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Synthesis and Characterization of Novel Polyurethanes Based on Tall Oil

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Amide and ester type polyols were synthesized from different kinds of tall oil and two types of ethanolamine (diethanolamine and triethanolamine). Poly(urethane amides) and polyester urethanes based on the synthesized polyols were prepared. The influence of the chemical structure of the obtained polyurethanes on density, glass transition temperature, thermal stability, mechanical properties and adhesive strength was investigated. The effect of the content of rosin acids in original tall oil on the specified characteristics was estimated. It has been found that poly(urethane amides) have higher 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, mechanical properties, thermal stability.

1. INTRODUCTION

The synthesis of reactive compounds used in the production of different polymeric materials is one of the traditional fields of the use of vegetable oils' fatty acids [1, 2]. In recent years, vegetable oils' fatty acids are attracting great attention, because they are renewable raw materials [3]. On their basis, new types of reactive compounds, used in the production of polymeric coatings, adhesives and foams, are synthesized [4 – 6]. The properties of new polyurethanes, based on the polyols obtained on the basis of vegetable oils' fatty acids, have been considered in detail in [7 – 10]. In these studies, the effect of the chemical structure of the polyols and isocyanates on the main properties of the material is shown by the example of various types of polyurethanes.

Tall oil, a by-product of Kraft pulping, is another popular source of fatty acids for polymer synthesis [11]. In contrast to vegetable oils, in which fatty acids are present in the form of fatty acid glycerides, tall oil contains free fatty acids. Besides fatty acids, the composition of crude tall oil includes rosin acids and unsaponifiables, the chemical composition and amount of which depend on the wood species. The products of the vacuum distillation of tall oil are tall oil fatty acids with a minimal content of rosin acids (ISO 8623:1997), distilled tall oil with the designed content of rosin acids and tall rosin. The former two products are widely used in the production of alkyd resins and other polymeric products. Tall rosin is used not only as a modifier of polymeric coatings, but also as an adhesive [12 – 14]. Besides, based on the listed products, polyurethane coatings and foams can be obtained [15 – 18].

In the production of polyurethanes, tall oil esters are mainly used, for producing of which triethanolamine or glycerol are used in the synthesis. If diethanolamine or other alkanolamines, instead of triethanolamine that is traditional for the synthesis of esters, are used, then fatty acids diethanolamide and the corresponding poly(urethane amide) can be obtained. The properties of such urethanes have recently aroused known interest and are considered, in particular, in [19 – 23]. However, there are yet no sufficient data in the literature on the poly(urethane amides) based on tall oil fatty acids.

In the present study, new amide-type polyols were synthesized from tall oil fatty acids and diethanolamine. Based on the synthesized polyols, new poly(urethane amides) were prepared, and their mechanical, thermal and other properties were investigated. The properties of the new poly(urethane amides) were compared with those of traditional polyurethanes based on tall oil fatty acids and triethanolamine esters. In addition, the effect of the content of rosin acids on the properties of the mentioned polyurethanes was studied.

2. EXPERIMENTAL

2.1. Materials

Polyisocyanate Voratec SD 100 (NCO content 31.5 %, functionality 2.7) was supplied by Dow Deutschland GmbH (Germany). Tall oil fatty acids (TOFA) FOR2 and distilled tall oil (DTO) of different grades were supplied by Forchem OY (Finland). The specifications of the mentioned oils are listed in Table 1.

Table 1. Specifications of oils

Oil grade	FOR2	FOR10	FOR20	FOR30
Acid value, mg KOH/g	195	194	190	190
Free fatty acids, %	96	87	76	70
Free rosin acids, %	1.9	10	20	28
Saponificatioin value, mg KOH/g	198	196	194	192
Unsaponifiables, %	1.9	3	3	3
Density at 20 °C, kg/m^3	904	920	930	945
Viscosity at 20 °C, mPa·s	30	50	70	85

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

2.2. Synthesis of polyols

To obtain tall oil diethanolamides, pure diethanolamine was used in the synthesis. Molar ratio (NH+OH)/COOH was 1.15. First, tall oil was heated in an agitated reactor up to 140 °C. Then diethanolamine, heated up to 70 °C, was added. Polyol synthesis was performed at (145 ±5) °C in an inert atmosphere [24]. Synthesis duration (about 4 h) was controlled from the change in the amine number of the polyol. The corresponding analysis was carried out according to the requirements of the standard ISO 25761:2008. After accomplishing the synthesis, distillation of the formed water was carried out during 1.5 h at a lowered pressure (200 mbar).

