TECHNOLOGICAL SCHEME FOR PRODUCING OLIGOURETHANES AND EPOXYURETHANES.

Abstract:

This paper examines the technological features of producing oligourethanes and epoxyurethane polymers without the use of toxic di- and polyisocyanates. The synthesis of urethane-containing oligomers based on hydroxyl-containing compounds and their subsequent interaction with epoxy resins to form spatially cross-linked epoxyurethane structures are investigated. Optimal process parameters for producing polymer systems with a high degree of cure and improved physical and mechanical properties are established. The resulting epoxyurethane materials were shown to possess high adhesion, chemical resistance, low water absorption, and increased resistance to aggressive environments. Comparative analyses have demonstrated that epoxy-urethane polymers produced using the developed method are capable of competing with existing thermosetting polymers. The potential applications of the developed materials as anticorrosive coatings and protective composite systems for the oil and gas, chemical, and construction industries were explored. A technical and economic evaluation of the developed technology demonstrated the potential for industrial implementation of epoxyurethane polymers.The resulting polymeric materials are characterized by high adhesion, chemical resistance, low water absorption, enhanced impact strength, and resistance to aggressive environments. It has been established that the incorporation of urethane moieties into the epoxy matrix helps reduce the intrinsic brittleness of the polymers and improve their deformation and strength properties.

Keywords: oligourethanes; epoxyurethanes; polymeric materials; isocyanate-free synthesis; anti-corrosion coatings.

Introduction

Modern developments in the chemical technology of polymeric materials are aimed at creating highly efficient thermosetting systems with enhanced physicomechanical, anticorrosive, and operational properties. Among these materials, oligourethanes and epoxy-urethane polymers occupy a special place due to their high adhesion, chemical resistance, mechanical strength, and stability in aggressive environments [1, 2, 3, 4].

Epoxy-urethane compositions are widely utilized in mechanical engineering, the oil and gas industry, construction, chemical engineering, and protective coating production, owing to their ability to form robust, spatially cross-linked structures. Combining epoxy and urethane moieties within a single polymer network makes it possible to simultaneously achieve the high mechanical strength characteristic of epoxy resins and the flexibility inherent to polyurethanes.

Traditional methods for synthesizing polyurethanes rely on di- and polyisocyanates, which exhibit high toxicity and pose environmental hazards [5, 6]. Consequently, non-isocyanate routes for producing oligourethanes have gained significant relevance, as they reduce the toxicity of the technological process and improve the ecological safety of production [7, 8, 9, 10].

The development of process flowcharts for synthesizing oligourethanes and epoxy-urethanes, along with evaluating their properties and technical-economic efficiency, represents a crucial objective in modern chemical industry. The implementation of such materials substantially extends the service life of metallic structures, reduces corrosion losses, and enhances the operational reliability of industrial equipment [11, 12, 13].

It was established that the presence of polar urethane groups enhances intermolecular interactions between the coating and the metal substrate, thereby increasing bond strength and reducing the likelihood of delamination under mechanical and thermal stresses. Significant attention was devoted to investigating the water absorption and chemical resistance of the materials [14, 15]. The resulting epoxy-urethane polymers were characterized by low permeability to moisture and aggressive liquids, ensuring effective corrosion protection for metals. During testing in acidic and alkaline environments, the coatings maintained their structural integrity and operational properties over extended periods [16]. The high mechanical and deformation performance of the epoxy-urethanes is attributed to the combination of rigid epoxy segments and more flexible urethane moieties. This structural architecture allows the material to absorb impact and vibrational loads without cracking or coating degradation [17]. Table 1 outlines the key advantages of materials based on epoxy-urethane polymers.

Table 1. Main advantages of epoxy-urethane materials

Property	PracticalSignificance
High adhesion	Reliable bonding to metal
Lowwaterabsorption	Corrosionprotection
Chemical resistance	Performanceinaggressiveenvironments
Enhancedflexibility	Resistancetodeformation
Wearresistance	Extendedservicelife
Thermalstability	Operationatelevatedtemperatures

Materials and Methods

The preparation of oligourethanes constitutes one of the most critical stages in the synthesis of epoxy-urethane polymeric materials. In the investigated technology, the synthesis was carried out without the use of toxic di- and polyisocyanates, ensuring the environmental safety of the process and reducing operational risks.

