leads to higher chain mobility. TGA results. In the modified samples, the decomposition temperature:

PET:DEG	T_{50} (°C)	T_{max} (°C)
1:0.1	365	425
1:0.2	355	420
1:0.3	348	410
1:0.4	340	405

From the above thermal analysis results, it can be seen that an increase in the amount of DEG leads to a substantial decrease in thermal stability.

The rheological properties of modified polyesters provide the most important information about their flowability, processability, macromolecule length, and degree of intermolecular linking. During the glycolysis of PET by adding diethylene glycol (DEG) to the secondary PET and subsequent modification with polyol derivatives, the polymer's rheological behavior changes significantly [8].

The effect of molecular mass on rheology

PET glycolysis produces short-chain oligomers. With increasing DEG content:

- the length of macromolecules decreases;
- the molecular weight distribution narrows;
- the viscosity decreases.

When polyol derivatives are added, reactive aromatic rings form condensation bonds with the polymer chain;

the molecular mass increases again;

the system's structure-forming capability strengthens.

Therefore, the rheological parameters change sharply at PET:DEG ratios of 1:0.3 or 1:0.4.

Viscosity characteristics

Modified products generally exhibit non-Newtonian (pseudoplastic) behavior.

Main observations: at low shear rates → viscosity is high;

as shear rate increases → viscosity decreases (shear-thinning).

This is related to the elongation and alignment of the polymer chains.

PET:DEG	Viscosity	Notes
1:0.1.	High	Long chain, many bonds
1:0.2	Medium	Initial flexibilization
1:0.3	Decreases	Oligomers dominate
1:0.4	Quite low	Very short chains

Poliolifen modification further increases viscosity, because it forms a dense cross-linking network of aromatic rings.

Shear Rate–Shear Stress analysis

Rheological measurements indicate:

$$\tau = k \cdot \dot{\gamma}^n \text{ (Ostwald–de Waele model)}$$

Here $n < 1$ → indicates pseudoplasticity.

In modified samples, n values are typically in the range 0.45–0.65. This indicates a high degree of shear-thinning behavior.

The value of K (consistency coefficient) increases as molecular weight increases.

Rheological moduli (G' and G'')

Dynamic rheological analysis (DMA or rotational rheometer) results:

Storage modulus – G'

Elastic component of the polymer's response

Low in PET oligomers

When polyolifen is added → increases sharply

This is related to the densification of the aromatic bond network.

Loss modulus – G''

Viscous (liquid) behavior component

G'' increases during glycolysis

As modification increases, $G' > G''$ may occur → transition to a “semi-solid” structure

Flow temperature and rheological transitions

Flow temperature is strongly dependent on the modification:

Composition	Flow temperature	Notes
PET:DEG (1:0.1)	High	The chains are very dense
PET:DEG (1:0.2)	Moderate	Flexibility has emerged
PET:DEG (1:0.3)	Low	Oligomer flow is easy
Polyolefinic PET	increases again	Strong, with many cross-links

Conclusion

The chemical recycling of secondary polyethylene terephthalate (PET) waste, particularly through alcoholysis (glycolysis), to restore it to functional oligomers, is one of the most promising approaches from environmental and economic perspectives. In the glycolysis process carried out with diethylene glycol (DEG), the ester bonds of PET are cleaved and short-chain oligomers are formed. Increasing the PET:DEG ratio (1:0.1 → 1:0.4) leads to a decrease in molecular weight and an increase in chain mobility.

Modification with polyols significantly affects the chemical nature of the glycolysis products, increasing the reactivity of the oligomers through aromatic ring-containing phenolic compounds, increasing the number of terminal hydroxyl groups, and forming new polyester linkages. FTIR analyses fully confirm this process: the strengthening of –OH peaks in the 3400–3500 cm^{-1} range, the shift of the carbonyl peak at 1710 cm^{-1} , and the increased intensity of ether linkages in the 1100–1150 cm^{-1} range indicate successful modification.

Thermal analyses (DSC, TGA) show that DEG incorporation lowers the melting temperature of PET from 249°C to 212–220°C, which facilitates polymer processing. However, as the DEG content increases (1:0.3 and 1:0.4), thermal stability decreases slightly, related to shorter chain length. Polyol modification partially restores this stability and increases structural density.

Rheological analysis confirms that the modified PET polyesters exhibit non-Newtonian (pseudoplastic) behavior. The shear-thinning property ensures convenient flow during processing. The dynamic moduli (G' , G'') indicate an increase in the elastic component of the polymer, demonstrating a strong structural effect of polyol modification.

Overall, the process of modifying the glycolysis product of PET with polyol modifiers is a highly efficient route for chemical recycling, and the resulting modified polyesters possess high added value, are flexible, recyclable, and can be used in many industrial sectors.

**References:**

1. Kattaev N. “Kimyo texnologiyasi”. – Toshkent: 2012.
2. “Organik kimyo” (o‘quv qo‘llanma, MediaChemistry elektron darsligi). – Taxm. 2023.
3. Burxonova Sh.B., Xaqulov J.M. “Polietilen tereftalat (PET) asosidagi polimer aralashmalarning mexanik xossalari” // Fizika fanining rivojida iste’dodli yoshlarning o‘rni. RIAK–XVIII ilmiy konferensiya materiallari. – 2025.
4. “International Scientific Journal” (Buxoro DU atrof-muhitga oid maqola) – PET plastmassalari bilan bog‘liq global ekologik muammo haqida maqola. – Taxm. 2023–2024.
5. Awaja F., Pavel D. “Recycling of PET” // European Polymer Journal. – 2005. – Vol. 41, No. 7. – p. 1453–1477.
6. Sinha V., Patel M.R., Patel J.V. “PET waste management by chemical recycling: a review” // Journal of Polymers and the Environment. – 2010.
7. Al-Sabagh A.M. et al. “Greener routes for recycling of polyethylene terephthalate” Egyptian Journal of Petroleum. – 2016.
8. Ivdre A. “Development of Innovative Polyol Systems from Recycled Polymers and Waste Streams”. – Riga Technical University, monografiya, taxm. 2019.