The synthesis of tall oil esters was realized by a similar procedure, using pure triethanolamine. The synthesis was conducted at a higher temperature [25] equal to (180 ± 5) °C. Molar ratio OH/COOH was 1.33. Synthesis duration was controlled from the change in the acid number of polyol (ISO 660:2009). The mentioned molar ratios were chosen by analogy with the methods of polyol synthesis for rigid polyurethane foams [14, 20].

Water content and OH value of the synthesized polyols were determined according to the requirements of the ISO 14900:2001 and ISO 14897:2002 standards. The dynamic viscosity of polyols at 25 °C according to the standard ISO 12058:1997 was determined using a falling ball viscometer KF10 (RheoTec Messtechnik GmbH). All measurements were done at the working angle of the cylindrical glass tube 80°. The calibrated balls (No. 3 or No. 4, depending on polyol viscosity) were chosen in such a way that minimum falling times were no shorter than 30 s, but no longer than 300 s.

2.3. Preparation and characterization of polyurethanes

Further, based on the synthesized polyols and polyisocyanate, polyurethanes in the form of free films (ASTM D 4708-99) were prepared. In this case, toluene was used as a solvent. Toluene (up to 50 %) was added to the polyol. Isocyanate and polyol components were mixed in the molar ratio NCO/OH = 1.1. The films as well as adhesive compounds were hardened at a temperature of (21 ±2) °C during 7 days. After curing, 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 Perkin Elmer). Scanning range was from 4000 cm^{-1} to 500 cm^{-1}, resolution 4 cm^{-1}, and averaging scans 32.

Polyurethanes' density was determined by 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. Width and length of all strips were 10 mm and 100 mm respectively. Distance between the jaws of the grips was 70 mm; testing speed 7 mm/min. Besides the jaws displacement, a variation of distance between the marks on the specimen (initial distance 50 mm) was measured visually using the millimetre scale. However, for the established maximum elongations of all tested specimens, the difference in the two methods of measurement appeared to be negligible. For each type of polyurethane 6 specimens were tested. Coefficients of variation for modulus of elasticity, tensile strength and elongation did not exceed 5, 8 and 15 %, respectively.

Shear strength of wood-to-wood (ISO 6237:2003) and aluminium-to-aluminium (ISO 4587:2003) polyurethane adhesive bonds was determined on a Zwick/Roell Z010 (10 kN) testing machine. Two-ply tension shear wood specimens were glued from standard non-abraded birch veneer with a thickness of 1.5 mm. Before and after gluing, veneer and wood samples were conditioned at a relative humidity of (50 ±5) % and a temperature of (21 ±2) °C for 7 days. Moisture content of wood samples was about 10 %. Samples width and length of overlap were 25 mm and 20 mm respectively. Distance between the jaws was 40 mm.

For the second test, aluminium strips (100×25×2.0) mm were used. Before gluing, aluminium strips were abraded and degreased. Length of overlap was 12.5 mm. Distance between the jaws was 110 mm. Testing speed in both adhesive tests (4 and 2 mm/min respectively) was chosen so that samples failed within (60 ±20) s. For each type of polyurethane 8 specimens were tested. Coefficients of variation for shear strength did not exceed 15 %.

Thermal stability and glass transition temperature of polyurethanes were determined using TGA/SDTA 851^e and DSC 851^e METTLER TOLEDO, respectively. Sample weight in both tests was about 8 mg; heating rate 10 °C/min. TGA test was carried out in airflow of 20 cm^3/min, and DSC in a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1. Properties of polyols

The main characteristics of the synthesized polyols are listed in Table 2. As follows from the presented data, with increasing content of rosin acids in the original tall oil, the content of OH groups in the synthesized polyols slightly decreased. In this case, the viscosity of all the polyols tended to increase.

