

Structure and properties of polyurethane foams obtained from rapeseed oil polyols

Uldis Stirna^{a*}, Irina Sevastyanova^a, Maria Misane^a, Ugis Cabulis^a,
and Ilze Beverte^b

^a Latvian State Institute of Wood Chemistry, 27 Dzerbenes Str., LV-1006 Riga, Latvia

^b Institute of Polymer Mechanics, University of Latvia, 23 Aizkraukles Str., LV-1006 Riga, Latvia

Received 24 October 2005, in revised form 2 January 2006

Abstract. By transesterifying rapeseed oil with triethanolamine or glycerol, polyols with a hydroxyl number of 290–310 mg KOH/g were synthesized. Water-blown rigid polyurethane foams (PUFs) with an isocyanate index of 150–250 were obtained from rapeseed oil polyols. Studies on the effect of the concentration of potassium oleate, the cyclotrimerization catalyst of isocyanate groups, on the conversion degree of isocyanate groups were carried out using FTIR spectroscopy. The optimal physical and mechanical properties of the obtained PUFs were achieved at an isocyanate index of 150–200. Water-blown PUFs from rapeseed polyols, in contrast to water-blown PUFs from petrochemical polyols, are characterized by quite high hydrophobicity.

Key words: water-blown polyurethane foams, rapeseed oil polyols, isocyanate index, physical properties, mechanical properties.

INTRODUCTION

Increasing attention is paid to obtaining polymer materials from renewable resources [1]. The interest in synthesizing rigid polyurethane foams (PUFs) from various vegetable oils, especially soy, sunflower, palm, and rapeseed oils, is also increasing [2–4]. By incorporating long fatty acid C₁₂–C₂₀ side chains in the PUF polymer matrix, it is possible to enhance the hydrophobicity of the PUFs [5], and such foams have a higher thermal stability than PUFs based on propylene oxide polyols [4]. Owing to the dramatic development of bio diesel production, obtaining rapeseed oil has increased also in the Baltic States. This promotes studies on the use of this product for obtaining PUFs.

* Corresponding author, ripors@edi.lv

It is known that the thermal stability, fire resistance, and dimensional stability of PUFs can be enhanced by incorporating isocyanurate rings in their polymer matrix, although mainly blowing agents of hydrogen chlorofluorocarbons (HCFCs) type are used for foam preparation [6]. An environmentally friendly blowing agent is carbon dioxide, which is obtained in the reaction between polyisocyanate and water, but the dimensional stability of the foams of this type is not sufficient. All water-blown PUFs containing isocyanurate rings in the polymer matrix and exhibiting excellent fire resistance properties were reported recently [7]. However, all water-blown PUFs containing isocyanurate rings pose several problems. They are polyol premix systems having poor dimensional stability as well as poor surface friability. Studies of water-blown polyisocyanurate foam preparation were conducted by Naruse et al. [8]. Water-blown PUF foam preparation from vegetable oil polyols involves some problems, and the main reasons are as follows: vegetable oil polyols are very hydrophobic products and do not form homogeneous polyol premix systems even with small quantities of water, and the collapse is observed in their blowing process. The main drawback of the HCFC-blown PUFs prepared from polyols of different epoxidized vegetable oils is their low dimensional stability and inadequate fire resistance [2–4]. This drawback can be eliminated by incorporating isocyanurate rings and urea groups in the polymer matrix.

In the present study, the results on the water-blown isocyanurate ring-containing PUFs obtained from rapeseed oil polyols, which are synthesized by way of transesterification of rapeseed oils with triethanolamine, are presented.

EXPERIMENTAL

Materials

Rapeseed oil (Iecavnieks, Latvia) with a saponification number of 180 mg KOH/g was used for polymer synthesis. The typical formulation used in this study was polyols from rapeseed oils and an oxypropylated glycerol – Lupranol 3300 (hydroxyl number 420 mg KOH/g) – from BASF AG. As additives, tris β -chloropropyl phosphate (TCPP) as a flame retardant and silicone surfactant were used. N,N-dimethylethanolamine and potassium oleate were used as catalysts. As an isocyanate, polymeric diphenylmethane diisocyanate (MDI) supplied by BASF AG was used.

