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Doctoral Thesis

# Polyols bearing azosulphonate units as novel additives for polyurethane foams

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# AFFIDAVIT

I declare on oath that I wrote this thesis independently, did not use other than the specified sources and aids, and did not otherwise use any unauthorized aids.

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# Abstract

This PhD thesis presents new polyurethane foams with a polar surface-active component that have other morphological and thermal properties than conventional PU foams do have. The novel PU foams were produced with polar additives and tested for thermal properties, showing successful results.

The modification of PU foam with polar azo components has not been considered in the published literature yet. These azo components, indeed, possess some special properties, they are polar, water-soluble, surface-active, light sensitive and non-toxic. Hence, a new PU foam based on commercial polyols and isocyanates with a novel synthesized azo polyol was developed to achieve enhanced thermal properties.

The selection of the modified system in this work was based on the required foam properties and processing, therefore a polar 3-carboxyphenyl-azosulphonate was chemically bonded to the standard polyol in such a way that it does not react with isocyanate during PU foam manufacturing. For the manufacturing of foams under laboratory conditions, the components of the reagent mixture were consequently premixed with each other by an automatic mixer. Taking into account the importance of foam cell gas analysis, an improved gas chromatography-mass spectrometry (GC-MS) method for detection of foam cell gas content was developed. The effect of additive incorporation and mixing parameters on foam kinetics, cellular structure, foam gas phase and the overall thermal conductivity of the foam was investigated as well.

# Kurzfassung

In dieser Doktorarbeit werden neue Polyurethanschäume mit polaren oberflächenaktiven Komponenten vorgestellt, die sich durch ihre morphologischen und thermischen Eigenschaften von herkömmlichen PU Schäumen unterscheiden. Diese neuartigen PU Schäume konnten mit Hilfe von polaren Additiven hergestellt werden und zeigen hinsichtlich ihres Wärmedammverhaltens vielversprechende Ergebnisse.

Die Modifikation von PU Schäumen durch polare Azo-Komponenten wurde vor dieser Arbeit noch nicht in der Literatur veröffentlicht. Die verwendeten Azo-Komponenten zeichnen sich durch spezielle Eigenschaften wie Polarität, Wasserlöslichkeit, Oberflächenaktivität, Lichtsensitivität aus. Dies führte dazu, dass neuartige PU Schäume auf Basis herkömmlicher Polyole und Isocyanate durch Zugabe von synthetisiertem Azo-Polyols mit verbesserten Eigenschaften entwickelt werden konnten.

Die Auswahl der Komponenten für das in dieser Arbeit verwendete modifizierte System wurde durch die erforderlichen Schaumeigenschaften und die Verarbeitung bestimmt. Hierfür wurde ein 3-Carboxyphenyl-Azosulphonat chemisch an ein Standardpolyol derartig gebunden, so dass es während der Polyaddition nicht mit dem Isocyanat reagiert. Für die Schaumherstellung unter Laborbedingungen wurden die einzelnen Komponenten gemeinsam in einem speziellen Mischsystem dispergiert. Wegen der bedeutenden Rolle der Zellgasuntersuchung wurde eine neuartige Methode auf Basis der Gaschromatographie-Massenspektrometrie (GC-MS) zur Detektion des Schaumzellgasinhalts entwickelt. Zusätzlich wurden in dieser Arbeit die Additivaufnahme, der Einfluss der Mischparameter auf die Schaumkinetik, die Zellstruktur, die Gasphase selbst und die Wärmeleitfähigkeit des Schaumes untersucht und in Relation zueinander gestellt.