Table 2. Characteristics of polyols

Oil grade	FOR2	FOR10	FOR20	FOR30
Tall oil diethanolamides				
OH number, mg KOH/g	287	288	275	274
Water, %	0.08	0.11	0.10	0.25
Viscosity at 25 °C, mPa·s	612	754	1040	1770
Tall oil and triethanolamine esters				
OH number, mg KOH/g	350	347	345	325
Water, %	0.04	0.19	0.09	0.08
Viscosity at 25 °C, mPa·s	182	200	275	336

The viscosity of the amide polyols exceeded several times that of ester polyols. This fact, along with the other ones considered next, testified a strong intermolecular interaction in amide polyols. At a considerable increase in the viscosity of polyol, the distillation of the water formed in the synthesis process was hampered. However, in the majority of cases, the content of water in polyols did not exceed 0.1 %.

3.2. Structure of polyols and polyurethanes

As has been shown in a range of studies, upon the interaction of fatty acids with diethanolamine at an appropriate molar ratio, diethanolamides [19 – 21] of general structure (I) are formed (Fig. 1). If traditional triethanolamine is used in the synthesis, then, in this case, fatty acids and triethanolamine esters (II) are formed [25]. Upon the interaction of the mentioned compounds with diisocyanate, poly(urethane amides) and polyester urethanes are formed. In these polyurethanes, residues of fatty acids form long dangling (side) chains [8] attached to the polyurethane network backbone. In this case, the double bonds of the unsaturated fatty acids present in tall oil are not involved in the polyurethane curing process.

The idealized structure of the chain fragments of the mentioned poly(urethane amides) and polyester urethanes can be represented (Fig. 1) as structures (III) and (IV), respectively [16, 21]. As it can be seen, in the case of poly(urethane amide), the residue of fatty acid (R_1) is linked directly to the rigid amide group. In the case of polyester urethane, the ester group with the residue of fatty acid is linked to the N atom via a thermodynamically flexible short ethylene chain – $(CH_2)_2$–.

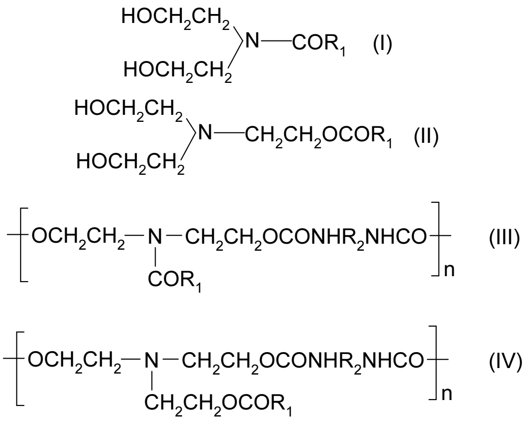

Fig. 1. Chemical structure of the synthesized polyols and polyurethanes, where R_1 – residue of saturated and unsaturated fatty acids (C_{16}–C_{24}) and R_2 – residue of aromatic diisocyanate

If distilled or crude tall oil is used in the synthesis, then a part of the side chains (R_1) will be formed also by the residues of rosin acids present in the oil. The role of those spatial branchings is assumed to increase with increasing content of rosin acids in the original tall oil.

The mentioned (Fig. 1) distinctions in the chemical structure are qualitatively confirmed by IR-spectroscopy data. The spectra of both the types of polyols had practically the same absorption bands at 2924 cm^{-1} and 2854 cm^{-1}, assigned to asymmetric and symmetric stretching vibrations of –CH_2– groups (Fig. 2). The absorption bands assigned to the valent vibrations of OH groups had a shift from 3389 cm^{-1} (ester polyols) to 3378 cm^{-1} (amide type polyols).

