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International Scientific Conference «Social and Cultural Transformations in the Context of
Modern Globalism»**LOW WASTE AND ENVIRONMENTALLY FRIENDLY METHODS
FOR PRODUCING POLYMERS AND COMPOSITIONS**

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364906, Russia; asldzam@mail.ru**Abstract**

Diols (glycols) are a class of organic compounds, the molecule of which contains two hydroxyl groups, these are dihydric aliphatic alcohols (the simplest glycol is ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$). The general formula for diols is $\text{C}_n\text{H}_{2n}(\text{OH})_2$. They are used in the production of polyester resins, polyurethanes, plasticizers, detergents, etc. Diols are one of the monomers to produce aliphatic and polyesters. Aliphatic polyesters are the polycondensation products of diols and aliphatic hydroxycarboxylic acids or aliphatic polycarboxylic acids. The general formula of dicarboxylic (dibasic) acids is $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$. This class includes such acids as oxalic malonic, succinic, sebacic, adipic, cork, and others. Aliphatic hydroxycarboxylic acids are lactic, malic, tartaric, citric, and others. Complex polyesters are polycondensation products of diols and aromatic carboxylic acids. The article describes methods for producing aliphatic and aromatic polymers and compositions based on various diols of ethylene glycol, propylene glycol, butanediol, and others, with aliphatic hydroxy acids, aliphatic polycarboxylic, and aromatic acids, developed by domestic and foreign scientists.

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1. Introduction

Diols (glycols) are a class of organic compounds, the molecule of which contains two hydroxyl groups, these are dihydric aliphatic alcohols (the simplest glycol is ethylene glycol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$). The general formula for diols is $\text{C}_n\text{H}_{2n}(\text{OH})_2$. They are used in the production of polyester resins, polyurethanes, plasticizers, detergents, etc.

Diols are one of the monomers to produce aliphatic and polyesters. Aliphatic polyesters are the polycondensation products of diols and aliphatic hydroxycarboxylic acids or aliphatic polycarboxylic acids. The general formula of dicarboxylic (dibasic) acids is $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$.

This class includes such acids as oxalic malonic, succinic, sebacic, adipic, cork, and others. Aliphatic hydroxycarboxylic acids are lactic, malic, tartaric, citric, and others.

Complex polyesters are polycondensation products of diols and aromatic carboxylic acids.

Glycols (diols) are widely used as one of the monomers to produce aliphatic and polyesters (Khasbulatova et al., 2022).

2. Problem Statement

There are many ways to make diols. Method to produce aliphatic α , ω -diols C₄-C₁₂ by catalytic hydrogenation of α , ω -dicarboxylic acids C₄-C₁₂, which are reacted in the form of oligomeric esters with target diols. The catalysts used are catalysts formed from powders based on a mixture of Cu, Zn, and Al oxides, to which Fe, Co, Ni, and/or Mn oxides are added. Hydrogenation is carried out continuously at a temperature of 180–250° and an H₂ pressure of 100–400 bar. Examples of the preparation of 1,4-butanediol and 1,6-hexanediol are given.

3. Research Questions

Aliphatic polyesters are prepared by catalytic polycondensation in an organic solvent using ion exchange resins as a drying agent. Polyesters were obtained using aliphatic hydroxycarboxylic acids (lactic acid), aliphatic polycarboxylic acids (succinic acid), polymers of aliphatic hydroxycarboxylic acids, and 1,4-butanediol (Kultys, 1997).

4. Purpose of the Study

In (Jung et al., 1999), copolyester was synthesized by polycondensation (200–205°C) containing polyester units from succinic acid and 1,4-butanediol (polyester-1) and polyester units from succinic acid and 1,4-cyclohexanedimethanol (polyester-2) ... The ratio of polyester-1 / polyester-2 units in copolyester is 90 / 10–60 / 40. Copolyester have a characteristic viscosity of 1.187–1.568 dl/g (in chloroform, temperature 25°C.), $M_n = (5,34-5,78) \cdot 10^4$, volumetric melt flow index (MVR) – 2.1–2.4, melting point 64.7–111, glass transition temperature 0.4–10.8. It is shown that an increase in the content of polyester-2 units in copolyester leads to a decrease in their intrinsic viscosity, melting point, and degree of crystallization, and an increase in the glass transition temperature. The tensile strength of copolyester depends little on the content of polyester-2 units in them, and the elongation increases with an increase in

the concentration of the latter in the copolyester. For example, it is 620 and 150% for copolyester containing resp. 40 and 10 mol% polyester-2 units. The rate of the biodegradation process decreases with an increase in the content of polyester-2 units. Thus, the degree of conversion of carbon to CO₂ after 35 days is 17.5 and 8% for copolyester with a polyester-2 unit content of 10 and 40 mol%, respectively.

