Synthesis of Rigid Polyurethane Foams from Oligoester Alcohols Obtained from Dimethyl Terephthalate Production Wastes

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Synopsis

A study was conducted to synthesize oligoester alcohols from dimethyl terephthalate production wastes via transesterification with diethylene glycol and trimethylol propane. The oligoester alcohols obtained are suitable for preparing rigid polyurethane foams. The oligoester alcohols from trimethylol propane possess good physical and mechanical properties. The oxygen indices indicate that the polyurethane foams exhibit improved resistance to combustion due to the increased content of aromatic nuclei in the oligoester alcohols.

INTRODUCTION

The production of dimethyl terephthalate from *p*-xylene via oxidation and subsequent esterification with methanol yields waste products. Various methods for their utilization have been suggested: preparation of plasticizers for rubber articles[1,2]; preparation of unsaturated alkyd resin[3]; improving the water resistance of asphalt and concrete coatings[4]; binding additives for road pavements[5–9]; substitutes for asphalt, rosin, and masut[10]; fillers for common and typographic dyes[11,12]; resins used in the furniture industry[13]; pigments for textile fibers and film-forming polymers.[14]

The aim of the present work is the preparation of oligoester alcohols for the synthesis of rigid polyurethane foams; the former are obtained from waste products via transesterification with diols and triols.

EXPERIMENTAL

Starting materials: residue from distillation of crude dimethyl terephthalate (residue 1); residue from the multistage distillation of the filtrate from the recrystallization of dimethyl terephthalate (residue 3); residue from the recrystallization of the fraction dimethyl terephthalate/dimethyl isophthalate/isophthalic fraction obtained in the production of dimethyl terephthalate; diethylene glycol (commercial product); trimethylol propane (commercial product).

Transesterification of the Residue from the Distillation of Crude Dimethyl Terephthalate (Residue 1) with Diethylene Glycol

Residue 1 (100 g) (10.3% methoxycarbonyl groups, acidic value 2.4 mg KOH/g and diethylene glycol (150 g, 1.4 mol) with zinc acetate or tetrabutyl titanate as

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catalyst (0.1%) are placed in a four-necked flask provided with a stirrer, thermometer, condensor and nitrogen inlet. The reaction is conducted till 80% completion at 190°C and the temperature is then brought to 235°C. The temperature is allowed to drop to 135°C after distillation ceases and the unreacted diethylene glycol is removed under reduced pressure (1 mm). The product is a very viscous liquid; its characteristics are listed in Table III: acid and hydroxyl values, diethylene glycol content, methxycarbonyl groups, moisture, average molecular mass, and viscosity.

Under the same conditions, the transesterification with diethylene glycol of residue 3 and the isophthalic fraction were also conducted. The characteristics of the products are given (Table III).

Transesterification with Diethylene Glycol and Trimethylol Propane of the Residue from the Distillation of Crude Dimethyl Terephthalate (Residue 1)

In a four-necked flask provided with a stirrer, thermometer, condensor, and a nitrogen inlet are placed trimethylol propane (53.6 g, 0.40 mol), diethylene glycol (298, 2.8 mol), and tetrabutyl titanate (0.65 g). The mixture is heated to 130°C and residue 1 (221.6 g) is added, preliminarily brought to 80°C. At first the reaction is conducted at 190°C and, after distillation ceases, at 235°C and acid value of 1–1.5 mg KOH/g. The temperature is then allowed to decrease to 130°C and the unreacted diethylene glycol and trimethylol propane is removed under reduced pressure (1 mm). The product is a very viscous liquid characterized by acid and hydroxyl values, methoxycarbonyl group content, presence of diethylene glycol, trimethylol propane, moisture, average molecular mass, and viscosity (Table IV).

Under the same conditions the transesterification with diethylene glycol and trimethylol propane of residue 3 were also conducted. The characteristics of the products are given (Table IV).

Synthesis of Oligoester Alcohols from Residue 1, Trimethylol Propane, Diethylene Glycol at a 1:2:1 Mol Ratio ($OH/COOCH_3$ Ratio of 4:1)

The molecular mass of the residues is taken to equal dimethyl terephthalate. The synthesis is carried out as in the previous subsection, however, without removing the unreacted diethylene glycol and trimethylol propane at the end of the synthesis. The product is characterized by acid and hydroxyl values, content of methoxycarbonyl groups, diethylene glycol, trimethylol propane, moisture, and viscosity (Table V).