Methods

Polyols from rapeseed oils were synthesized in the transesterification process using glycerol or triethanolamine. Transesterification with glycerol was conducted at a temperature of 240°C and with triethanolamine at 180°C; the catalytic system was Pb acetate (0.3 wt %). The typical PUF formulation used in this study is shown in Table 1. Foams were prepared at $22 \pm 2^\circ\text{C}$ applying a hand mixing

Table 1. Typical formulation of a water-blown polyurethane foam

Raw material	Parts by weight
Rapeseed oil polyol	80
Oxipropylated glycerol	20
Tris β -chloropropyl phosphate	30
Silicone surfactant	1.5
Potassium oleate	2.0
N,N-dimethylethanolamine	3.0
Water	2.5
Polymeric MDI (isocyanate)	Index = 170

method. For the measurement of foaming reactivity, free rise density, and physical and mechanical properties, 50 g of the polyol premix and polymeric MDI were poured into an open box mould. Table 1 shows the formulation of the polymer premix. PUF foams were obtained also by the spraying method at the following process characteristics: volume ratio of the polymeric MDI to the polyol premix 1.2: 1.0, low-pressure equipment capacity 2.0 L/min, air pressure 5.0 ± 0.5 bar.

The physical and mechanical properties of the foams were measured in accordance with the following standards: foam density – DIN 53420, compressive strength – DIN 53421, dimensional stability at 70°C and relative humidity 95% for 48 h – ISO 2796, closed cell content – ISO 4590, and water absorbance after 7 days – DIN 53428. The compressive strength of PUFs was tested parallel and perpendicular to the foam rise, and the tensile strength perpendicular to the foam rise. Isocyanurate ring-containing polyester(urethane) films were moulded on Teflon sheets from polyol and polymeric MDI 30% solution in dry toluene; film thickness 150–250 μm . After the evaporation of the solvent, the films were heated at 110°C for 2 h to complete curing. The stress–strain characteristics of polyester(urethane) films containing isocyanurate rings were determined by tensile testing using dumbbell-shaped specimens on a Zwick/Roell at the deformation rate 50 mm/min. The spectra of the ground and KBr pellet pressed PUF samples were registered with a Perkin Elmer FTIR spectrometer.

RESULTS AND DISCUSSION

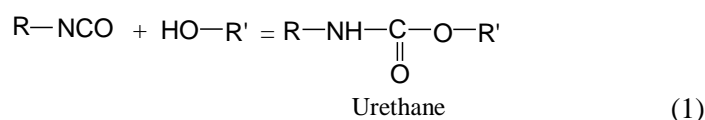
Rapeseed oils are triglycerides of fatty (C_{12} – C_{22}) acids, mainly consisting of mono-unsaturated fatty acids such as oleic acid, and poly-unsaturated fatty acids such as linoleic and linolenic acids. The synthesized polyols are low-viscosity, homogeneous products, except the polyols obtained in the transesterification of rapeseed oils with glycerol. These products crystallize at long storage. Vegetable oil transesterification with polyhydric alcohols and the chemical structure of the synthesized products are widely covered in the literature. The synthesized products represent a mixture of short-chain polyols, containing higher fatty acid mono- and diesters as well as free polyhydric alcohols [9]. The characteristics of the synthesized polyols are listed in Table 2.

Table 2. Characteristics of polyols synthesized from rapeseed oils

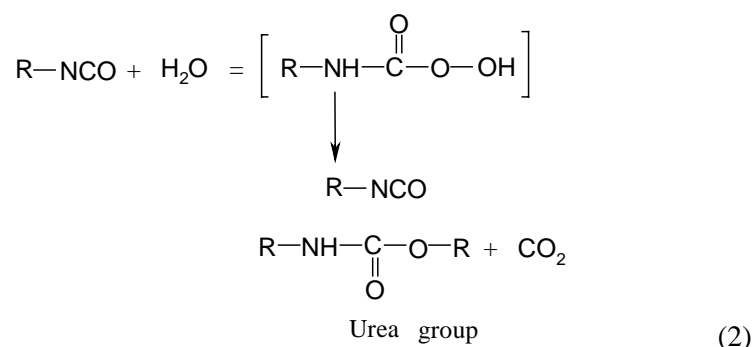
Alcohol	Vegetable oils/alcohol, mol/mol	Hydroxyl number, mg KOH/g	Viscosity, mPa · s at 25 °C
Glycerol	1 : 2.3	290	Crystalline
Triethanolamine	1 : 2.4	310	190

It follows from the data listed in Table 2 that, in terms of the hydroxyl number and viscosity indices, the polyols synthesized from rapeseed oil with triethanolamine meet the requirements for obtaining water-blown rigid PUFs from them.