In (Bajpai & Rai, 1998), polytetramethylene aspartate was synthesized by polycondensation in a melt of D.L-aspartic acid and 1.4. butanediol. The reaction of the obtained polymer with dimethyl sulfoxide gave complexes of divalent Mn, Co, Ni, Cu, Zn, Hg, Cd, Mg, Ca, Pb, as well as tetravalent Ce. The resulting complexes were characterized by elemental analysis methods: infrared spectroscopy, thermogravimetric analysis, and measurements of magnetic susceptibility.

5. Research Methods

Complex polyesters are obtained as a result of the interaction of diols with aromatic carboxylic (terephthalic, isophthalic, naphthalenedicarboxylic, and others) acids. Thus, hydroxyalkyl carboxylates containing <2.5% oxyethylene glycols are obtained by condensation of aromatic dicarboxylic acids (4,4'- or 3,4'-diphenyldicarboxylic or terephthalic acid, their diphenyl ethers, stilbenes, naphthalenedicarboxylic acid) with C₂-8(2-4) diols (ethylene glycol, propylene glycol, butanediol) at 200–260 °C, pressure 500–700 kPa without catalyst.

6. Findings

When copolyester is prepared from aromatic dicarboxylic acid and ethylene glycol, the authors of (Kultys, 1997), at the stage of practical completion of esterification, add 0.01–3% of inactive inorganic particles with an average diameter of 0 to the reaction product containing 100 g-eq / 106 g of terminal COOH groups., 5-5 microns. Example: to bis-β-hydroxyethyl terephthalate, obtained at a molar ratio of I to terephthalic acid of 1.15, at 250, a mixture of 86.5 terephthalic acid and 37.2 ethylene glycol is fed for 3.5 hours and the esterification is carried out at 250°, removing the resulting water. After the end of the mixture feeding, the temperature is raised to 255° and the esterification is continued for another 1 hour, obtaining a product containing 210 g-eq / 106 g of COOH groups. 104.8 of the resulting product is introduced into another reactor, a suspension of 0.1 Li₂O in 10 ethylene glycol, 0.03 trimethyl phosphate, and 0.03 Sb₂O₃ is added, after 20 minutes, 5 suspensions of CaCO₃ (average particle diameter 1.2 μm) are added to ethylene glycol (before by adding a suspension, the product contains 36 g-eq / 106 g of COOH groups) and polycondensation is carried out in the usual way. Get polyester polyethylene terephthalate with a viscosity [η] = 0.615, containing uniformly dispersed particles of CaCO₃.

When polyester resin is obtained by (re) esterification of an aromatic dicarboxylic acid or its ester-forming derivative with glycol followed by polycondensation, a suspension of particles inactive with respect to polyester resin is introduced into the system in a continuous or periodic manner at a temperature decrease of <50° glycol. Example: 0.04 Mn(OAc)₂·H₂O is added to a mixture of 90 dimethyl terephthalate and 57 ethylene glycol and transesterification is carried out, increasing the temperature of the mixture > 150° When reaching 200°, 90 suspension filtered through a filter with 2 μm pores obtained by dispersing 10 spherical particles is introduced into the system TiO₂ with an average

diameter of 0.3 microns in 90 ethylene glycols, at a rate that provides a temperature drop of 25°. In this case, the time for adding the suspension is 10 minutes. The mixture is heated to 240° and the transesterification is carried out at this temperature. 0.025 trimethyl phosphate and 0.04 Sb2O3 are added to the reaction product and polycondensation is carried out at 2900 / 0.2 mm to obtain a polyester resin with a viscosity $[\eta] = 0.59$, containing 10% TiO2 with an average particle diameter of 0.3 μm .

Low-colored polyesters are obtained by liquid-phase polycondensation of dicarboxylic acids and diols, followed by separation by distillation of the unreacted diol and polycondensation catalyst, filtration, and decolorization.

