Synthesis and Characterization of Novel Polyurethanes Based on Vegetable Oils Amide and Ester Polyols

Vladimir YAKUSHIN [*], **Uldis STIRNA, Oskars BIKOVENS, Maria MISANE, Irina SEVASTYANOVA, Dzintra VILSONE**

Latvian State Institute of Wood Chemistry, Dzerbenes 27, LV-1006, Riga, Latvia

Amide and ester type polyols were synthesized from rapeseed, sunflower and castor oils, and two types of ethanolamine (diethanolamine and triethanolamine) at different molar ratio. Poly(urethane amides) and polyester urethanes based on the synthesized polyols were prepared. The effect of the chemical structure of the obtained polyurethanes on density, glass transition temperature, thermal stability and mechanical properties was investigated. The influence of the content of OH groups in the synthesized polyols on the specified characteristics was estimated. It has been found that poly(urethane amides) have better mechanical characteristics, but their thermal stability is lower than that of polyester urethanes. The chemical structure of the synthesized polyols and polyurethanes is qualitatively confirmed by IR-spectroscopy data.
Keywords: poly(urethane amide), polyester urethane, vegetable oils, properties.

1. INTRODUCTION

Vegetable oils, being fatty acids glycerides, are widely used in the synthesis of different esters, which are used in producing various polymeric materials, including polyurethanes [1 – 2]. One of the traditional methods for obtaining reactive esters is transesterification of vegetable oils with polyhydric alcohols (glycerol, trimethylolpropane or pentaerythrite). Transesterification is carried out at such stoichiometric ratios that ensure obtaining of monoesters of those alcohols. Monoesters have free hydroxyl groups and form polyurethanes upon the interaction with isocyanates. The properties of different polyurethanes based on fatty acids esters, in comparison to those of other polyurethanes, are considered in numerous studies [2 – 4].

As a rule, the transesterification of vegetable oils with polyhydric alcohols is carried out at a relatively high temperature (240 °C – 260 °C). As a result of transesterification, an equilibrium mixture of monoesters with di- and triglycerides is always formed. The drawback of the given process is the tendency of some diglycerides of fatty acids to crystallize at room temperature.

If triethanolamine is used instead of the mentioned polyhydric alcohols, the transesterification process can be realized at a lower temperature (180 °C). In this synthesis, esters of fatty acids and triethanolamine are formed, and in these polyols, glycerides generally do not crystallize at room temperature. Similar ester polyols have found rather wide application in producing polyurethane foams [5].

Some of researchers have recently started using diethanolamine instead of triethanolamine in the polyol synthesis. As a result, diethanolamides of some oils (flax, nahar, and palm) have been synthesized, on the basis of which poly(urethane amides) with good characteristics have been obtained [6 – 8]. However, there is still scarce information about the poly(urethane amides) based on other oils that are more accessible to European manufacturers, and they are assigned mainly to polyurethane foams [9, 10].

The aim of the present study was to evaluate the effect of the synthesis parameters of sunflower, rapeseed and castor oil diethanolamides on the properties of monolithic polyurethanes. In the evaluation, the mechanical, physical and thermal properties of the poly(urethane amides) based on the mentioned oils were compared among themselves, and with those of the polyurethanes based on conventional esters of the same oils and triethanolamine.

2. EXPERIMENTAL

2.1. Materials

Sunflower crude oil grade 2 (GOST 1129-93) was supplied by the "Volgodonsk oil factory" Ltd. (Volgodonsk, Russia). Rapeseed oil grade 1 was supplied by the oil factory "Iecavnieks" Ltd. (Iecava, Latvia) and Castor oil First Special Grade (FSG) was obtained from Alberdingk Boley GmbH (Germany). Saponification value of oils was 190, 187 and 180 mg KOH/g, respectively. OH number of castor oil was 164 mg KOH/g. Acid value of all oils did not exceed 2.0 mg KOH/g

Diethanolamine [CAS 111-42-2] (min. 99 %) was supplied by Huntsman Holland BV (The Netherlands), but triethanolamine pure (min. 99.5 %) by BASF SE (Germany). Toluene pure (≥99.7 %), was obtained from Sigma-Aldrich Chemie GmbH (Germany).

Polyisocyanate Voratec SD 100 (NCO content 31.5 %, functionality 2.7) was supplied by Dow Deutschland GmbH (Germany).