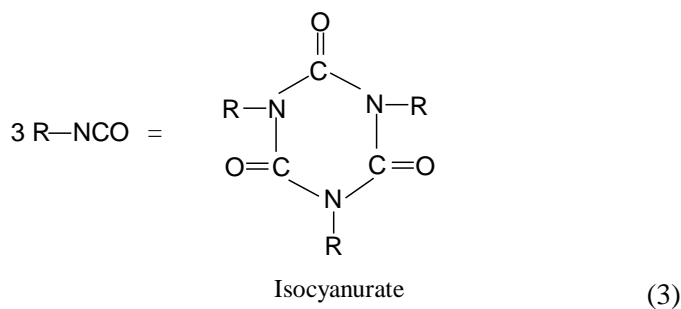
If PUFs are obtained by using water as a blowing agent, the following main chemical reactions occur: urethane formation, reacting hydroxyl groups with the isocyanate groups (1):



and urea groups formation, as water reacts with the isocyanate groups (2):

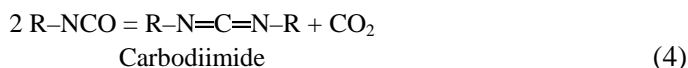


As NCO groups are capable of entering into reaction with urethane groups, allophanate groups can be formed, and as urea groups in turn enter into reaction with NCO groups, biuret groups can be formed. To enhance the thermo- and fire-resistance of the obtained PUFs, isocyanurate rings, which are formed as a result of the cyclotrimerization reactions of NCO groups, were incorporated into the structure of the polymer matrix of these PUFs (3):



This was achieved by increasing the isocyanate index values up to 150–250 in PUF compositions. The index is defined as the product of the number of NCO mols per OH and H₂O mol multiplied by 100. Potassium acetate, dissolved in water or ethylene glycol [8], is used most often for the catalysis of the cyclotrimerization reaction of isocyanate groups. However, it has been found in the course of experiments that this catalyst forms heterogeneous systems with vegetable oil polyols. Therefore, a new catalyst, potassium oleate, which forms homogeneous systems with vegetable oil polyols, was used. The efficiency of this catalyst with isocyanurate groups in obtaining PUFs has not been described. To determine the optimal concentration of potassium oleate in PUF compositions, its quantity was varied from 0.15 to 0.76 wt %, while the concentration of the blowing catalyst, N,N-dimethylethanolamine, was constant, namely 0.83 wt % of the total amount of the raw materials.

It can be seen from the FTIR spectra (Fig. 1) that the PUF polymer matrix has absorption bands at 2135 and 2275 cm⁻¹, which are typical of carbodiimide and isocyanate groups, respectively [4]. The analysis of FTIR spectra shows that they also have an absorption band at 3410–3450 cm⁻¹, which is typical of the polyurethane NH^{H free} group, while in this spectrum part a shoulder at 3300 cm⁻¹, which is typical of NH^{bonded}, is only slightly pronounced [10]. The NCO group conversion degree in the PUF polymer matrix, depending on the potassium oleate concentration, is judged from the intensity changes of the absorption bands at 2275 cm⁻¹. It can be seen in Fig. 2 that with the increasing of the potassium oleate concentration from 0.15 to 0.76 wt %, the absorption bands intensity ratio A_{2275}/A_{2925} corresponding to NCO and CH₂ groups decreases from 0.81 to 0.61. Figure 2 shows that the optimal potassium oleate concentration for obtaining PUFs modified with isocyanurate rings is about 0.45 wt %, and no notable decrease in the NCO group concentration in the polymer matrix of the foam occurs. It is known that the dimerization of NCO groups, as a result of which carbodiimide groups are formed, proceeds in the presence of catalysts such as phospholene derivatives [11]. In the presence of the chosen catalytic systems potassium oleate – N,N-dimethylethanolamine, also the dimerization of NCO groups occurs, with the formation of a carbodiimide group and the release of carbon dioxide according to Eq. 4:



It follows from Fig. 2 that with the increasing of the potassium oleate concentration from 0.15 to 0.76 wt %, the ratio between the absorption frequencies A_{2135}/A_{2925} increases from 0.18 to 0.38, which indicates an increase in the amount of the carbodiimide groups in the PUF polymer matrix as the catalyst concentration is increased, although the absorption peak intensity at 2135 cm⁻¹ is modest, which indicates that this reaction does not play a great role in the process of obtaining PUFs.

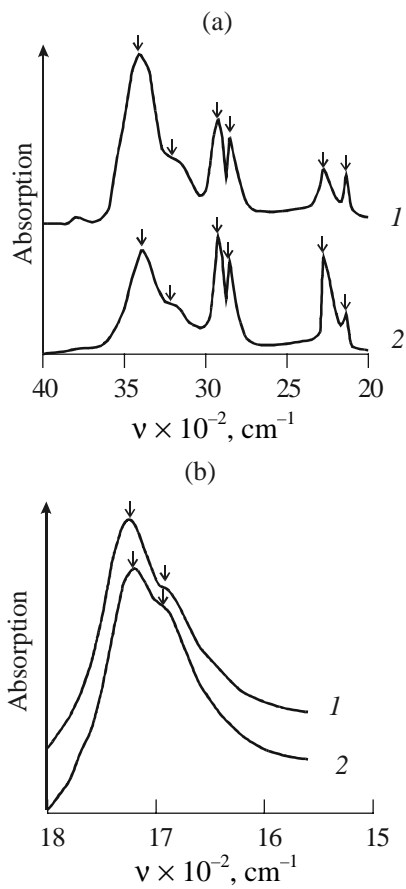


Fig. 1. FTIR absorption spectra of PUF with an isocyanate index of 150: potassium oleate concentration 0.76 wt % (1) and potassium oleate concentration 0.15 wt % (2) in the regions 3000 (a) and 1700 cm^{-1} (b).

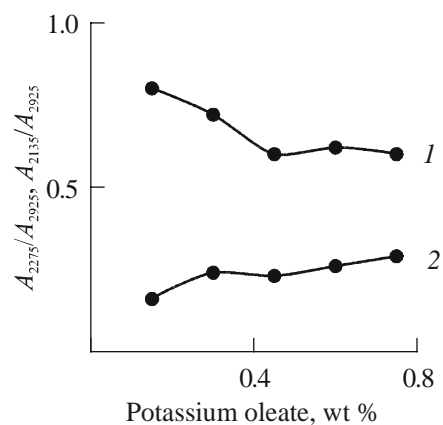


Fig. 2. The ratios A_{2275}/A_{2925} (1) and A_{2135}/A_{2925} (2) versus the potassium oleate concentration. PUF with an isocyanate index of 150.

To elucidate the effect of the isocyanurate ring on the properties of foams from rapeseed oil polyols, PUFs with the isocyanate indices (II) ranging from 150 to 250 were obtained. Table 3 lists the physical and mechanical properties of these PUFs.

As can be seen from the data listed in Table 3, with the increasing PUF isocyanate index, also the compressive strength, modulus of compression, and water absorption increase. The optimal complex of physical and mechanical properties for such PUFs is achieved at isocyanate indices from 150 to 200. The PUFs prepared at II = 125 are characterized by poor properties; namely, they have a high shrinkage and the closed pore content is lower by 50%. In turn, PUFs with II \geq 250 have a poor adhesion to metal structural members, and their water absorption capacity grows. The increase of water absorption at II \geq 250 can be explained by the fact that, owing to the steric factors, the prepared foams have an insufficiently high conversion degree of isocyanate groups. The free NCO groups present in the polymer matrix of PUFs act as a peculiar “water absorbent”, and this factor also promotes the growth in the hydrophilicity of foams, which are comparable with the water-blown PUF Lagopur 402 (Lagomat, Sweden). Isocyanurate rings-containing PUFs prepared from vegetable oil polyols are characterized by very low water absorption indices in comparison with the water-blown PUF Lagopur 402 prepared from petrochemical polyols. This can be explained by the fact that there are long fatty acid side chains of hydrophobic nature in the polymer matrix of the former foams. The optimum complex of the physical and mechanical properties of PUFs is achieved for PUF compositions with isocyanate indices of 150–175.