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# Contents

## List of abbreviations

| Abbreviation | Description |
|---|---|
| PU | Polyurethane |
| FTIR spectroscopy | Fourier transform infrared spectroscopy |
| GC-MS | Gas chromatography – mass spectrometry |
| NMR spectroscopy | Nuclear magnetic resonance spectroscopy |
| RT | Room Temperature |
| SEM | Scanning electron microscopy |
| UV/Vis spectroscopy | Ultraviolet/Visible light spectroscopy |
| pH | Scale specification for acidic/basic water-based solution |
| DMAP | 4-Dimethylaminopyridine |
| DCC | Dicyclohexylcarbodiimide |
| DCU | Dicyclohexylurea |
| F-St5; F-St10; F-St20; F-St40 | Standard PU foam mixed different period of time (5s, 10s, 20s, 40s) |
| F-0.5; F-3; F-5; F-10; F-20 | PU foam modified with different concentration of additive (0.5%, 3%, 5%, 10%, 20%) |
| MUL | Montanuniversität Leoben |

## List of symbols

| Symbol | Unit | Meaning |
|---|---|---|
| m | g | Mass |
| V | ml | Volume |
| M | g/mol | Molar mass |
| $\bar{M}_w$ | g/mol | Weight average molecular weight |
| ρ | $Kg/cm^3$ | Density |
| T | °C | Temperature |
| η | Pa·s | Viscosity |
| λf | $mW \cdot m^{-1} \cdot K^{-1}$ | Total thermal conductivity of foam |
| λg | $mW \cdot m^{-1} \cdot K^{-1}$ | Thermal conductivity of foam gas phase |
| λs | $mW \cdot m^{-1} \cdot K^{-1}$ | Thermal conductivity of foam solid polyurethane |
| λr | $mW \cdot m^{-1} \cdot K^{-1}$ | Radiative thermal conductivity |
| Wt% | % | Weight percentage |
| H | cm | Height |
| OH | - | Hydroxyl number |
| ε | l/mol·cm | Molar absorption coefficient |

# Chapter 1

## General Introduction

### *Motivation*

Standard polyurethane (PU) foam contains only 8 to 2% polyurethane and the rest is gas, by volume. This 92 - 98 % of gas by volume in the foam is a low thermal conductivity gas mixture consisting of two blowing agents (BA) $C_5H_{10}$ and $CO_2$ and diffused air from the surroundings.[1,2] Such material structure makes PU foam a popular product in thermal insulation applications in the temperature range from – 196 °C up to 130 °C, particularly in building, transportation and pipeline fields.[3-5] During service life of product, insulation foam ages, variations in thermal conductivity of the foam are significant in terms of commercial profile of product and in terms of calculating of energy saving in large scale. Thus, over the years, scientists have changed the blowing agent type and foam morphology due to requirements of business, ecology and technical standards on thermal properties of PU foam.[1,6]

For evaluation of thermal insulation ability of the foam, the heat transfer in PU foam has to be determined. There are four modes of heat transfer in PU foam, namely thermal conductivity of gas phase, thermal conductivity of solid polyurethane, radiation between cell walls and convection.[7,8] Generally there are two approaches to improve the thermal insulation ability of foam. One concerns the change of the initial foam thermal conductivity already during foam manufacturing, another one concerns the long-term value of foam thermal conductivity during service life of product. There are several mechanisms that cause deterioration of foam insulation ability. One of them is the diffusion of blowing gas molecules $C_5H_{10}$ and $CO_2$ out of the foam cells and the diffusion of atmospheric gases into the cells, which impact the gas phase thermal conductivity.[1] Another one is the influence of the environment conditions during product service life time, such as temperature, humidity, mechanical forces, which impact the solid polyurethane thermal conductivity.

Thus, the aim of the work is to develop a new PU foam, which has improved thermal insulation than conventional foams.

### *Research approaches towards the reduced permeability of polymers*

Generally polymers are permeable for gases and liquids due to their low density and structure. For the implementation of a barrier against gas transport through the mono material polymer, they can be combined with other polymer materials. There is a great variety of polymer types and combination techniques, that lead to the better barrier against permeant. The process, by which the gases, vapors, liquids and aromas can be transportable, depends on the structure of the solid polymer material. Polymers show different permeation coefficients for gases. There are many factors and effects that influence the permeation, diffusion and solubility, which will be summarized below.[9]

*Effect of carbon chain length of permeant*

Several studies on carbon chains showed that longer molecular chains demonstrate higher affinity to migration of the permeant into the polymer than the shorter one.[9-12]