The synthesis base consisted of ethylene glycol, glycerol, phthalic anhydride, urea, and formaldehyde. During the synthesis, urethane groups were formed through the interaction of hydroxyl-containing compounds with carbamide components. The resulting oligomers contained reactive functional groups capable of subsequently reacting with epoxy resins to yield three-dimensional cross-linked epoxy-urethane structures. The technological process flow for the synthesis of oligourethanes is presented in Table 2.

Table 2. Technological processes for the synthesis of oligourethanes

ProcessStage	MainOperations	Purpose
Rawmaterialpreparation	Purification and dosing of components	Ensuringsynthesisstability
Reagentmixing	Introduction of polyols and carbamide compounds	Formation of the reaction medium
Polycondensation	Heatingandstirring	Formationofurethanegroups
Heattreatment	Maintenanceoftargettemperature	Reactioncompletion
Cooling	Producttemperaturereduction	Obtaining a stableoligomer

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At the LLC Tashkent Scientific Research Institute of Chemical Technology, synthetic methods were developed for non-isocyanate urethane oligomers utilizing local raw material resources. Non-isocyanate oligourethane formulations based on ethylene glycol, glycerol, and phthalic anhydride were established. A distinctive feature of the proposed technology for synthesizing urethane-containing oligomers is the complete elimination of di- and polyisocyanates from the production process.

The resulting products are highly viscous resins. The technological processes involved in obtaining these products are simplified, operating without elevated temperatures or the need for high pressure. These methods allow sampling at each stage of the process, thereby enabling precise control over the physicochemical properties of the final product via laboratory analysis. Polymeric materials derived from these oligomers exhibit high physicochemical parameters [7, 8, 18–25].

The aim of this study is the development of a technological process scheme for the production of urethane oligomers, as well as identifying the technical-economic and environmental efficiency.

The developed production technology will make it possible to obtain three types of urethane oligomers: 1-urethane oligomer based on ethylene glycol; 2-urethane oligomer based on glycerol; 3-urethane oligomer based on phthalic anhydride. Also, this technology will make it possible to obtain urethane-epoxy two-component prepolymers based on the resulting urethane oligomers.

For pilot-industrial production, four samples of epoxy-urethane thermosets were selected and coded under the names indicated below:

EPU-15EG – the mass ratio of the ethylene glycol-based urethane oligomer and KER 828 brand epoxy resin is 1.5:1;

EPU-30G – the mass ratio of the glycerol-based urethane oligomer and KER 828 brand epoxy resin is 3.0:1;

EPU-70F – the mass ratio of the phthalic anhydride-based urethane oligomer and KER 828 brand epoxy resin is 7.0:1;

EPU-100F – the mass ratio of the phthalic anhydride-based urethane oligomer and KER 828 brand epoxy resin is 10:1.

Table 3 outlines the compositions of the obtained epoxy-urethane polymers based on oligourethanes from ethylene glycol, glycerol, phthalic anhydride, and KER 828.

Table 3. Composition of the epoxy-urethane polymer with oligourethane based on ethylene glycol, glycerol, phthalic anhydride, and KER 828

SampleNo.	Startingmaterials,		
	Oligourethane	**Resin KER 828**	**Hardener PEPA)**
	Mass ratio of starting materials		
ЭПУ-15ЭГ	1,5	1	0,025
ЭПУ-30Г	3	1	0
ЭПУ-70Ф	7,0	1	0,03
ЭПУ-100Ф	10,0	1	0,01

The above-listed samples of epoxy-urethane thermosets were selected based on the results of the conducted physicochemical, deformation-strength, and technical-economic studies. Epoxy-urethane polymeric materials obtained on the basis of these urethane oligomer samples possess optimal physicochemical, anticorrosive, and tribotechnical characteristics when utilized as anticorrosive polymeric structural materials and coatings for protecting metal equipment against corrosion and wear.

Among the epoxy resin grades ED-20 and KER 828, the KER 828 grade epoxy resin was chosen as the epoxy component of the urethane-epoxy two-component polymer system. Comparative analysis of the physicochemical, deformation-strength, tribological, and anticorrosive properties of epoxy-urethane polymer samples synthesized using both grades of epoxy resins revealed that the epoxy-urethane polymers produced with either epoxy resin grade exhibit closely similar property parameters. However, the KER 828 grade epoxy resin is economically more feasible.Figure 1 shows the technological flowchart for the production of urethane oligomers and epoxy-urethane polymers based on them.