Polyesters with acetaldehyde content $< 5 \cdot 10^{-4}\%$ for the manufacture of containers are obtained by liquid-phase polycondensation as follows. Initially, the interaction of dicarboxylic acids (terephthalic acid), or their esters and diols (ethylene glycol) or their esters with monocarboxylic acids is carried out. The reaction is carried out in the liquid phase at an elevated temperature and a polyester with a reduced viscosity of 0.7–1.5 dl / g (o-chlorophenol) is obtained. polyester is recrystallized, determining the crystallization temperature within $< 200^\circ$, in 1 min – 4 h, treated with hot water at 60–130° for 5 min – 10 h, dried for 0.5–6 h at 110–150° and heat treated 1–10 h at 160–200°.

Thermoplastic polyester resin is obtained by polycondensation of diols with dicarboxylic acids in the presence of compounds of alkalis or alkaline earth metals (alcoholates) in an amount of < 1 (0.1–0.9) mmol / kg.

Complex copolyesters, are obtained by transesterification of alkyl diesters of naphthalene dicarboxylic acid with an aliphatic diol, polycondensation of the resulting bis (hydroxyalkyl naphthalate) to a degree of polymerization of 20–100, and subsequent polycondensation of the resulting product with phthalic acid (the usual secondary terephthalic copolymer) and the second diol to form a statistical copolyether.

Thermosetting polyester for the manufacture of the polymer composition is obtained by polycondensation of a mixture (mol%) of 90–100 aromatic acids (iso-, tere- and orthophthalic acids) and/or anhydrides and 10–0 non-aromatic polycarboxylic acids (adipic, succinic acid) or anhydrides and (mol%) > 60 2-butyl-2-ethyl-1,3-propanediol, 0–20 neopentyl glycol and 10–20 triols (trimethylolpropane, trimethylolethane) as chain branching agents. As a second component, the compositions contain crosslinking agents (melamine, benzoguanamine, urea formaldehyde, blocked polyisocyanates).

Complex (co) polyesters (polybutylene terephthalate or polyethylene terephthalate) are obtained by polycondensation or transesterification in the presence of a catalyst consisting of a titanium or zirconium compound and a lanthanide or hafnium compound; the catalytic composition may contain phosphates or phosphites of alkali metals.

A description of the interaction of various diols (butanediol, 1,4-bis (methyl) cyclohexanediol, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol and tripropylene glycol) with isocyanate groups is given. Thus, in (Bajpai & Rai, 1998), a method was developed for producing a vinyl ester urethane oligomer by the reaction of (a) a polyester of general formula I where $m = 1-100$; where $n = 2-6$; Y- (CH₂)_n, where $n = 2-4$, or 1,2-phenylene, 1,3-phenylene or 1,4-phenylene, with a diisocyanate (b) selected from the group consisting of toluene diisocyanate, 4,4-

diphenylmethane diisocyanate, tetramethylxylene diisocyanate, isophorone diisocyanate, 4,4-dicyclohexylmethane diisocyanate and n-hexane diisocyanate, or polyisocyanates having two or more functional groups, and with oxymonovinyl ether (c) "where $CR = 0$ ", where R is CH-0 and R "is hydrogen, alkyl groups containing 1–10 carbon atoms; Z – bivalent residue of butanediol, 1,4-bis (methyl) cyclohexanediol, ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol and tripropylene glycol, with a molar ratio of hydroxyl groups of compounds (a) and hydroxyl groups (c) 0.5: 5.0 at a molar ratio of hydroxyl groups of compounds (a) and (c) and isocyanate groups of compound (c) 1: 1, and the remainder of unreacted hydroxyl groups in vinyl ester urethane is less than 1 mol.% of those initially participating in the reaction. The polymer was obtained by curing the vinyl ester urethane oligomer.

Data were obtained on the properties of a differential scanning calorimetry thermogram, infrared spectra, X-ray diffraction patterns, and dependence on elastic moduli and temperature losses for crosslinked and uncrosslinked polyurethanes (PU) based on diphenylmethane diisocyanate, 1,4-butanediol and polyester resin from adipic acid and 1.5–24-diethyl or 3-methyl-pentamethyl diol. It is noted that the introduction of side groups into polyether diol has little effect on the mechanical properties of PU, but noticeably improves their hydrothermal resistance.