2.2. Synthesis of polyols

Polyols' syntheses were carried out according to the methodology, similar to that of the synthesis of diethanolamides and esters of tall oil, described in detail in [11]. The only distinction was that, to ensure the transesterification of oils, the catalyst Zinc acetate

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[*] Corresponding author. Tel.: +371-2659899, fax: +371-67550635.
E-mail address: *yakushin@edi.lv*. (V. Yakushin)

dehydrate $Zn(CH_3COO)_2 \cdot H_2O$ in an amount of 0.15 % of the polyol mass was used in both cases. The molar ratio of oil (triglyceride) to ethanolamine 1 : 2.0, 1 : 2.5 and 1 : 3.0 were used. Duration of the synthesis of diethanolamides (amide type polyols) at $(143 \pm 3)\,°C$ was about 40 min. Duration of oils' esterification with triethanolamine (synthesis of ester type polyols) at $(173 \pm 3)\,°C$ was about 100 min. The ending of both the syntheses was controlled by the solubility of the polyol in ethanol at a ratio of 1 : 1.

OH number, water content and the dynamic viscosity of the synthesized polyols at 25 °C were determined according to the standards ISO 14900:2001, ISO 14897:2002 and ISO 12058:1997, respectively.

2.3. Preparation and characterization of polyurethanes

As in the previous study [11], based on the synthesized polyols and polyisocyanate, polyurethanes in the form of free films (ASTM D 4708-99) were prepared. Isocyanate and polyol components were mixed in the molar ratio NCO/OH = 1.1. The films were hardened at a temperature of $(21 \pm 2)\,°C$ during 7 days. The thickness of most of the films was 150 μm – 200 μm.

Chemical structure of the obtained polyols and polyurethanes was identified by IR-spectroscopy using a Spectrum One FT-IR spectrometer with an ATR polarization accessory (of PerkinElmer Inc.).

Polyurethanes' density was determined by a Gas Pycnometer AccuPyc 1340 (Micrometrics Instrument Corporation).

Tensile tests of polyurethane films were performed on a universal testing machine Zwick/Roell DO–FB0.5TS (500 N) according to the requirements of the standard ASTM D 882-10. For each type of polyurethanes, at least 6 strips $100\ mm \times 10\ mm$ were tested. Coefficients of variation for modulus of elasticity, tensile strength and elongation did not exceed 5, 8 and 15 %, respectively.

Thermal stability and glass transition temperature of polyurethanes were determined using TGA/SDTA 851^e and DSC 851^e METTLER TOLEDO, respectively. TGA test was carried out in the airflow of 20 cm^3/min. DSC test was performed in a nitrogen atmosphere.

Details for all listed tests of polyurethanes and polyols are described in [11].

3. RESULTS AND DISCUSSION

3.1. Properties of polyols

Theoretically, at a molar ratio of 2.0 in the synthesis of amide polyols, two molecules of monoamide (I) and one molecule of monoglyceride (II) of fatty acids must be formed, the general structure of which is shown in Fig. 1. In the synthesis of ester polyols, instead of monoamide, an equivalent amount of triethanolamine and fatty acids monoester of the general structure (III) must be formed (Fig. 1). If castor oil is used in the synthesis, then in the presented structural formula, in most cases, the ricinoleic acid residue of the total formula $-C_{10}H_{18}CH(OH)C_6H_{13}$ will act as R_1.

At a higher molar ratio, besides monoamides (monoesters), the corresponding amount of moles of free

trifunctional glycerol must be still formed. Correspondingly, varying the molar ratio from 2.0 to 3.0, both the average functionality of the polyol and the content of OH groups therein must vary.
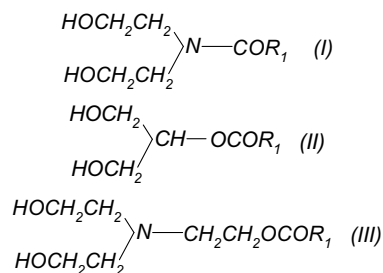

Fig. 1. Chemical structure of the synthesized polyols, where R_1 – residue of saturated and unsaturated fatty (C_{16} – C_{24}) or ricinoleic acids and R_2 – residue of aromatic diisocyanate

Actually, an equilibrium mixture of mono-, di- and triesters as well as glycerol and ethanolamine is always present in all synthesized polyols, which is extremely difficult to characterize. Correspondingly, it is rather difficult to establish also the actual average functionality of polyols. Therefore, all synthesized polyols were characterized by another integral index, namely, total content of OH groups. Proportionally to the content of OH groups in polyols, both the content of urethane groups and average degree of crosslinking of the polyurethanes must change.

