*ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 14, No. 4. 2008*

# Properties of Sprayed Polyurethane and Polyisocyanurate Foams Obtained from Vegetable Oil Polyols

**Vladimir YAKUSHIN***, **Uldis STIRNA**, **Irina SEVASTYANOVA**, **Laimonis DEME**, **Viesturs ZELTIŅŠ**

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

*Received 29 May 2008; accepted 11 September 2008*

A technology of the synthesis of polyols with the hydroxyl value (310 – 320) mg KOH/g from rapeseed and sunflower oils by way of their transamidisation with diethanolamine has been developed. Based on these polyols, compositions for producing polyurethane and polyisocyanurate foams have been formulated. The technology of spraying these compositions both with low-pressure and high-pressure machines has been developed. The comprehensive studies of these foams have shown that, in terms of both mechanical and thermal insulation characteristics, they compare well with commercial PUR foams. The reaction to fire of these foams conforms to the requirements of the E class (EN 13501-1:2002).

*Keywords*: vegetable oil polyols, polyurethane and polyisocyanurate foams, physical and mechanical properties.

## 1. INTRODUCTION

In production of polymer materials, the problem of replacing petrochemical products by new renewable raw materials becomes increasingly urgent. Polyols, synthesised from vegetable oils, could have a significant place in producing rigid polyurethane foams [1 – 3].

In the previous works [4 – 6] the applicability of polyols obtained by way of amidisation of vegetable oils in compositions for producing polyurethane and polyisocyanurate foams has been considered. The studies were conducted mainly on the foams produced by the hand mixing method.

In the present work, results of the investigation of the properties of polyol mixtures and polyols, synthesised in pilot-scale reactors as well as the properties of the foams produced on the basis of the foams sprayed both with low-pressure and high-pressure machines are presented.

## 2. EXPERIMENTAL

### 2.1. Polyols synthesis

Polyols on the basis of vegetable oils, suitable for obtaining polyurethanes, can be obtained by different methods. Most often the transetherification or epoxidation of oils are applied. In the present work, for obtaining polyols, the method of transamidisation of vegetable oils with diethanolamine was applied.

Firstly, in laboratory conditions, optimum synthesis conditions of polyols, suitable for obtaining rigid polyurethane foams and polyisocyanurate foams were determined. The synthesis process was controlled from the diethanolamine conversion degree.

In compliance with the developed technology, the experimental batches of rapeseed and sunflower oil polyols in a small 50-L reactor were synthesised at the temperature 150 °C and reaction time 2 hours.

It should be mentioned that the temperature of conducting synthesis is much lower than in the case of the synthesis of polyols by way of transetherification (170 °C) or epoxidation (170 °C). Besides, as a result of the synthesis, no by-products such as, for example, water are produced. From this viewpoint, the given method of polyol synthesis is a low energy-consuming and environmentally friendly process. It meets the “green” chemistry requirements, as no harmful emissions are formed.

As a result, polyols with the hydroxyl value (310 – 320) mg KOH/g were obtained. The functionality of the synthesised polyols is not high, namely 2.0, therefore, they are especially suitable for obtaining PIR foams.

### 2.2. Development of formulations of rigid polyurethane foams and polyisocyanurate foams

Based on the synthesised polyols, compositions for sprayed polyurethane (PUR) and polyisocyanurate (PIR) foams have been formulated. In the composition’s formulation, besides the synthesised polyols, the following additives were used: tris-chloropropyl phosphate (TCPP) as a flame retardant, Solkane 365 mfc/227ea as a blowing agent, silicone surfactant Tegostab B8870, potassium acetate (30 % dyetheleneglycol solution) and N-Dimethylethanolamine (DMEA) as a catalyst. All the listed components comprise the so-called polyol mixture “A”. To increase the average functionality of the mixture, another polyol, Lupranol 3422, was added therein. As an isocyanate or component “B”, polymeric MDI (Lupranat M20R supplied from BASF AG) was used. A typical formulation of the compositions for obtaining polyisocyanurate (PIR) foams is listed in Table 1.

The formulation of the compositions was developed taking into account the possibility of obtaining foams at the volume ratio of the components “A” : “B” = 1 : 1.

In the process of developing compositions for obtaining polyurethane foams and polyisocyanurate foams, both technological characteristics of the compositions

---

*Corresponding author. Tel.: +371-755-2581; fax: +371-755-0635.
E-mail address: *yakushin@edi.lv* (V. Yakushin)

(viscosity and compatibility of the mixture's components, start time, gel time, etc.) and the physical and mechanical characteristics of the plastic foams manufactured by the hand mixing method were evaluated.