*Effect of polymer structure*

Besides influence of molecular structure of polymer, the nature of permeant influences the permeation. The following factors were summarized from the literature:

- Micro holes. They can appear from the effect of the temperature, they have considerable impact on the gas transportation.
- Crystallinity. It shows its impact in such a way that solubility of gas happens just in the amorphous phases and not in crystal phases of the polymer.
- Polarity.
- Branching degree. It influences the hardness of the polymer. Orientation or expansion properties of polymer depend on the method of manufacturing and are closely related to the mechanical properties of the polymer. They increase the crystallinity of the semi-crystalline polymers (PE) and decrease their permeation and diffusion (PE, PP, PVC, PC, PET).
- Additives. They decrease the glass transition temperature and increase the number and size of micro holes, which lead to the higher permeation and diffusion.
- Polymer blends that have an impact on the permeation in any case.[9,10]

*Effect of functional groups and polarity of permeant*

Nonpolar molecules diffuse faster and easier through the nonpolar polymer, than those which contain polar groups. Thus, nonpolar gases such as oxygen, nitrogen, carbon dioxide or cyclopentane dissolve better in the nonpolar polymers such as Polyethylene (PE) or Polypropylene (PP). Polarity is described as the permanent change of charge distribution in the molecules or parts of molecules. In the study of Fayoux about sorption properties it was shown that in two chemically similar terpenes (Lime and Carvone) with different polarity the faster diffusion happens on the side of lower polar lime.[9,10]

## *Concept of this PhD thesis*

The concept of this PhD thesis was based on the formation of surfactant barrier layer on the cell wall of the foam for preventing the permeation of the cell gas through the foam in such a way that thermal conductivity of the foam remains constant low (Figure 1-1). Scientific idea towards the reduction of permeation of gas through the polymer was built up on two approaches selected from the above described variety of approaches namely on additive and polarity.

For implementation of the polarity approach the polar material 3-carboxyphenyl-azosulphonate was selected. This substance is classified as surface active agent, surfactant, which contains polar and nonpolar groups in its molecule. Generally azo substances are known in literature as highly polar materials.[13]

For implementation of the additive approach several tasks were set. Firstly, attention was paid to the state of the additive, the priority was given to the liquid state, while solid incorporations might lead to the micro holes in the PU foam matrix increasing the permeation and diffusion of permeant. Secondly, attention was paid to the compatibility of the additive with the PU foam matrix and to the way of incorporation of additive into the PU foam matrix. For this purpose one of the main components of PU foam formulation, polyol, was modified. This method is one of the most common in literature.[5,14-16]

Finally, it was decided to combine these two approaches and to modify the polyol with 3-carboxyphenyl-azosulphonate (azo polyol). Thus, the concept of this PhD thesis is to make PU foam in a way that classical PU foam components – isocyanate and polyol are added together with a modified polyol component. The azo polyol should be synthesized without free hydroxyl groups, in order not to disturb the stoichiometry of PU foam formulation. In this case, firstly, highly polar additive is added to the nonpolar PU foam and decreases permeation of nonpolar gases, such as $N_2$, $O_2$, $CO_2$ and $C_5H_{10}$. Secondly, the new additive is chemically compatible with PU foam matrix. Thirdly, the new additive is applied in a liquid state to prevent micro holes in the PU foam matrix. The accumulation of azo polyol interfacial surfactant is carried out at the boundary layer in such a way that a new polar layer is formed on the cell wall (Figure 1-1).