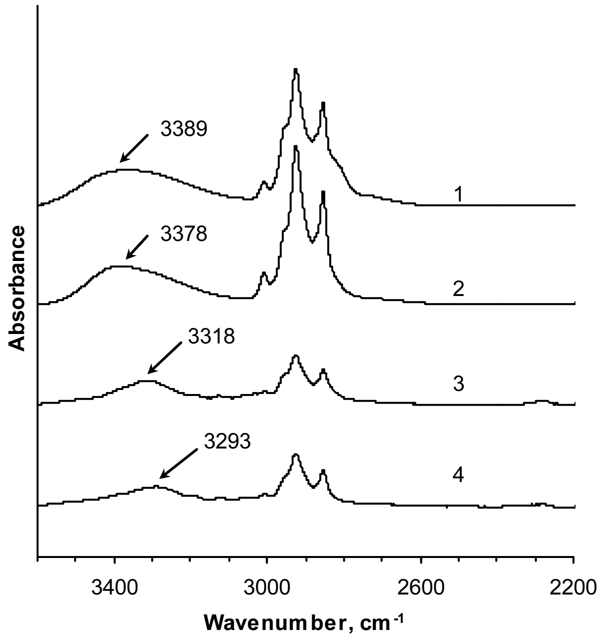

Fig. 2. IR-spectra of polyols (1, 2) and urethanes (3, 4), based on tall oil FOR2 esters (1, 3) and diethanolamides (2, 4)

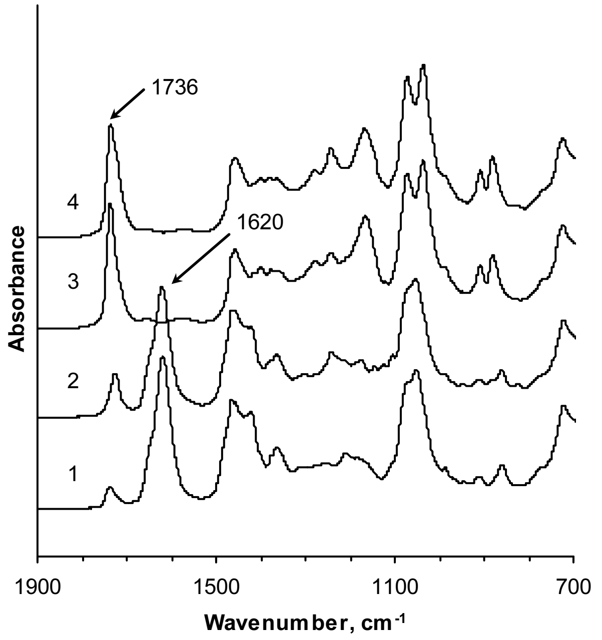

Fig. 3. IR-spectra of tall oil diethanolamides (1, 2) and esters (3, 4), containing 2 % (1, 3) and 20 % (2, 4) of rosin acids

However, the greatest distinction in the spectra of the synthesized polyols was observed in the middle part of the spectrum (Fig. 3). If ester polyols had a strong absorption band at 1736 cm^{-1}, typical for ester carbonyl, then diethanolamides had an adsorption band of such intensity at 1620 cm^{-1}, typical for amide [26]. A weak adsorption band at 1736 cm^{-1} was observed also in the spectra of diethanolamides. The presence of such an adsorption band testifies that, in the synthesis of diethanolamides, a side reaction, with the formation of diethanolamine ester, occurs [27]. However, the main product of this synthesis is diethanolamide, the intensity of the adsorption band of which (1620 cm^{-1}) in the polyols spectrum is much higher.

The spectra of the synthesized polyols differ also in terms of intensity and the form of peaks in the ranges, typical for the deformation vibrations of –CH$_2$– groups (1457 – 1466 cm^{-1}). Besides, the spectra of ester polyols had adsorption peaks at 1278 cm^{-1} and 1165 cm^{-1}, typical for the stretching vibrations of C–O bond in alcohols and esters [26]. The increase in the content of rosin acids in the original tall oil did not considerably influence the spectra of ester polyols. The spectra of diethanolamides with different contents of rosin acids differed from each other in the intensity of separate adsorption bands.