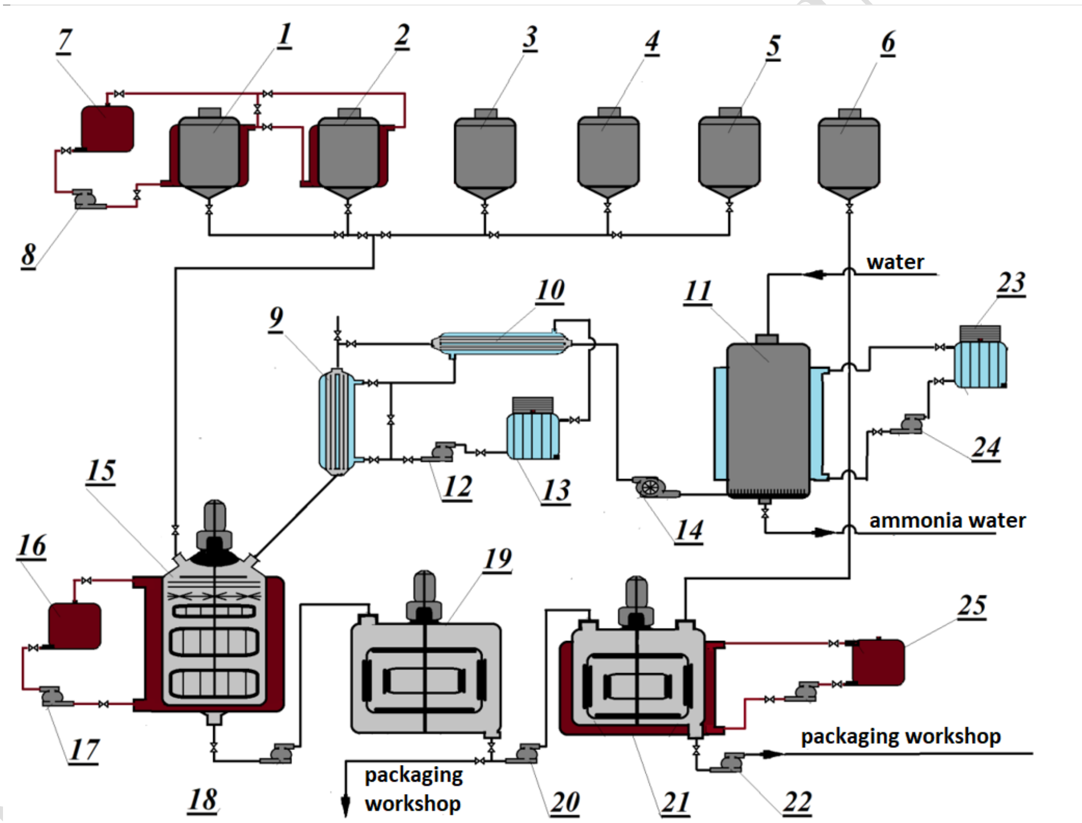

Figure 1. Technological flowchart for the production of oligourethanes and epoxy-urethane polymers based on them

1 – jacketed tank for ethylene glycol; 2 – jacketed tank for glycerol; 3 – tank for aqueous formaldehyde solution; 4 – hopper for urea; 5 – hopper for phthalic anhydride; 6 – tank for epoxy resin; 7, 16, 25 – heat transfer fluid heaters; 8, 12, 17, 18, 22, 24 – pumps; 9 – reflux condenser; 10 – gas condenser; 11 – absorber; 13, 23 – heat exchanger cooling radiator; 14 – vacuum pump; 15 – reactor for the

synthesis of urethane oligomers; 19 – mixer for oligourethane adjusting/standardization; 21 – jacketed mixer for obtaining urethane-epoxy polyblends.

During the synthesis, the process temperature, reaction duration, and ratio of starting components were of great importance. Optimization of these parameters made it possible to obtain oligourethanes with an average molecular weight of up to 3800 and a high degree of reactivity. The resulting oligourethanes were characterized by increased adhesion, chemical resistance, and good compatibility with epoxy resins. The presence of urethane and hydroxyl groups ensured the effective formation of intermolecular bonds during the formation of epoxy-urethane polymers. Obtaining epoxy-urethane polymers. In the next stage, the synthesized oligourethanes were used to prepare epoxy-urethane polymer systems. Epoxy resin grades ED-20 and KER-828, possessing high reactivity and good film-forming properties, were utilized as the epoxy component. Polyethylenepolyamine (PEPA) was used as the hardener. The technological process for obtaining epoxy-urethanes included: 1. preparation of the oligourethane component; 2. mixing with epoxy resin; 3. introduction of the hardener; 4. mechanical stirring; 5. degassing of the composition; 6. molding and thermal curing. The process of obtaining epoxy-urethanes is based on the chemical interaction of the epoxy groups of the resin with the active functional groups of the oligourethanes. As a result of the reaction, a three-dimensionally cross-linked structure with a high degree of chemical cross-linking reaching 96% is formed. Table 4 presents the main characteristics of the obtained epoxy-urethane polymers.