Oligoesters containing diethylene glycol fragments are used to obtain hydroperoxides. In (Shugurova et al., 1999), a method was proposed for the synthesis of alpha hydroperoxides by ozonolysis of an oligoester based on diethylene glycol and endic anhydride in the presence of proton donor compounds according to the reaction: $(I) + O_3 \rightarrow (II) \text{ } n = 20-45, G = OR, OCOR$. The kinetics of ozonolysis of oligoester was studied depending on the chemical nature of the proton-donor compound, its concentration, concentration of ozone, solvent, outlet temperature and stability of the resulting oligomeric alpha-hydroperoxides. Compatibility of mixing PET and two types of polyetherethers (PEE) in the melt with varying composition of the components was investigated. The PETs used contain rigid polybutylene terephthalate segments (PBTPS) in large or small amounts. The resulting blends were analyzed using dynamic mechanical analysis, strength tests, and optical microscopy. Both mixtures have good strength properties, which is attributed to the compatibility of the segregated PBTFs domains in PE with PET. Dynamic mechanical analysis data indicate higher compatibility when the PBTPS content in PEE is high than when it is low. Depending on the composition of the blends have a wide range of strength properties: properties of thermoplastics at high content of PBTPS and properties of reinforced elastomers at their low content (Collet-Sabé, 2023; Manakbayeva, 2023; Sheveleva, 2024).

Complex (co) polyesters of diols and terephthalic acid (polybutylene terephthalate or polyethylene terephthalate) are obtained by polycondensation or transesterification in the presence of a catalyst consisting of a titanium or zirconium compound and a lanthanide or hafnium compound; the catalytic composition may contain phosphates or phosphites of alkali metals.

The compositions contain (%) 90–10 modified polyolefin having epoxy, hydroxyl, or carboxyl groups and 10–90 PA or aromatic polyester [polyethylene terephthalate or polybutylene terephthalate]. Crystalline modified polyolefin has a melt index of 0.01–500 g/10 min (230°, 2.16 kg), an elastic modulus of 50–800 MPa and a crystallinity (CR) > 10% and can contain 0.05–30 mol% non-conjugated

diene phenols $\text{CH}_2=\text{CH}[\text{C}(\text{R}_5)(\text{Rir})]_n-\text{CR}_3=\text{CR}_2-\text{R}_1$, where R_1 = alkyl (C1-8), R_2 -5-H alkyl (C1-8) and $n=1-10$, (copolymerization of propylene with 7-methyl-1,6-octadiene or methyl-1,4-hexadiene).

Hydroxy-modified polyolefine is obtained by radical polymerization of crystalline copolymerization of olefin and 0.1–10% (by weight of copolymerization) 2-hydroxymethyl (ethyl) (propyl) (meth) acrylate, epoxy-modified polyolefine – by copolymerization polymerization and 0.1–10% glycidyl ether α , β -unsaturated acids and carboxy-modified PO – by copolymerization polymerization and α , β -unsaturated carboxylic acid (maleic anhydride). PA-6 and PA-66 are used as P polyamides. Example: copolymerization of propylene with 2.7 mol. % 7-methyl-1,6-octadiene melt index 1.7 g/10 min, CR 45%) is mixed with 75 2-hydroxyethyl methacrylates (I) in 5 L of xylene, heated in a nitrogen flow at 110 °, 25 Bz202 is introduced into 500 ml of xylene, heated for 5 h. At 110°, the modified polyolefin is precipitated in acetone, filtered, washed and dried. The grafted copolymerization contains 2% 75 2-hydroxyethyl methacrylate and has a melt index of 1.8 g/10 min. Compositions obtained by mixing (including) 1 modified polyolefin and 1 PA-6 or 1 polybutylene terephthalate has Izod impact strength corresponding to 5.0 and 7.5 kg/cm and the particle size of PA and polybutylene terephthalate 1–2 and 1 μm

Compositions based on unsaturated polyester with improved strength properties contain, as a strengthening additive, a block copolymerization of the ABA structure, where A are blocks with a molecular weight of 100–600 based on saturated alkylene oxides or alkyldiols and dicarboxylic acids and their anhydrides in a mixture with ≥ 50 mol % unsaturated acids and anhydrides. Unsaturated polyester blocks with a glass transition temperature ≤ 00 .

Compositions for products with surface gloss $\leq 20\%$ (at 45° reflection angle) contains 100 polyacetal, 1–50 polyalkylene terephthalate (pour point ≤ 210 °) – a polycondensation product of an acid component containing (mol%) 90–60 terephthalic acid and 10–60 > 1 other acid (isophthalic, naphthalenedicarboxylic or adipic acid), and ≥ 1 diol [1,4-butanediol, (di) ethylene glycol, 1,4-cyclohexanedimethylol] and 1–10 (un) modified. (di) isocyanate or (di) isothiocyanate, their dimer or trimer [4,4'-methylene di (phenylisocyanate), isophorone- (1), 1,5-naphthalene-, 1,6-hexamethylene-, or 2,4 (2,6)-toluene diisocyanate, their di- or trimers. Example: mix 100 PMO, 20 polybutylene terephthalates in which 30 mol % of the acid component is isophthalic acid and 3, 0 trimer. The mixture is extruded, granulated and samples are cast at 180–200°, pressure 65 MPa and mold temperature 80°. The obtained composition and the control polyacetal are well extruded, respectively, the surface of the samples matte and shiny, gloss 7.1 and 77%, tensile strength 64 and 60.5 MPa, elongation 20, 60% and flexural strength 101 and 86 MPa. The composition with a matte and non-shiny surface is used for automotive finishes and optical instruments where reduced light reflection is required (Mele, 2022; Nikulin, 2023; Rawel, 2022).