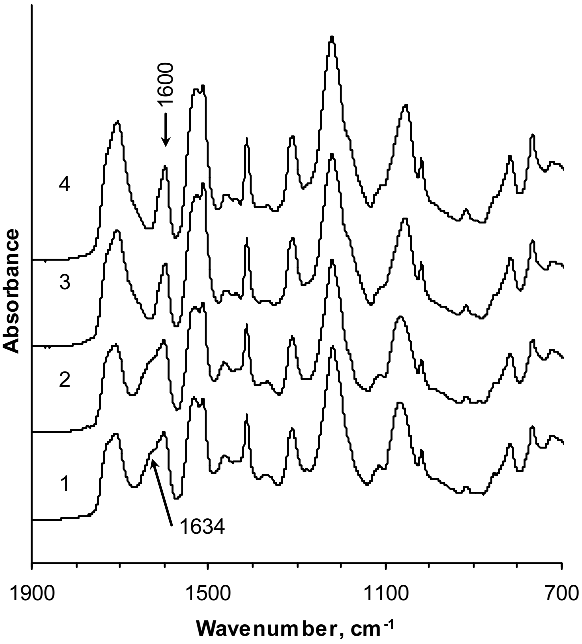

Fig. 4. IR-spectra of polyurethanes based on tall oil diethanolamides (1, 2) and esters (3, 4), containing 2 % (1, 3) and 20 % (2, 4) of rosin acids

There was no essential difference in the spectra of poly(urethane amides) and polyester urethanes, in contrast to those of polyols. In the spectra of all polyurethanes, weak absorption bands were observed (Fig. 2), assigned to the valent vibrations of the unreacted NCO groups of the polyisocyanate excess (2275 cm^{-1}). The intensity of the double absorption bands of the –CH$_2$– groups (2924 cm^{-1} and 2854 cm^{-1}) substantially decreased. In the same region of the spectrum, absorption bands at 3318 cm^{-1} for polyester urethane and 3293 cm^{-1} for poly(urethane amide) were present, assigned to hydrogen-bonded –NH groups [28 – 30]. The intensity of these absorption bands, in comparison with other ones, was not high; however, the observed shift of the poly(urethane amide) absorption band to the low-frequency region, as in the case of amide polyol, indicated a more intensive intermolecular interaction in poly(urethane amide), determined also by the intensity of hydrogen bonds.

As in the case of polyols, more essential difference in the absorption spectra was observed in the middle part of the spectrum (Fig. 4). All the polyurethanes had amide I (1707 – 1709 cm^{-1}), amide II (1511 – 1527 cm^{-1}) and amide III (1218 cm^{-1}) bands, typical for polyurethanes, differing for various polyols only in terms of intensity. In this case, the higher was the content of rosin acids in the original tall oil, the higher was the intensity of the absorption peaks. A similar pattern was observed also relative to the peaks typical for the vibrations of the groups: –CH$_2$– (1413 cm^{-1}), C–O (1310 cm^{-1}) and O–C=O (1054 – 1065 cm^{-1}). However, the main distinction in the spectra of poly(urethane amides) from those of polyester urethanes was the presence of a double absorption band of amide carbonyl (1600 cm^{-1} and 1634 cm^{-1}). All the polyester urethanes in the given region had a single absorption band of 1600 cm^{-1}.

3.3. Properties of polyurethanes

A study of the physical properties of the polyurethanes produced on the basis of the synthesized polyols showed that polyester urethanes (PEU) had a higher density than the corresponding poly(urethane amides) (PUA). Most likely, the high mobility of the side chains of polyester urethanes favoured the denser packing of the structural elements of the crosslinked polymer. With increasing content of rosin acids in the original tall oil, the density of the polyurethanes of both the types increased (Fig. 5).