As follows from the data listed in Table 4, the spray PUFs modified with isocyanurate rings have good physical and mechanical properties. Similarly to other spray PUFs [12], also these foams are anisotropic materials, which this property being more pronounced for samples with a low density. The high degree of anisotropy of these PUFs is testified by a great distinction in the values of the modulus of elasticity E and Poisson’s ratio in the parallel (//) and perpendicular (\perp) directions to the foam rise. The obtained PUFs with isocyanate index values from 150 to 175 are hydrophobic materials owing to the fact that higher saturated and unsaturated fatty acids’ side chains are incorporated in their polymer matrix.

Table 3. Physical and mechanical properties of PUFs with different isocyanate indices

Parameter	II = 150	II = 175	II = 200	II = 250	Lagopur 402
Density, kg/m ³	48.9	49.8	37.6	37.9	39.2
Compressive strength, MPa	0.17	0.15	0.13	0.18	0.18
Modulus of compression, MPa	4.80	6.33	4.50	6.29	5.12
ΔV at 70 °C, 95% RH \times 48 h, %	1.30	1.24	0.72	1.30	0.82
Water absorption, vol. %	1.36	1.62	2.37	2.73	3.70
Closed cell content, %	85	89	88	90	92

It is known that the urethane formation reaction proceeds with an exothermal effect of 83.2 kJ/mol, but the isocyanate groups cyclotrimerization reaction with 66.5 kJ/mol [13]. The conversion of isocyanate groups in PUF samples can be judged from the fixed maximum temperature (T_{\max}) of conducting the samples' foaming in adiabatic conditions. It can be seen from Fig. 3 that when the potassium oleate concentration increases from 0.3% to 0.76%, T_{\max} grows from 135 to 163 °C, which testifies an increase in the conversion degree of functional groups. During the PUF blowing process, the highest T_{\max} values are achieved at 0.45–0.60 wt % potassium oleate concentration. An increase in the catalyst concentration above 0.60 wt % does not influence the T_{\max} values any more. These results correlate well with FTIR spectroscopy data on NCO groups' conversion dependence on the potassium oleate concentration in PUF compositions (Fig. 2).

Table 4. Physical and mechanical properties of the spray polyurethane foams with the isocyanate index of 170

Parameter	$\rho = 50$ kg/m ³	$\rho = 65$ kg/m ³	$\rho = 80$ kg/m ³
Compressive strength //, MPa	0.28	0.31	0.56
Compressive strength \perp , MPa	0.12	0.26	0.56
Modulus of compression //, MPa	19.6	29.2	33.7
Modulus of compression \perp , MPa	3.0	10.7	20.2
Poisson coefficient of compression //	0.62	0.32	0.45
Poisson coefficient of compression \perp	0.16	0.26	0.28
Tensile strength \perp , MPa	0.27	0.46	0.45
Modulus of elasticity (E) in tension \perp , MPa	7.5	19.2	28.0
Water absorption after 7 days, vol. %	1.7	1.60	1.50
Closed cell content, %	91	93	90
$E_{//}/E_{\perp}$	6.5	2.7	1.7

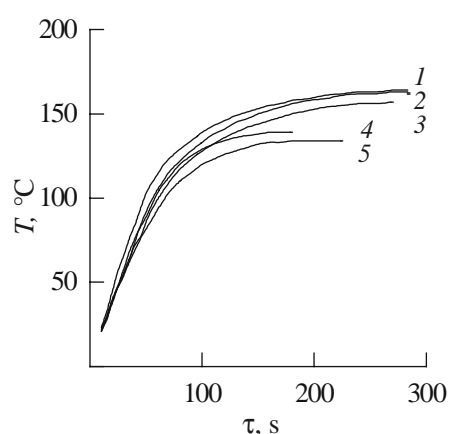


Fig. 3. Dependence of temperature on time in the PUF adiabatic foaming process. Potassium oleate concentrations: 0.76 (1), 0.60 (2), 0.45 (3), 0.30 (4), and 0.15 (5) wt %.