Table 1. Characteristics of polyols

Oil grade	Sunflower	Rapeseed	Castor
Vegetable oil diethanolamides			
OH number, mg KOH/g	297–372	297–374	404–472
Water, %	0.03–0.09	0.03–0.10	0.06–0.08
Viscosity at 25 °C, mPa·s	157–213	138–156	513–751
Esters of vegetable oil and triethanolamine			
OH number, mg KOH/g	300–395	312–385	420–512
Water, %	0.06–0.18	0.05–0.18	0.06–0.20
Viscosity at 25 °C, mPa·s	477–695	605–826	1700–2500

The ranges of the change in the total content of the OH groups of the synthesized polyols, in parallel with other characteristics, are given in Table 1. As follows from the listed data, the OH number of all polyols varied within wider ranges than those for the above-mentioned average functionality of polyols. Polyols based on sunflower and rapeseed oil, obtained under equal conditions of synthesis, differed little from each other in terms of the OH number. The OH number of the polyols based on castor oil was much higher owing to the presence of OH groups in the residues of ricinoleic acid, which made up about 90 % from the total amount of fatty and hydroxyl acids in the initial castor oil.

The viscosity of amide polyols exceeded several times that of ester polyols. The high viscosity of amide polyols, obtained at a maximum molar ratio, considerably hampered the distillation of water at the final stage of synthesis. Therefore, the content of water therein was high enough (0.18 % – 0.20 %). In all other polyols, the content of water did not exceed 0.1 %.

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3.2. Structure of polyols and polyurethanes

The difference in the chemical structure of the synthesized amide and ester polyols was qualitatively confirmed by IR-spectroscopy data. It should be mentioned that the spectra of the polyols of the same type and the polyurethanes based on different oils practically did not differ from each other in terms of the location of the characteristic absorption bands. In its turn, some difference in the intensity of particular absorption bands was proportional to the content of OH groups in the synthesized polyol. Therefore, as an example, Figs. 2 and 3 show spectra of amide and ester polyols and their corresponding polyurethanes based on only one oil, namely, castor oil. In this case, the content of OH groups therein was the highest.

All polyols had a wide absorption band, assigned to the valence vibrations of OH groups in the region $(3340–3370)$ cm^{-1}, like polyols in [11]. The shift of the given absorption band to the low-frequency region for amide polyols in comparison with ester polyols at the same absorption band was negligible.

The main distinction of the polyol spectra (Fig. 2) was that all amide polyols had an absorption band at 1620 cm^{-1}, typical for amide [12]. All ester polyols had an absorption band at 1736 cm^{-1}, typical for ester carbonyl. Amide polyols also had an absorption band at 1738 cm^{-1}, although with a lower intensity. The presence of this absorption band is explained by the presence of both some amount of diethanolamine ester as a by-product of the reaction [13] and the corresponding amount of monoglycerides in the polyol. However, the intensity of the absorption band at 1620 cm^{-1} in amide polyols was much higher.

The spectra of the amide type polyols also had not so intensive, but clear enough absorption band at 1365 cm^{-1}, assigned to C–N stretching [14]. Still another absorption band, connected with C–N stretching, was observed in the spectra of amide polyols at 1420 cm^{-1} beside the absorption band at 1465 cm^{-1} (–CH$_2$– bending), common for both types of polyols [12].

The spectra of all ester polyols differed from those of amide polyols by the presence of absorption bands at 1278, 1242 and 1165 cm^{-1}, typical for the stretching vibrations of the C–O bond in esters [12]. The intensity of 1165 cm^{-1} was much higher than those of the other absorption bands.

In contrast to the polyol spectra, the spectra of poly(urethane amides) and polyester urethanes did not differ so greatly from each other in detail. The spectra of the polyurethanes of both types had amide I $(1705$ cm$^{-1}–1709$ cm$^{-1})$, amide II $(1510$ cm$^{-1}–1515$ cm$^{-1})$ and amide III $(1218$ cm$^{-1})$ bands [15], differing for various polyurethanes only in terms of intensity.