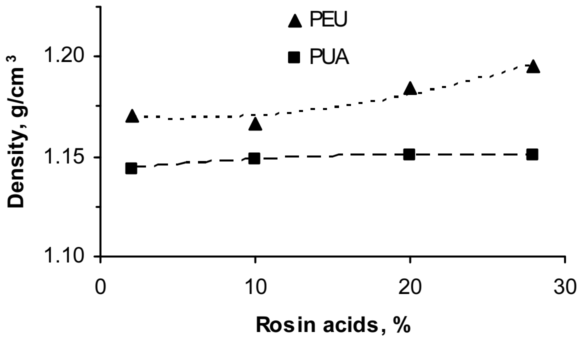

Fig. 5. Density of polyurethanes versus the content of rosin acids

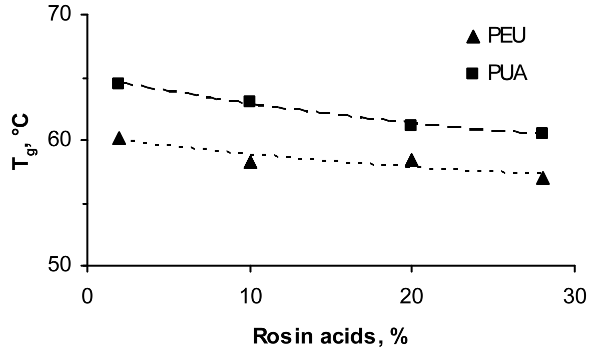

Fig. 6. T_g of polyurethanes versus the content of rosin acids

In contrast to density, the glass transition temperature (T_g) of polyester urethanes was lower than that of poly(urethane amides) (Fig. 6). With increasing content of rosin acids in the original tall oil, the T_g of polyurethanes of both types decreased practically linearly.

Modulus of elasticity (Fig. 7) and tensile strength (Fig. 8) of poly(urethane amides) with a small content of rosin acids exceeded almost twice the modulus and strength of polyester urethanes. These facts, as well as the higher T_g, have confirmed the presence of a stronger intermolecular interaction in poly(urethane amides), the structure of which is formed by hard urethane-amide segments. In polyester urethanes, the intermolecular interaction is weakened by dangling chains with an ester bond, acting as a plasticizer.