Preparation of Components A and B

Component A of the following composition is prepared on the basis of the synthesized oligoester alcohols: oligoester alcohol—100 weight fractions: tris(β-chloroethyl)phosphate—10 weight fractions; silicon L 540—1 weight fraction; stannous octanoate—0.08 weight fraction; amine catalyst—1.2 weight fraction; water—0.2 weight fraction; polyethylene glycol (mol mass 200, hydroxyl value 372)—20 weight fractions; ethylene glycol—6 weight fractions; freon—11–22 weight fractions.

Component B = polymeric diphenylmethanediisocyanate. For the oligoester alcohol on the basis of: residue 1—188 weight fractions; residue 3—174 weight fractions; isophthalic fraction—183 weight fractions.

The rigid polyurethane foams were obtained by mixing in a 250-mL beaker component A and component B, stirring with a propeller stirrer (1350 rev/min), and pouring out on the polyethylene sheet or into the form. During the synthesis the starting time, gellation time, and time of the end of the rise (by the standard of Schwarzheide-DDR) were followed (Table VI).

Characterization of the Oligoester Alcohols and Polyurethanes

Acid value = titration of sample with potassium hydroxide in the presence of phenolphthalein. The hydroxyl value is determined by the acetylation method; methoxycarbonyl groups are determined by gas chromatography; moisture is determined by the Fischer method; diethylene glycol content is determined by gas-chromatography; trimethylol propane is determined by gas chromatography. The average molecular mass is determined by the vapor pressure method; viscosity is determined by the rheo-test Brookfield, model LVT; the characteristics of the polyurethane foams were determined by standard procedures.

RESULTS AND DISCUSSION

Residue 1—the residue from the distillation of crude dimethyl terephthalate—, residue 3—the residue from the multistage distillation of the filtrates of recrystallizing dimethyl terephthalate—and the residue lastly from recrystallizing the dimethyl terephthalate/dimethyl isophthalate (isophthalic fraction) fraction have the composition listed in Table I.[15]

The presence of the products listed in Table I in the wastes from the production of dimethyl terephthalate has been determined by gas chromatography.

The organic compounds present in the three residues are either methyl esters

TABLE I
Composition of Dimethyl Terephthalate Production Wastes

Composition	Residue 1 (%)	Residue 3 (%)	Isophthalic fraction (%)
Di- and trimethyl esters of diphenyltricarboxylic acids	Up to 10	5–10	—
Dimethyl esters of diphenyldicarboxylic acids	20–25	10–15	—
Dimethyl esters of 3,4-benzocoumaric acid	10–15	5–10	—
Monomethyl terephthalate	2–3	3	—
Dimethyl terephthalate	8–10	10–20	20—25
Dimethyl isophthalate	—	15	45–50
Dimethyl orthophthalate	3–4	—	9–14
Methyl ester of *p*-toluylic acid	1–2	0.5–2	3
p-Toluylic acid	1–2	0.5–2	3
Methyl benzoate	0.2–0.5	Traces	0.5
Benzoic acid	8	5–10	—
Terephthalic aldehyde	—	—	—
Resinous substances	Up to 20	10–15	3
Unidentified products	2	—	3

TABLE II
Characteristics of Waste Products from Production of Dimethyl Terephthalate

Characteristics of waste products	Residue 1	Residue 3	Isophthalic fraction
Acid value (mg KOH/g)	2.4	6.8	1.8
Content of OCH_3 groups (%)	10.30	14.79	32.98
Moisture content (%)	0.01	0.01	0.01

of aromatic carboxylic acids or pure carboxylic acids which can participate in transesterification or esterification reactions with hydroxyl-group containing compounds. Some of the aromatic carboxylic acids in residues 1 and 3 possess more than two functional groups, thus permitting the synthesis of oligoester alcohols with an increased content of hydroxylic groups. Since the extent of the transesterification and esterification processes is estimated by the content of methoxy groups and the acid value respectively, these two characteristics of the waste products were determined prior to carrying out the reaction (Table II).

The waste products were subjected to transesterification and esterification with the view to establishing whether the methoxy and carboxylic groups can take part in these reactions. Residues 1 and 3 and the isophthalic fraction were treated with diethylene glycol separately. The obtained values for methoxycarbonyl group content and acid values for the waste products treated with diethylene glycol (Table III) indicate that in the transesterification process almost all methoxycarbonyl groups take part, while the carboxylic groups participate to a lesser degree. The hydroxyl group content can also provide information on the degree of the transesterification reaction and oligomerization. Even though, the waste products lack a strictly defined molecular mass and there is no simple relationship between hydroxyl values and molecular mass, the hydroxyl value of the isophthalic fraction is lowest (48.7), while the determined molecular mass is highest (994). Taking into consideration the composition of the isophthalic fraction (Table I), its hydroxylic value is lowest in comparison with residues 1 and 3, which contain up to 10% trifunctional compounds. The dynamic viscosity is very high.