The main distinctions between poly(urethane amides) and polyester urethanes were observed in two zones of the spectra. In the high-frequency zone of the spectrum, all polyester urethanes had an absorption band, assigned to hydrogen-bonded –NH groups at 3319 cm^{-1}. At the same time, the spectra of poly(urethane amides) had a similar absorption band approximately at 3293 cm^{-1}. The value of the shift to the low-frequency region, testifying a more intensive intermolecular interaction [26] in poly(urethane amide), slightly increased with increasing content of OH groups in polyols.
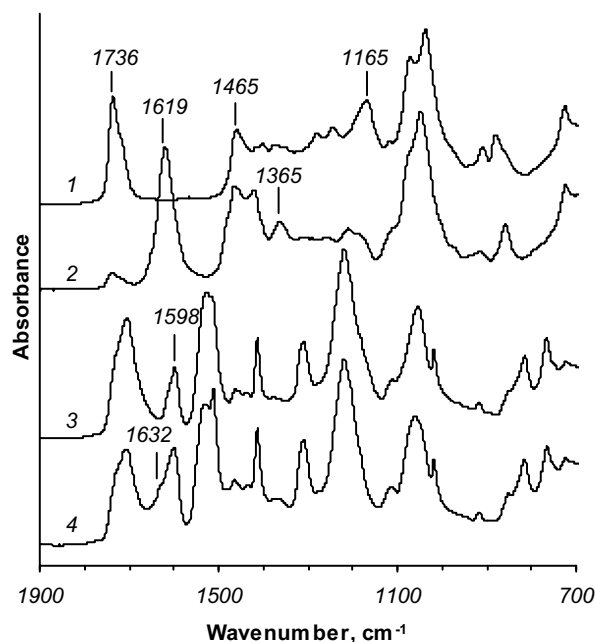
Fig. 2. IR-spectra of polyols (1, 2) and polyurethanes (3, 4), based on castor oil esters (1, 3) and diethanolamides (2, 4)
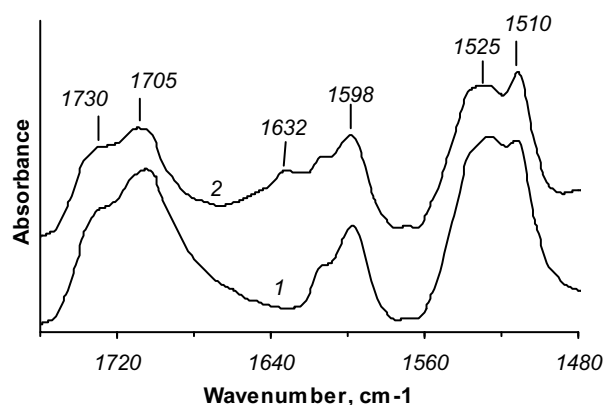
Fig. 3. Deconvoluted IR-spectra of polyester urethane (1) and poly(urethane amide) (2)

Still another essential distinction was observed in the middle part of the spectrum (Fig. 2). All poly(urethane amides) had an absorption band at 1632 cm^{-1} of amide carbonyl [16]. This absorption band neighboured with the absorption band 1598 cm^{-1} common for both types of polyols, assigned to the C=C stretching of isocyanate aromatic rings. These absorption bands are more evident on the deconvoluted spectra shown in Fig. 3. The use of deconvolution also allowed finding overlapped absorption bands of free and H-bonded carbonyls at 1730 cm^{-1} and 1705 cm^{-1}, respectively, and the overlapped absorption bands of amide II (1525 cm^{-1}) and aromatic skeletal vibrations (1510 cm^{-1}). The intensity of the mentioned absorption bands in the spectra of similar polyurethanes slightly increased with increasing content of OH groups in the synthesized polyols, because, as a result, the content of urethane groups in polyurethanes also increased proportionally.

Thus, IR-spectroscopy data confirmed not only the qualitative distinction of the synthesized polyols and

polyurethanes obtained on their basis, but also indicated a strong intermolecular interaction in poly(urethane amides), including that at the expense of hydrogen bonds. Another important distinction is that fatty acids' residues, forming long dangling (side) chains in poly(urethane amides), are linked directly to the rigid amide group. In polyester urethanes, the ester group with the residue of fatty acid is linked to the nitrogen atom via a thermodynamically flexible short ethylene chain $-(CH_2)_2-$. These structural peculiarities have been clearly demonstrated (Fig. 1) in the previous study [11].