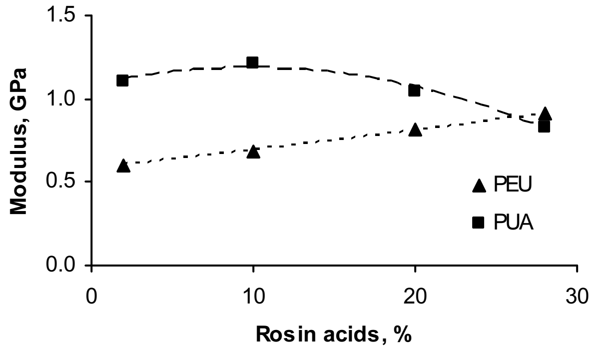

Fig. 7. Modulus of elasticity of polyurethanes versus the content of rosin acids

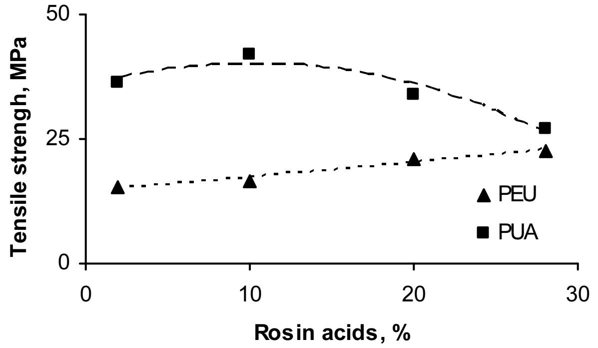

Fig. 8. Tensile strength of polyurethanes versus the content of rosin acids

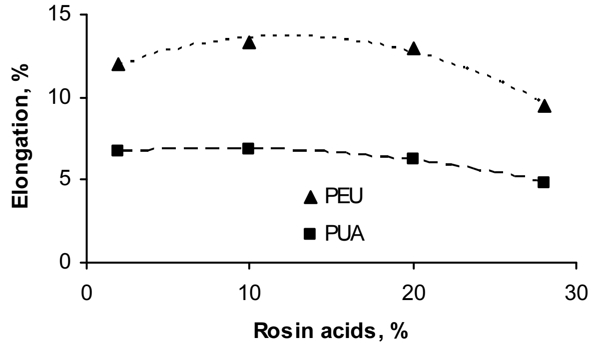

Fig. 9. Elongation at break of polyurethanes versus the content of rosin acids

The tensile strength and modulus of elasticity of polyester urethanes considerably increased with decreasing content of rosin acids. Consequently, in this case, the presence of spatial residues of rosin acids in the side chains had a favourable effect on the mechanical properties of polyurethanes. Quite a different pattern was observed in poly(urethane amides). At a rosin acid content of more than 10 %, the strength and modulus of elasticity of poly(urethane amides) essentially decreased. Obviously, at a considerable content, the spatial residues of rosin acids, linked directly to the nitrogen atom of the hard urethane segment, essentially weakened the intermolecular interaction in poly(urethane amides).

Elongation at break for poly(urethane amides) was almost twice lower than the elongation of polyester-urethanes (Fig. 9). Moreover, with an increasing of rosin acids content this elongation at break for poly(urethane amides) decreased up to 4.8 %. With increasing content of rosin acids up to 20 % in the original tall oil, elongation at break of polyester urethane changed negligibly. At higher content of rosin acids, elongation decreased. It seems that the rigidity of polyester urethanes at 20 % content of rosin acids reaches such an extent, above which its elongation at break for cross-linked polyurethane begins to decrease.

Shear bond strength of the studied polyester urethanes was higher than that of poly(urethane amides). Shear bond strength of polyester-urethanes to wood (birch veneer) and aluminium substrate was about the same at a low content of rosin acids. Shear bond strength of poly(urethane amides) to aluminium substrate was 1.5 – 2 times lower than that to wood (birch veneer). With increasing content of rosin acids, adhesion to both wood and aluminium decreased practically linearly (Fig. 10). The most probable reason for all these effects is the fact that the viscosity of diethanolamides is higher than that of the ester polyols. The viscosity of polyols and the polyurethane composition increased with increasing content of rosin acids; as a result, the wetting of the substrate surface with polyurethane worsened.

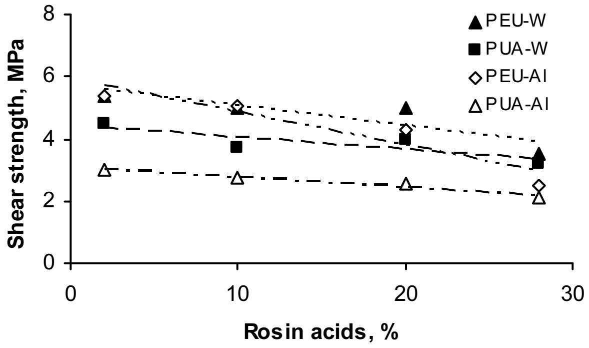

Fig. 10. Shear bond strength to wood (W) and aluminium (Al) for polyurethanes versus the content of rosin acids

To evaluate the thermal stability of polymers by the TGA method, different indices are used. In some studies, the temperature, at which a 5 % or 10 % mass loss of the polymer ($T_{5\,\%}$ and $T_{10\,\%}$) occurs, is taken for the initial decomposition temperature [17, 31]. In other studies, the thermal stability of polymers is evaluated from the initial (onset) decomposition temperature of the first and second steps of decomposition ($T_{1\mathrm{ON}}$ and $T_{2\mathrm{ON}}$) and the temperatures of the maximum rate of weight loss for the first and second steps of decomposition ($T_{1\mathrm{MAX}}$ and $T_{2\mathrm{MAX}}$) [32, 33]. For comparison of thermal stability, also characteristics such as char yield at 600 (m_{600}), 700 or even 800 °C are used. The use of the mentioned characteristics in the study has shown (Table 3) that the chemical composition of polyurethane has a similar effect on all characteristics of the same type. The difference is only in the absolute values of these characteristics.