Table 4. Main properties of the obtained epoxy-urethane polymers

Property	TestMethod	Value
Degreeofcuring	(ISO 14322:2012, MOD)	upto 96%
Adhesionstrength	(ГОСТ 14760-69)	high
Waterabsorption	(ГОСТ 4650-2014)	low

Property	**TestMethod**	**Value**
Chemicalresistance	ГОСТ 9.403-80. (СТ СЭВ 5260-85)	high
Impactresistance	ГОСТ Р 53007- 2008 (ИСО 6272-1:2002, ИСО 6272-2:2002)	increased
Thermalresistance	(ГОСТ 32618.1-2014 (ISO 11359-1:1999)	high

Results and Discussion

The ratio of system components was of particular importance, as varying the content of oligourethanes significantly influenced the physicochemical and mechanical properties of the final material. At the optimal concentration of the urethane component, an increase in elasticity, impact strength, and coating adhesion to the metallic surface was observed. The conducted thermomechanical and deformation-strength studies showed that the introduction of urethane fragments contributes to reducing the internal brittleness of the epoxy matrix and increases the resistance of polymers to dynamic loads. The resulting epoxy-urethane materials can be effectively utilized as protective coatings, structural polymers, lining materials, and anticorrosive compositions for operation in aggressive environments. The specimens were prepared in the form of plates with a cross-sectional area of 20 mm^2. The working gauge length of the specimen is 50 mm. Based on the results of this study, stress-strain curves under tension were obtained.