3.3. Properties of polyurethanes

The performed studies revealed the effect of all the listed peculiarities of the chemical structure on the physical and mechanical properties of poly(urethane amides) and polyester urethanes. The density of polyurethanes of both types increased with increasing content of OH groups in the synthesized polyols and the corresponding increase in the content of urethane groups in polyurethanes.

If density in polyurethanes based on rapeseed (R) and sunflower (S) oil increased practically linearly, then in polyurethanes based on castor oil (C), the growth in density was slowed down with increasing content of OH groups in the polyol (Fig. 4). Obviously, the formation of a denser packing of the crosslinked polymer at a high content of hydroxyl groups is hampered.
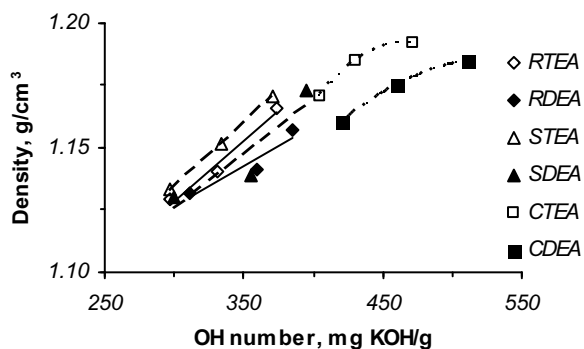

Fig. 4. Density of polyurethanes versus the content of OH groups in polyols

Another important point is that the density of polyester urethanes based on all three oils (RTEA, STEA and CTEA) is higher than that of the corresponding poly(urethane amides) (RDEA, SDEA and CDEA). In this case, obviously, the high mobility of the side chains of polyester urethanes favoured the denser packing of the structural elements of the crosslinked polymer. The density of both types of polyurethanes based on sunflower oil was slightly higher than that of the corresponding polyurethanes based on rapeseed oil.

It was just on the contrary for glass transition temperature (T_g). For all poly(urethane amides), T_g was higher than that for the corresponding polyester urethanes (Fig. 5). In this case, the main factor was the presence of a stronger intermolecular interaction in poly(urethane amides), which was confirmed, in particular, by a shift in the absorption band of hydrogen-bonded –NH groups in IR spectra. T_g for all polyurethanes increased moderately with increasing OH groups in polyols. T_g for polyurethanes based on sunflower oil polyols was somewhat lower than

that for the corresponding polyurethanes based on rapeseed oil. Still lower was the T_g of the polyurethanes based on castor oil polyols despite the highest content of OH groups in those polyols. The latter can be explained by a more complex structure of crosslinked polyurethanes based on castor oil. In this case, not only hydroxyls of amides and esters, but also those of ricinoleic acid residues in side chains participated in the formation of an urethane network. Correspondingly, also the main polyurethane chain was formed not only by rigid urethane-amide fragments [11], but also the hydrocarbon chains $-C_{10}H_{18}-$ of the ricinoleic acid molecule fragment.
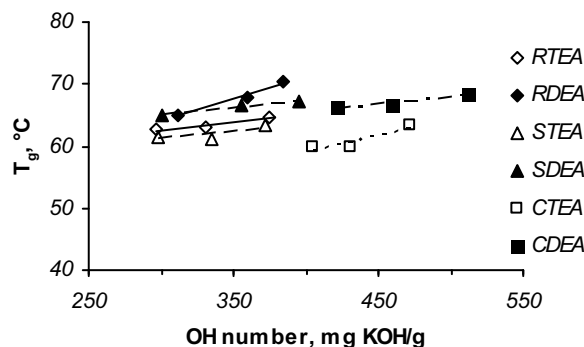