To improve processing, surface properties of products, compositions are prepared containing (%) 95, -99.99 ethylene polymer obtained with CT of Ziegler, Phillips or metallocene, 0.01–5 thermoplastic polyester with a melting point ≤ 150 °, synthesized from 30–60 a mixture containing 30–70 adipic acid or an ester-forming derivative, 30–70 terephthalic acid or its ester, 0–5 compounds with 3 ester-forming groups, 40–70 dioxy compounds C210, 0– diisocyanate, divinylether, 2.2 – bisoxazoline or mixtures thereof. The components are mixed at 100–150 °. Example: mix 99 copolymerization of ethylene and 10

butene (polydispersity coefficient, melt index 1.8 at 19072.16 kg, density 0.902 g/cm³) and 1 polyester obtained from (kg) 1.82 prepolymer based on butanediol and adipic acid (OH number 56), 1.17 dimethyl terephthalate, 1.7 butanediol in the presence of 4.7 g of titanium tetrabutylate at 180 ° and 230. After 2 hours, 6.54 g of pyromellitic dianhydride is introduced, after another 1 hour 0.4 g of H₃P₀₄ (concentration 50%), 15 g of hexamethylene diisocyanate is introduced at 200°, a polyester is obtained with OH-number 2, molecular weight 98350, melting point. 98°, glass transition temperature –31°. Films are extruded from the composition at a speed of 80–100 kg/h under pressure. 350 kg/cm² without melt rupture, and from PE without polyester under a pressure of 450 kg/cm² at a rate of 30 kg/h, the melt breaks. Vials from the resulting composition have improved gloss and crack resistance (Skafidas & Kalfoglou, 1997).

The composition used, for example, as a polymer component for glass fibers or a binder in the manufacture of molded articles, contains a crystalline polyester, the crystal lattice of which is built from the condensation product of 1 or 2 polyhydric alcohols and an unsaturated polycarboxylic acid, and contains an unsaturated monomer as inclusions. Example: 1725 maleic anhydride, 166 propylene glycol, 1611.2 neopentyl glycol and 0.3 toluene hydroquinone are placed in a reactor. The reaction mass is heated in a stream of N₂ to 190° and after distillation of 220–225 ml of liquid products, 2 ml of piperidine are added. The temperature is reduced to 205° and the reaction is carried out until the viscosity becomes 35 P (at 175°) and the alkaline number 25–28. The resulting polyester (in the form of a melt at 150°) is added to a composition containing 1210 styrene, 056 parabenzoquinone, 0.25 hydroquinone stabilizers at a rate such that the temperature does not exceed 80° (Furukawa et al., 1999). After cooling, the composition is granulated and crushed.

7. Conclusion

Biodegradable polymers and molded packaging are prepared from aqueous dispersions of polyester and aliphatic prepolymers. diisocyanates containing as chain extenders the Na-salt of diaminosulfonate (N- (2- (aminoethyl) -2-aminoethanesulfonic acid (I)) and ethylenediamine. Example: a composition containing 83.4 complex polyester based on adipic acid and a mixture (1, 4:1) ethylene glycol and 1.4 butanediol (molecular weight 2000) and 3 adducts of butanol and a mixture (1: 7.1) of propylene oxide and ethylene oxide: (molecular weight 2240) after degassing in vacuum (120 °, 30 min) treated with 0.1 BZCI and 13.7 hexamethylene diisocyanate for 1 h at 120°. The resulting prepolymer, containing 2.84% NCO-groups, is dissolved at 50° in 300 acetones, a mixture of 4.8 of 50% solutions of I is added, 1.15 ethylenediamine and 20 water, add 230 water, distill off acetone and obtain 337 of a 30% aqueous dispersion The film obtained from the aqueous dispersion decomposes biologically in 8 weeks.

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