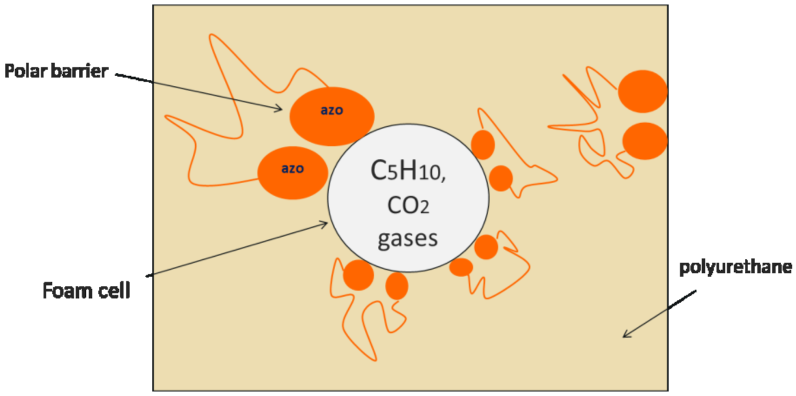

**Figure 1-1** Formation of a surfactant polar layer on the cell wall of PU foam

## *Outline of work*

This PhD thesis concerns the development of PU foam based on commercial polyol and isocyanate with novel synthesized azo polyol. The new foams have other morphology and thermal properties than conventional foams do (Chapter 5).

Considering that PU foam is a nonpolar material and its cell gases $N_2$, $O_2$, $CO_2$ and $C_5H_{10}$ are also nonpolar, the selection of the barrier system in this work was based on highly polar additive, 3-carboxyphenyl-azosulphonate. Thus, 3-carboxyphenyl-azosulphonate was chemically bonded to the standard polyol in such a way in order not to react with isocyanate during PU foam manufacturing (Chapter 4). Additive synthesis has been followed by its incorporation into PU foam matrix and controlling of foaming process in lab conditions (Chapter 5).

Taking into account that measurement of gas content in polyurethane foams has been rarely considered in the published literature[17,18], an enhanced gas chromatography-mass spectrometry (GC-MS) method for the separation of cell gases in PU foam was developed. The thermal conductivity of cell gas mixture is considered as an example of the potential application of this novel GC-MS method (Chapter 2).

The complex analysis of new modified foam density, the presence of open cells, cell size and thermal conductivity of cell gas mixture was uniquely done to contribute to the understanding of PU foam thermal conductivity.

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# Chapter 2

## Materials and Methods

### 2.1 Materials

**Table 2-1** List of applied materials

| Chemical reagent | Description | CAS-No. | Supplier |
|---|---|---|---|
| *PU foams manufacturing* | | | |
| Polyol | Elastopor* H 2130/88/OT Mixture of polyol, catalyst, additives | | BASF Polyurethanes GmbH |
| Isocyanate | IsoPMDI 92140 | | BASF Polyurethanes GmbH |
| Cyclopentane | 98% | 287-92-3 | Sigma-Aldrich |
| Azo polyol | | | Synthesized internally |
| *Azo polyol synthesis* | | | |
| 3-Carboxyphenyl-azosulphonate sodium | | | Synthesized internally |
| Polyol | Elastopor* H 2130/88/OT Mixture of polyol, catalyst, additives | | BASF Polyurethanes GmbH |
| N,N’-Dicyclohexyl-carbodiimide | DCC, puriss., ≥99.0% (GC) | 538-75-0 | Sigma-Aldrich |
| 4-(Dimethyl-amino)-pyridine | DMAP, ReagentPlus, ≥99% | 1122-58-3 | Sigma-Aldrich |
| Dichloromethane | $CH_2Cl_2$, Rotisolv, ≥99.9%, GC Ultra Grade | 75-09-2 | Carl Roth |
| Acetic acid | Rotipuran 100% | 64-19-7 | Carl Roth |
| *3-carboxyphenyl-azosulphonate sodium* | | | |
| 3-Aminobenzoic acid | 98% | 99-05-8 | Sigma-Aldrich |
| Hydrochloric acid | HCl, 37% solution | 7647-01-0 | ACROS Organics, Carl Roth GmbH + Co. KG |
| Sodium carbonate | $Na_2CO_3$, water free, | 497-19-8 | Carl Roth GmbH + |

| | | | |
|---|---|---|---|
| | ≥99% | | Co. KG |
| Sodium nitrite | $NaNO_2$ | 7632-00-0 | Sigma-Aldrich |
| Sodium sulphite | $Na_2SO_3$, BioUltra, anhydrous, ≥98% (RT) | 7757-83-7 | Sigma-Aldrich |