Fig. 5. T_g of polyurethanes versus the content of OH groups in polyols

Modulus of elasticity of polyurethanes based on rapeseed and sunflower oil increased practically linearly with increasing content of OH groups in the synthesized polyols (Fig. 6). In the polyurethanes based on castor oil, the growth in modulus of elasticity, as well as density, was slowed down with increasing content of OH groups in the polyol. As also the glass transition temperature, modulus of elasticity for all poly(urethane amides) was higher than that of the corresponding polyester urethanes. However, the difference in moduli of elasticity was more considerable. The greatest modulus of elasticity was in poly(urethane amides) based on castor oil with the maximum content of OH groups in the polyol (1.75 GPa). Modulus of elasticity for poly(urethane amides) and polyester urethanes based on sunflower oil was somewhat higher than that for the corresponding polyurethanes based on rapeseed oil.
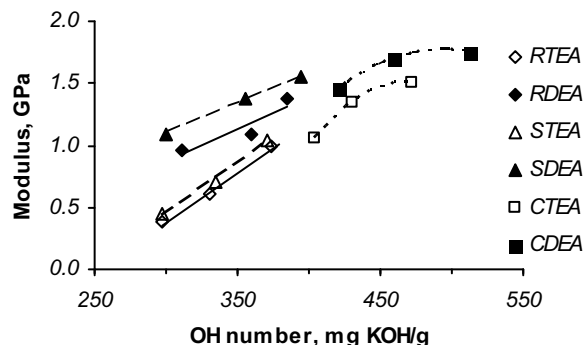

Fig. 6. Modulus of elasticity of polyurethanes versus the content of OH groups in polyols

Tensile strength of polyurethanes based on rapeseed and sunflower oil, as well as modulus of elasticity, increased practically linearly with increasing content of OH groups in the synthesized polyols (Fig. 7). Tensile

strength of poly(urethane amides) based on castor oil reached its maximum (56.7 MPa) at the content of hydroxyl groups in the polyol on the level of (460 – 470) mg KOH/g. With the further increase in the content of hydroxyl groups in the polyol, elongation at break of poly(urethane amides) decreased and strength somewhat decreased. Owing to the stronger intermolecular interaction, the tensile strength of poly(urethane amides) was greater approximately 1.5 times than that of the corresponding polyester urethanes. The difference in the tensile strength of polyurethanes based on sunflower and rapeseed oil was no longer so obvious.
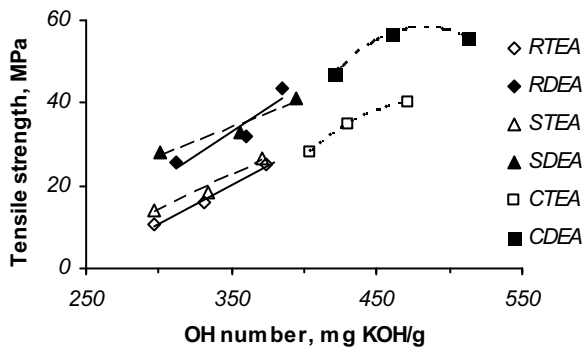

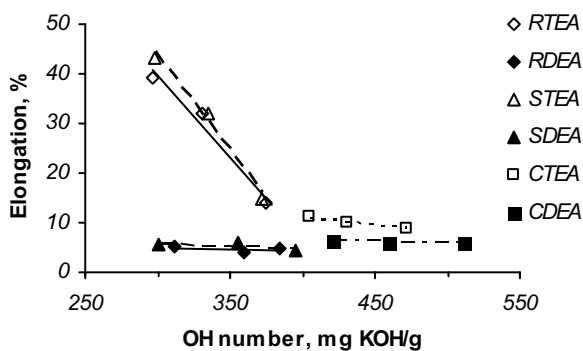**Fig. 7.** Tensile strength of polyurethanes versus the content of OH groups in polyols

Fig. 8. Elongation at break of polyurethanes versus the content of OH groups in polyols

Elongation at break of polyester urethanes considerably decreased with increasing content of OH groups in the synthesized polyols (Fig. 8). Correspondingly, the least was elongation for polyester urethanes based on castor oil (9 % – 11 %). Elongation at break of poly(urethane amides) was much lower than the elongation of the corresponding polyester urethanes. Practically all poly(urethane amides) behaved at tension as brittle materials. At rupture, most of the samples of poly(urethane amides) disintegrated into pieces. Poly(urethane amides) based on rapeseed and sunflower oil (elongation at break 4.2 % – 5.5 %) turned to be the most brittle ones. Elongation at break for poly(urethane amides) based on castor oil was somewhat higher (6.0 % – 6.5 %). With increasing content of OH groups in polyols, elongation at break of poly(urethane amides) decreased insignificantly.