**Table 1.** Typical composition for producing PIR foam

| Component | Pbw |
|---|---|
| Vegetable oil polyol | 70 |
| Lupranol 3422 | 30 |
| Solkane 365 mfc/227 ea | 35 |
| Water | 1.0 |
| Tegostab B 8870 | 1.5 |
| Tris-chloropropyl phosphate | 30 |
| N-Dimethylethanolamine | 6.0 |
| Potassium acetate | 2.0 |
| Polyisocyanate | (isocyanate index 200) |

The stability of the chemical composition (pH) and technological characteristics (start time and gel time of gel formation) of the developed mixtures "A" both on the basis of rapeseed oil polyol and sunflower oil polyol upon storage were checked within 6 months.

## 2.3. Spraying of the developed compositions

The final modification of the composition of polyurethane and polyisocyanurate foams was realized during processing of foams spraying with low-pressure and high-pressure machines at the volume ratio of the components "A" : "B" = 1 : 1.

As a low-pressure spraying machine with mixing the components with compressed air, without the preliminary heating of the components was used. The pressure of the compressed air for mixing the components in the mixing head was 6 bar.

As a high-pressure spraying machine, the Reactor™ E-10 machine (Graco Inc.) was used. Upon spraying, the components were heated up to 30 °C. Fluid working pressure in "A" and "B" side – 110 bar – 120 bar.

The spraying of the foams was carried out at the ambient temperature 20 °C – 21 °C. The foam was sprayed on plywood 12 mm in thickness in compliance with the general requirement of the standard ISO 8873-1 on manufacturing of control samples – panels [7]. The panels were sprayed both in one pass of the maximum possible thickness (40 mm – 50 mm) and in 2 – 3 passes, each 15 mm – 20 mm in thickness.

## 2.4. Determination of the physical and mechanical characteristics of foams

The main physical and mechanical characteristics of foams were determined in accordance with the requirements of the corresponding ISO or EN ISO standards.

Besides conventional mechanical characteristics, the interlaminar adhesive strength between the successively sprayed layers (passes) of the foam in the panel upon transversal tensile force was determined. For the tests, (40 × 40) mm samples with the thickness ~30 mm were used. The samples were cut-out in such a way that the boundary of the layers would locate approximately in the centre of the sample. Metal plates with hubs for fastening to rods with hinged joint to the test machine, were glued to the foam samples from two sides. Test speed was 10 % / min from the sample's thickness.

# 3. EXPERIMENTAL RESULTS AND DISCUSSION

## 3.1. Properties of synthesised polyols

The developed technology of the laboratory synthesis of polyols turned to be fully suitable in conditions of experimental and industrial production. The properties of the polyols, synthesised according to the same technology in experimental and industrial reactors turned to be identical to the properties of polyols, synthesised in laboratory conditions. In all cases, the synthesis process was controlled from the diethanolamine conversion degree.

Polyols from rapeseed and sunflower oils, synthesised according to the developed technology, had practically the same hydroxyl value (310 – 320) mg KOH/g. The polyols with such values of the hydroxyl index could be used for obtaining rigid polyurethane or polyisocyanurate foams.

The viscosity of these polyols differs somewhat. Polyols from rapeseed oil have viscosity at 25 °C 477 mPa·s, while the viscosity of sunflower oils polyol is equal to 605 mPa·s.

In comparison with polyether and polyester polyols, which are obtained from petrochemical products, these polyols at any ratios can be mixed with all blowing agents, including also with n-pentane, isopentane and cyclopentane.

## 3.2. Technological properties of polyol mixture

The synthesised polyols turned to be well compatible with all components, which are commonly used for producing polyol mixtures. The mixtures prepared on their basis are also well compatible with different blowing agents in a rather wide range of concentrations. Upon storage, the polyol mixtures "A" did not laminate and, within the whole period of observation (6 months), remained homogeneous and transparent. The polyol mixtures on the basis of rapeseed oil amide have the density 1.11 g/cm$^3$ and viscosity at 25 °C 176 mPa s.

The polyol mixtures on the basis of sunflower oil amide have the density 1.09 g/cm$^3$ and viscosity at 25 °C 120 mPa s.

In terms of the technological parameters of foaming, both the phenolic mixtures are practically equal. At the temperature of 20 °C – 21 °C, start time and gel time for the sprayed compositions are equal to 3 s and 10 s, respectively.