The methoxycarbonyl and carboxylic groups participate in the transesterification and esterification reactions under the conditions of synthesis, i.e., oligoester alcohols from the dimethyl terephthalate production waste products can be prepared. A reduction in their viscosity and increase in hydroxyl group content is, however, necessary.

TABLE III
Characteristics of Oligoester Alcohols Obtained on Treating Waste Products with Diethylene Glycol

Characteristics of oligoester alcohols	Residue 1	Residue 3	Isophthalic fraction
Acid value (mg KOH/g)	1.83	1.67	1.26
Hydroxyl value (mg KOH/g)	159	262	48.7
Methoxycarbonyl groups (%)	0.33	Traces	2.24
Moisture (%)	0.15	0.14	0.19
Diethylene glycol content (%)	Traces	Traces	Traces
Average molecular mass	475	368	994
Viscosity, 25°C (cps)	75,000	68,000	—

TABLE IV
Characteristics of Oligoester Alcohols Obtained on Treating Waste Products with Diethylene Glycol and Trimethylol Propane

Characteristics of oligoester alcohols	Residue 1	Residue 3	Isophthalic fraction
Acid value (mg KOH/g)	2.2	4.4	2.37
Hydroxyl value (mg KOH/g)	251	326	282
Methoxycarbonyl groups (%)	0.50	0.68	5.8
Moisture (%)	0.18	0.16	0.15
Diethylene glycol content (%)	Traces	Traces	Traces
Trimethylol propane content (%)	Traces	Traces	Traces
Average molecular mass	366	350	329
Viscosity (cps) 25°C	44,000	32,230	20,280
75°C	860	684	380

The waste products were therefore transesterified and esterified with diethylene glycol and trimethylol propane. The hydroxyl values increased and approached those of the polyols employed in the synthesis of polyurethane foams (Table IV). The dynamic viscosity of the prepared oligoester alcohols is two times lower (at 25°C) than that of the oligoesters synthesized with diethylene glycol; it is, however, still unsuitable for preparing polyurethane foams.

The viscosity of oligoester alcohols[16] decreases upon the introduction of low-molecular glycols and triols into their molecules in amounts of up to 20% and 22%, respectively. The waste products were esterified and transesterified with diethylene glycol and trimethylol propane at a 1:1:2 mole ratio (OH/CH_3OOC and $COOH$ = 4:1). The oligoester alcohols contain, at this initial ingredients' ratio, free glycols (diethylene glycol) from 9% to 18% and triols (trimethylol propane) between 10% and 22%. The presence of free diethylene glycol and trimethylol propane results in a marked decrease in the viscosity and an increase in the hydroxyl value (Table V) of the oligoester alcohols.

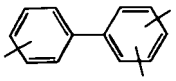
The oligoester alcohols prepared in this manner satisfy the requirements for synthesizing polyurethane foams; the acid values are in the limits of 0.9–1.3; the hydroxyl values are between 425 and 480; the viscosity at 25°C is close to that of the polyols employed in the synthesis of polyurethane foams.

TABLE V
Characteristics of Oligoester Alcohols Obtained by Treating Waste Products with Diethylene Glycol and Trimethylol Propane at $OH/COOCH_3$ and $COOH$ at a Ratio of 4:1

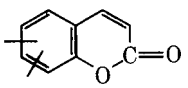
Characteristics of oligoester alcohols	Residue 1	Residue 3	Isophthalic fraction
Acid value (mg KOH/g)	1.2	1.3	0.9
Hydroxyl value (mg KOH/g)	480	425	460
Methoxycarbonyl groups (%)	1.05	1.1	1.2
Moisture (%)	0.12	0.14	0.10
Diethylene glycol content (%)	12	18	9.3
Trimethylol propane content (%)	16	10	22.1
Viscosity, 25°C (cps)	8129	10,384	9285

The following aromatic moieties are present in the prepared oligoester alcohols on the basis of residues 1 and 3:

(a) substituted biphenyls:



(b) substituted coumarinic acid:



(c) substituted aromatic rings:

The oligoester alcohols were used for preparing component A and in the synthesis of rigid polyurethane foams. The characteristics of the polyurethane systems are listed in Table VI.