In contrast to mechanical characteristics, the thermal stability of poly(urethane amides) appeared to be lower than that of analogous polyester urethanes. In this case, the difference in the indices, characterizing the initial step of

decomposition, such as the temperature of the maximum rate of weight loss for the first step of decomposition (T_{1MAX}) or the temperature of 5 % mass loss of the polymer ($T_{5\%}$) for all poly(urethane amides) and polyester urethanes under study was (Fig. 9) approximately 50 °C – 60 °C. With increasing content of OH groups in the synthesized polyols, the corresponding temperatures decreased practically linearly by 5 °C – 7 °C. It should be mentioned that the given temperatures, characterizing the initial step of the thermal decomposition of poly(urethane amides), agreed with the data obtained by other researchers [6 – 7].
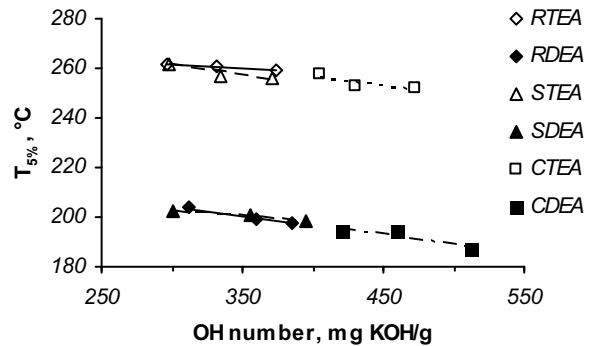

Fig. 9. $T_{5\%}$ of polyurethanes versus the content of OH groups in polyols

Upon the further decomposition, the difference in the indices between both the types of polyurethanes decreased and the difference between the temperatures of the maximum rate of weight loss for the final step of decomposition (T_{fMAX}) for poly(urethane amides) and polyester urethanes was only 10 °C (Fig. 10).
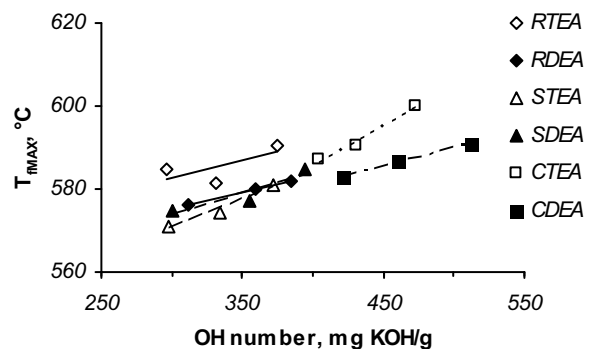

Fig. 10. T_{fMAX} of polyurethanes versus the content of OH groups in polyols

In this case, with increasing content of OH groups in the synthesized polyol, this temperature increased practically linearly on the average by 6 °C – 10 °C for each type of polyurethane. The value of the char yield of polyurethanes also changed in a similar way. In this case, at 600 °C, it was by 3 % – 4 % higher for polyester urethane than that for poly(urethane amide).

In general, the study on the properties of new poly(urethane amides) based on sunflower, rapeseed and castor oil has shown that their tensile strength and modulus of elasticity are proportional to the content of hydroxyl groups in polyols. Correspondingly, the polyurethanes based on the polyols, synthesized at the maximum molar ratio of oil: ethanolamine 3.0, have the best characteristics.

At such ratios, the mechanical characteristics of new poly(urethane amides) are comparable with the properties of the best polyurethanes based on vegetable oils polyols of other types [2].

In terms of tensile strength and modulus of elasticity, the new poly(urethane amides) considerably excel the polyester urethanes based on the esters of the same oils and triethanolamine. However, the thermal stability of the novel poly(urethane amides) is much worse than that of analogous polyester urethanes. The latter fact is in complete agreement with the data of other researchers, who noted the high thermal stability of polyurethanes based on esters [3, 5].

4. CONCLUSIONS

The effect of the synthesis parameters of amide and ester type polyols based on sunflower, rapeseed and castor oil on the properties of polyurethanes was investigated. It has been found that the polyurethanes, synthesized at the maximum molar ratio of oil to ethanolamine have the highest tensile strength and modulus of elasticity.

Novel poly(urethane amides) have higher tensile strength, modulus of elasticity and glass transition temperature than the analogous polyester urethanes. Polyester urethanes, in their turn, are better than analogous poly(urethane amides) in terms of thermal stability. They are also characterized by higher elongation at break and density.

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