As it can be seen from Fig. 11, the decomposition of poly(urethane amides) had started much earlier than that of polyester urethanes. If $T_{5\,\%}$ was taken for the initial decomposition temperature, then the difference between the temperatures of decomposition of poly(urethane amide) and polyester urethane reached 40 °C. In this case, the obtained values of the initial decomposition temperature of poly(urethane amides) agreed with the data obtained in other studies [19 – 21]. With increasing content of rosin acids in the original tall oil, the initial decomposition temperature of polyurethanes changed negligibly.

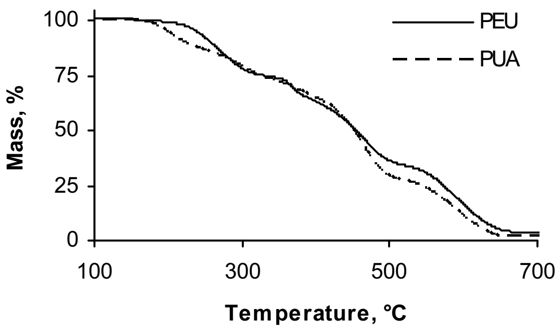

Fig. 11. TGA curves of polyurethanes with the content of rosin acids of 2 %

Table 3. Thermal stability of polyurethanes

Oil grade	FOR2	FOR10	FOR20	FOR30
Poly(urethane amides)				
$T_{5\,\%}$, °C	199	201	204	205
$T_{10\,\%}$, °C	225	226	233	232
$T_{1\mathrm{MAX}}$, °C	203	199	205	202
$T_{2\mathrm{MAX}}$, °C	304	308	304	306
T_{fMAX}, °C	591	582	582	581
m_{600}, %	16.8	13.4	18.6	16.8
Polyester-urethanes				
$T_{5\,\%}$, °C	241	247	249	241
$T_{10\,\%}$, °C	261	265	266	261
$T_{1\mathrm{MAX}}$, °C	257	254	259	258
$T_{2\mathrm{MAX}}$, °C	353	362	375	370
T_{fMAX}, °C	596	581	608	583
m_{600}, %	11.3	12.2	13.1	12.9

The high thermal stability of polyester urethanes was indicated (Table 3) also by the value of the char yield at 600 °C (m_{600}). It was higher than that of the corresponding poly(urethane amides). With increasing content of rosin acids up to 28 %, the char yield of all the polyurethanes increased negligibly. However, at higher content of rosin acids, the char yield of polyester urethanes decreased. At higher temperatures, such a clear dependence of the char yield on the composition of polyurethane was not already observed. It should be added that there was no considerable difference also between the temperatures of the maximum rate of weight loss for the final steps of decomposition (T_{fMAX}) for poly(urethane amides) and polyester urethanes.

Thus, in mechanical characteristics, the obtained poly(urethane amides) excel noticeably the traditional polyester urethanes. In terms of the values, the characteristics of poly(urethane amides) are comparable with those of the best samples of polyurethanes, based on vegetable oils. However, there are scarce data for such a comparison. Only in some of the mentioned works, polyurethanes have been tested as polymeric films or adhesives [8]. In many studies, results of specific tests for polymeric coatings such as scratch hardness, impact resistance, etc. are presented. However, in terms of thermal stability, poly(urethane amides) are inferior to polyester urethanes. This, however, agrees with the results of other studies. The higher thermal stability of polyester urethanes, in comparison with the case of other polyurethanes, is indicated, in particular, in the studies [7, 10].

4. CONCLUSIONS

Amide type polyols were synthesized on the basis of tall oil and diethanolamine. The properties of the poly(urethane amides) obtained on their basis were investigated.

Tensile strength and modulus of elasticity of poly(urethane amides) with a low content of rosin acids considerably exceed those of analogous polyester urethanes. On the contrary, the elongation at break of poly(urethane amides) is considerably lower than that of analogous polyester urethanes.

With increasing content of rosin acids in the original tall oil, the mechanical characteristics of poly(urethane amides) worsen, but, on the contrary, the characteristics of polyester urethanes are improved.

The initial decomposition temperature of polyester urethanes is much higher than that of analogous poly(urethane amides).

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