The kinetic parameters of the polyurethane systems based on oligoester alcohols from dimethyl terephthalate production waste products are comparable to the ones of the SH4050/1/17/system.[17]

These polyurethane systems were used for making rigid polyurethane foams (Table VII). The determined characteristics—density, resistance to pressure and bending, and heat transfer coefficient—are the same as the ones of rigid polyurethane foams based on SH 4050/1 and PUF-317. A significant difference is observed in the resistance to combustion. The determined oxygen index (Table VII) indicates that the rigid polyurethane foams based on oligoester alcohols from dimethyl terephthalate production wastes exhibit an improved resistance to combustion compared to the ones prepared on the basis of SH 4050/1

TABLE VI
Characteristics of Polyurethane Foam Systems

Characteristics of polyurethanes systems	System based on oligoester alcohol from residue 1	System based on oligoester alcohol from residue 3	System based on oligoester alcohol from isophthalic fraction
Viscosity at 20°C cps			
Component A[a]	750	700	650
Component B[b]	500	500	500
Hydroxyl value of component A	726	672	706
Ratio of A:B	1:1.1	1:1.1	1:1.1
Foaming coefficient[c]	108	108	108
Technological time intervals at 20°C (s)			
Start	25	21	22
Gel formation	65	55	64
End of rise	110	100	108

[a] Hydroxyl-group-containing component.

[b] Isocyanate component.

[c] Expressed in percentage with respect to the taken amount of isocyanate vs. the stoichiometrically necessary.

TABLE VII
Characteristics of Rigid Polyurethane Foams

Characteristics of polyurethanes	PUF[a] on basis of oligoester alcohols from residue 1		PUF on basis of oligoester alcohols from residue 3		PUF on the basis of oligoester alcohol from isophthalic		PUF on the basis of system SH 4050/1 (GDR)		PUF 317 (USSR)	
	Free foaming	Foaming in a mold[b]	Free foaming	Foaming in a mold	Free foaming	Foaming in a mold	Free foaming	Foaming in a mold	Free foaming	Foaming in a mold
Density (kg/m^3)	39.8	77.4	37.0	77.0	39.0	66.6	40.0	62.0	40.0	60.0
Resistence to pressure (kg/cm^2)	2.2	5.3	2.2	5.3	3.0	6.1	2.3	25.4	2.1	24.2
Resistence to strain (kg/cm^2)	4.1	10.6	3.55	11.5	4.35	11.6	3.9	—	4.2	9.8
Open cells (%)	1.7	7.7	8.1	6.9	7.3	8.5	—	—	—	—
Closed cells (%)	89.0	85.7	88.9	87.7	89.6	85.6	86.0	88.0	—	—
Water absorption after 7 days (cm^3/m^2)	296	165	198	167	184	125	—	—	—	—
Coefficient of heat transfer (kcal/m·h·°C)	0.023	—	0.023	—	0.022	—	0.024	—	0.025	—
Oxygen index (% O_2)	24.3	25.0	24.8	25.9	23.8	24.6	21.0	—	21.0	22.5
Fire tube										
Ignition (s)	10.0	50.0	10.0	15.0	12.5	20.0	2.5	—	—	—
Independent combustion (s)	20.0	15.0	10.0	15.0	12.5	50.0	Burns	—	—	—
Weight loss (%)	49.0	43.0	56.0	36.0	67.0	47.0	100	—	80.0	—

[a] PUF–polyurethane foam.

[b] Form-filling coefficient; for PUF 317 = 1.7; for PUF on the basis of oligoester alcohols from waste products = 1,3.

and PUF-317. These results are also corroborated by data obtained from fire tube tests. The polyurethanes based on oligoester alcohols from waste products ignite after a fourfold longer interval of time than the polyurethanes based on SH 4050/1 and PUF-317. They burn, while the ones shown self-extinguish. The two systems taken for comparison suffer weight losses of 100% and 80%, respectively, while the polyurethane foams based on the waste products oligoester alcohols exhibit weight losses of 49%, 56%, and 67%. The better resistance to combustion of the latter is due to the increased content of aromatic compounds in the oligoester alcohols. The oxygen indexes of the polyurethane foams based on residue 1 and 3 are higher than the oxygen index of the foam based on the isophthalic fraction. This difference is again caused by the higher presence of aromatic compounds in residues 1 and 3 than in the isophthalic fraction.

The waste products from the production of dimethyl terephthalate can be employed in the synthesis of oligoester alcohols, which find application as a hydroxyl-group-containing component in the preparation of rigid polyurethane foams.

The polyurethanes obtained from these oligoester alcohols can be used as a construction material in building and in the refrigeration industry.

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