CONCLUSIONS

- Water-blown PUFs containing isocyanurate rings were obtained from rapeseed oil polyols with isocyanate index values from 150 to 250. The obtained PUFs are characterized by good mechanical properties and very low water absorbance indices.
- The conversion degree of isocyanate groups in the polymer matrix of the water-blown PUF can be controlled with a potassium oleate – N,N-dimethyl-ethanolamine catalytic system.
- Spray PUFs with good physical and mechanical properties were obtained from rapeseed oil polyol.

REFERENCES

1. Heidbreder, A., Höfer, R., Grützmacher, R., Westfechtel, A. & Blewett, W. C. Oleochemical products as building blocks for polymers. *Lipid-Fett*, 1999, **101**, 418–424.
2. Badri, K. H., Ahmad, S. H. & Zakaria, S. J. Production of a high-functionality RBD palm kernel oil-based polyester polyol. *J. Appl. Polym. Sci.*, 2001, **81**, 384–389.
3. Javni, I., Zhang, W. & Petrovic, Z. S. Effect of different isocyanates on the properties of soy-based polyurethanes. *J. Appl. Polym. Sci.*, 2003, **88**, 2912–2916.
4. Javni, I., Petrovic, Z. S., Guo, A. & Fuller, R. Thermal stability of polyurethanes based on vegetable oils. *J. Appl. Polym. Sci.*, 2000, **77**, 1723–1734.
5. Stirna, U. K., Tupureina, V. V., Sevastyanova, I. V., Dzene, A. V., Misane, M. M. & Vilsonne, D. M. Synthesis, structure, and properties of poly(ester urethanes) based on glycerol monostearate. *Polymer Sci.*, 2003, **45**, 765–772.
6. Moss, E. K. & Skinner, D. K. Modified isocyanurate foams. *J. Cellul. Plast.*, 1978, **14**, 143–145.
7. Moriya, K., Naruse, A., Kurita, M. & Sasaki, K. Fire resistant all water blown polyisocyanurate foam. In *Proceedings of Polyurethane Expo'96, October 20–23, 1996, Las Vegas, Nevada*, 349–355.
8. Naruse, A., Nanno, H., Kurita, M., Inohara, H. & Fukami, T. Development of all water-blown polyisocyanurate foam system for metal-faced continuous sandwich panels. *J. Cellul. Plast.*, 2002, **38**, 385–401.
9. Grone, D., Metternich, H. J. & Schoenfelder, W. Quantitative NMR-spektroskopische Analyse der Zusammensetzungen von Glycerinfettsäureestermischungen. *Fett/Lipid*, 1998, **100**, 64–69.
10. Yokoyama, T. Hydrogen bonding in urethanes. *Adv. Urethane Sci. Technol.*, 1978, **6**, 1–29.
11. Buist, J. M. *Developments in Polyurethane - I*. Applied Sci. Pol. Ltd., London, 1978.
12. Yakushin, V. A., Zhmudj, N. P. & Stirna, U. K. Physicomechanical characteristics of spray-on rigid polyurethane foams at normal and low temperatures. *Mech. Compos. Mater.*, 2002, **38**, 273–280.
13. Welte, R. E. Calculation and measurement of reaction temperature in rigid polyurethane and polyisocyanurate foams. *J. Cellul. Plast.*, 1984, **20**, 351–356.

Rapsiõli polüoolidest saadud poliüuretaanvahtude struktuur ja omadused

Uldis Stirna, Irina Sevastyanova, Maria Misane, Ugis Cabulis
ja Ilze Beverte

Kasutades puhumisagendina vett, on rapsiõli transesterdatud polüoolidest saadud erineva isotsüanaatrühmade sisaldusega vahtpolüüretaanid, millele on määratud füüsikalisi-mehaanilisi omadusi. Optimaalse isotsüanaatrühmade sisaldusega vahtudele on iseloomulik kõrge hüdrofoobsus.