Upon the prolonged storage of the polyol mixtures at the temperature of 20 °C – 22 °C, their activity (start time and gel time) begins to change negligible only after 2 months of storage.

## 3.3. Physical and mechanical properties of the foams

In contrast to PUR and PIR foams, which are obtained from the polyols synthesised from petrochemical products, the polymeric matrix of these foams is characterised by the absence of ester or ether groups in the polymeric main chain as well as the presence of long saturated and unsaturated fatty acid $C_{12} – C_{22}$ side chains.

This peculiarity of the chemical structure of the foams' polymeric matrix must promote the decrease of the water absorption of these foams, which is important so that the thermal insulation would retain a high insulation ability for a long time. For the same reason, the foams must be more stable to hydrolysis.

Apart from this, long side chains are capable of screening the polar urethane and isocyanurate groups and promoting the intermolecular plasticisation of the polymeric matrix. As a result of this plasticisation, the friability of the PIR foams must decrease.

The studies of the physical and mechanical properties of the produced foams confirmed the specified suggestions. As can be seen from the data summarised in Table 2, sprayed PIR foams are characterised by a high closed cell content, a very low water absorption and rather high mechanical properties.

**Table 2.** Properties of sprayed foams obtained from different vegetable oils. Isocyanate index = 200

| Parameters | Rapeseed oil polyol | Sunflower oil polyol |
|---|---|---|
| Density, kg/m$^3$ | 38 | 34 |
| Compressive strength, MPa | 0.18 | 0.18 |
| Compressive modulus, MPa | 4.3 | 3.6 |
| Tensile strength, MPa | 0.12 | 0.11 |
| Tensile modulus, MPa | 2.75 | 2.1 |
| Elongation at break, % | 4.7 | 5.4 |
| Water absorption 7 days, *V*, % | 2.42 | 2.23 |
| Dimensional stability (volume change at 60 °C), % | +3.7 | – |
| Closed cell content, % | 96 | 91 |
| Fire classification (EN 13501) | E | E |

Fig. 1 shows the dynamics of water absorption changes for both foams within 30 days. As can be seen, the water absorption of the foams on the basis of sunflower oil polyol is somewhat greater than that in the case of the foam on the basis of rapeseed oil polyol.

The fire classification of these foams, in compliance with the requirements of the standard EN 13501-1:2002, was determined from the reaction to fire (EN ISO 11925-2 – test method). According to the results of the tests and the classification of EN 13501-1:2002, both these foams conform to the E class requirements.

The thermal conductivity of both the foams, determined using a guarded hot plate apparatus (ISO 8302:2001) at the temperature 20 °C is 0.028 W/m·K.

It should be also mentioned that the synthesised polyols have the properties of the active substance of the non-ionogeneous surface. This circumstance makes it possible to obtain especially fine porous foams. In practice, all samples of the foams produced both by the hand mixing and sprayed with low-pressure and high-pressure machines had the average pore size 200 μm – 300 μm. The microstructure of a typical foam sample is shown in Fig. 2.

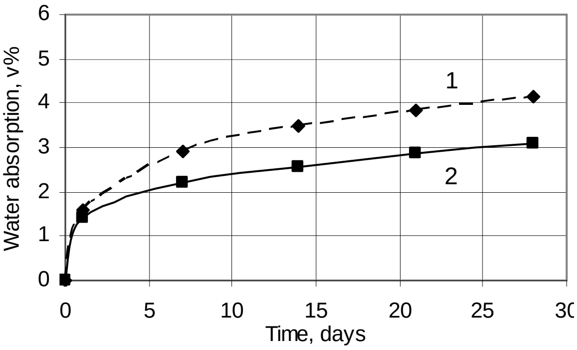

**Fig. 1.** Dependence of the water absorption versus the time for foams on base of: 1 – sunflower oil polyol, 2 – rapeseed oil polyol