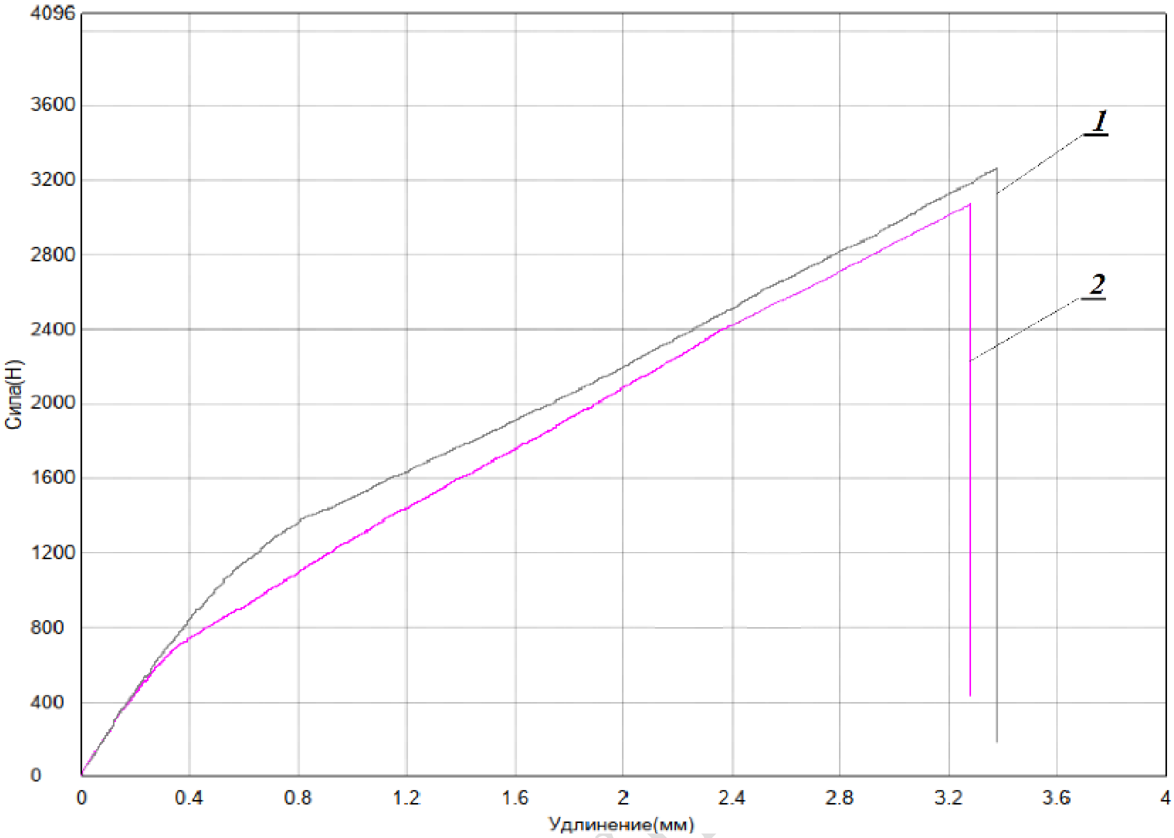

Figure 2. Stress-strain curves under tension for epoxy polymers: *Curve 1 – ED-20-based epoxy polymer;Curve 2 – KER 828-based epoxy polymer*

Initially, the study was carried out on epoxy polymer samples based on ED-20 and KER 828. The obtained data were used for comparative analyses with epoxy-urethane polymers. Figure 2 shows the results of tensile strength testing for the epoxy polymer samples. The calculated results of tensile strength and modulus of elasticity for the epoxy polymer samples are presented in Table 5.

Table 5. Tensile strength properties of epoxy polymer samples

Sample	Breakingforce, N	Elongation, mm	Tensile strength σ_t, N/mm²	Modulus of elasticity, N/mm²
ED-20	3248	3.35	162.4	1480,37
KER 828	3067	3.28	153	1479,92

Technical and Economic Efficiency.

The development of technology for obtaining oligourethanes and epoxy-urethane polymers is of not only scientific but also major industrial significance.

The application of the non-isocyanate synthesis method makes it possible to lower the toxicity of the manufacturing process, reduce costs for personal protective systems, and enhance the environmental safety of production. One of the key advantages of the developed technology is the utilization of accessible raw materials and the feasibility of tailoring the properties of the resulting materials by adjusting the ratio of components. This enables the production of epoxy-urethane compositions for various applications without significantly complicating the technological process.

The economic efficiency of the technology is driven by:

1. increasing the service life of metal structures;
2. reducing corrosion losses;
3. lowering equipment repair costs;
4. decreasing the consumption of paint and varnish materials;
5. enhancing the operational reliability of industrial facilities.

A significant advantage is the high durability of epoxy-urethane coatings. Due to enhanced adhesion and chemical resistance, the need for frequent renewal of the protective layer is minimized, which substantially reduces operational expenses for industrial enterprises.

Table 6. Technical and economic advantages of the developed materials

Indicator	**Effect**
Corrosionreduction	Increasedequipmentservicelife
Highadhesion	Reducedcoatingconsumption
Chemicalresistance	Reductioninrepairwork
Wearresistance	Loweringoperationalcosts
Non-isocyanatesynthesis	Enhancementofenvironmentalsafety

Practical implementation of the developed epoxy-urethane materials at industrial facilities demonstrated high efficiency of their application as anticorrosive coatings and lining materials. The use of these polymers in oil and gas as well as mining and metallurgical enterprises made it possible to enhance equipment resistance to aggressive media and extend the mean time between overhauls. Thus, the developed technology for obtaining oligourethanes and epoxy-urethanes is promising for industrial deployment owing to the combination of high operational performance of the materials, environmental safety, and economic efficiency of production.

Conclusion

As a result of the conducted study, a technology for obtaining oligourethanes and epoxy-urethane polymers without the use of toxic di- and polyisocyanates was developed. It was established that the application of the non-isocyanate synthesis method allows obtaining urethane-containing oligomers with high reactivity and good compatibility with epoxy resins. It was shown that the interaction of the synthesized oligourethanes with epoxy resins leads to the formation of three-dimensionally cross-linked epoxy-urethane structures with a high degree of curing reaching up to 96%. Due to the combination of rigid epoxy segments and elastic urethane groups, high operational reliability of the coatings under mechanical and thermal loads is ensured. The developed epoxy-urethane materials can be effectively applied as anticorrosive coatings, lining compositions, and protective polymer systems in the oil and gas, chemical, construction, and mining-metallurgical industries. Industrial implementation demonstrated the possibility of increasing the service life of metal structures and reducing operational expenses. Thus, the developed technology for obtaining oligourethanes and epoxy-urethanes possesses high scientific and practical significance and is promising for further industrial application in the production of modern corrosion-resistant polymeric materials.

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