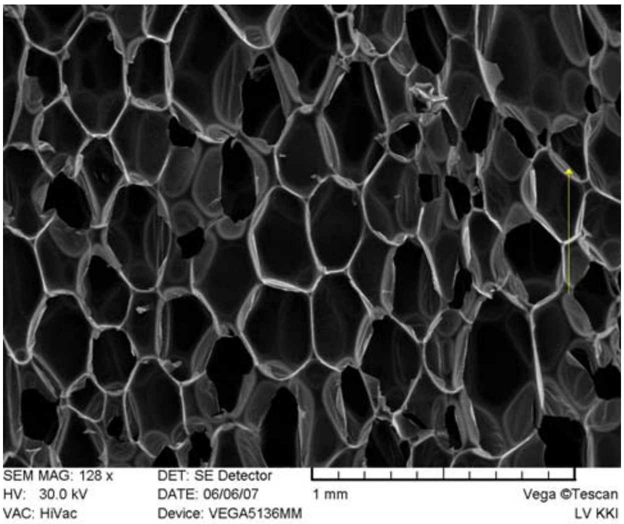

**Fig. 2.** Microstructure of sprayed foam on base of sunflower oil polyol

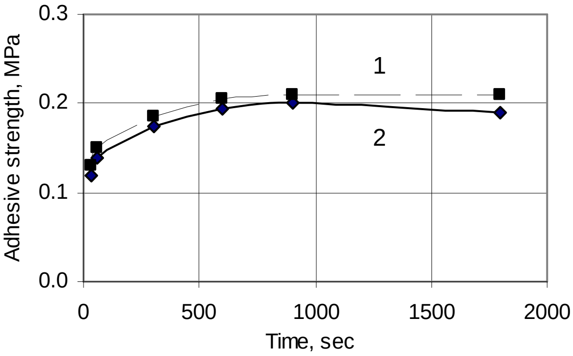

**Fig. 3.** Dependence of the interlaminar adhesive strength versus passes pause duration for PIR foams on base of: 1 – rapeseed oil polyol, 2 – sunflower oil polyol

In the process of upgrading the technology of spraying the developed foams, special attention was drawn to the investigation of the interlayer adhesion upon the spraying of the foam insulation in 2 – 3 layers. Such a method for spraying is recommended by many companies, producing components for sprayed polyurethane foams. Fig. 3

demonstrates typical dependencies of the interlaminar adhesion on the duration of the pause between the two successive sprayings. Based on the presented data, the spraying of the second layer of the foam should be performed no earlier than in 2 min after the accomplishment of the spraying of the previous layer. At a lesser duration of the pause, not only a lower adhesion strength but also local peel-off of the upper layer was observed.

## 4. CONCLUSIONS

1. Polyol synthesis, based on vegetable oils transamidisation, is an environmentally friendly process, and the obtained polyols are competitive with the polyols synthesised from petrochemical raw materials.
2. PUR and PIR foams from transamidised rapeseed and sunflower oils are characterised by an especially low water absorption ability.
3. The mechanical and thermal insulation properties of the new foams compare well with commercial PUR foams.

### *Acknowledgments*

Financial support from the Latvian State Science and European Regional Development Foundation (Activity 2.5.1.) is greatly appreciated.

## REFERENCES

1. **Hill, K.** Fats and Oils as Oleochemical Raw Materials *Pure and Applied Chemistry* 72 (7) 2000: pp. 1255 – 1264.
2. **Gandini, A., Belgacem, M. N.** Polymers Derived from Renewable Resources *Journal of Polymer and the Environment* 10 2002: pp.105 – 114.
3. **Hu, Y. H., Gao, Y, Wang, D. N., Hu, C. P.** Rigid Polyurethane Foam Prepared from a Rape Seed Oil Based Polyol *Journal of Applied Polymer Science* 84 (3) 2002: pp. 591 – 597.
4. **Stirna, U., Cabulis, U., Beverte, I.** Water-blown Polyisocyanurate Foams from Vegetable Oil Polyols *UTECH Europe 2006 Conference Papers*, Maastricht, Netherlands, 28 – 30 March, 2006: 14 p.
5. **Stirna, U., Yakushin, V., Misane, M., Sevastyanova, I.** New Polyurethane and Polyisocyanurate Foams Obtained from Vegetable Oil Polyols *Baltic Polymer Symposium 2007*, September 19 – 21, Druskininkai, Lithuania, p. 71.
6. **Stirna, U., Cabulis, U., Beverte, I.** Water-blown Polyisocyanurate Foams Vegetable Oil Polyols *Journal of Cellular Plastics* 44 2008: pp. 139 – 160.
7. ISO 8873-1:2006 Rigid Cellular Plastics-Spray-Applied Polyurethane Foam for Thermal Insulation. Part 1: Material Specification.

*Presented at the 17th International Conference*
*"Materials Engineering'2008"*
(*Kaunas, Lithuania, November 06 – 07, 2008*)

DOI: 10.5755/j02.ms.26201