## 2.2 Equipment

**Table 2-2** List of utilized equipment

| Equipment | Description |
|---|---|
| *Laboratory equipment* | |
| Analytical balances | "Kern ABT220-4M"<br>Weighing range: 0.01-220 g; weighing resolution: 0.1 mg; weighing accuracy; calibration:internal |
| Magnetic stirrer | "IKAMAG RCT Standard"<br>Rotation speed: 0-2000 rpm; heating capacity 600W; Temperature range: 0-310 °C; Temperature sensor: PT1000 |
| Mixer | „VM-200 Vortex Mischer StateMix"<br>Roration speed: 0-2000 rpm (0-100%); Rotation time: 0-60 sec; Mixing capacity: 200 g; Working temperature: 10 - 40°C |
| Vacuum drying chamber | "Binder", model VD 23<br>Volume: 23 L; Temperature range: RT - 200 °C |
| Rotation evaporator | "Heidolph Laborota 4000 Eco"<br>Temperature range of hot water bath: 20 - 100 °C |
| Filter paper | "Macherey-Nagel"<br>MN 615 ¼ Ø 240mm |
| *GC-MS test equipment* | |
| Desiccator – internal assembly | Desiccator Typ 5311, PC<br>Outer diameter 280 mm, inner diameter 251 mm; transparent; light; 0.95 bar inner pressure keeps for 24h; with silicon ring;<br>"Butoject Glove" for connection to desiccator; size 08, strength 0.7mm; butyl<br>Turn-over flange stoppers Ø 10.2 mm, silicone, code: 467010-50<br>Sticky tape for better connection between desiccator and its cover<br>Tube for connection between desiccator and argon isolation gas cylinder |
| Syringe | Trajan SGE Syringe<br>P/N 004279; 50R-V-GT; 50 µl |

| | |
|---|---|
| Needle | Trajan Side-Port needle<br>P/N 038815; NV25/2.5M-5/0.63H |
| Vials with caps | Rotilabo vials with thread (ND13, 4 mL)<br>Screw caps (PP, ND13) with septum (butyl/PRFE, 1.3 mm 55°) |
| Calibration Gas cylinder | "Linde Gas calibration mixture"<br>Carbon dioxide (0.041%) + C-pentane (1%) + Nitrogen (98.96%) |
| Argon Gas cylinder | Argon gas for desiccator atmosphere |
| *Spectroscopic and microscopic equipment* | |
| FTIR spectrometer | "Bruker VERTEX 70"<br>Wavelength range: 6000-130 $cm^{-1}$; resolution: 0.4 $cm^{-1}$ |
| NMR spectrometer | "Agilent"<br>NMR 400MHz resonance frequency; methods: $^1H/^{13}C$; various solvents |
| SEM/EDX | „Zeiss Auriga 60"<br>Crossbeam workstation; voltage accelerator: 0.1-30 kV; detector system: InLens, CZ BSD |
| UV/Vis spectrometer | "Agilent Cary 50"<br>Wavelength range: 190-1100 nm; scanning speed: up to 24 000 $nmmin^{-1}$; optical system: dual beam; light source: Xenon flash lamp |
| *Additional analytic equipment* | |
| Gas Chromatograph-Mass spectrometer | "Shimadzu GCMS-QP2010 Plus"<br>Fused silica capillary column (length 30 m, ID 0.25 mm). Flow rate of the carrier gas He |
| Water content meter | "899 Coulometer"<br>Measuring range: 10 µg – 200 mg absolute water |
| Rheometer | "Anton Paar", model MCR 102<br>Maximum torque 200 mNm; Min. torque (rotation) 5 nNm; Min. torque (oscillation) 7.5 nNm |
| *Instrument for measuring thermal conductivity* | |
| Thermal conductivity meter | "Hot Disk AB", model Hot Disk TPS 2500S<br>Temperature range: - 190 to 180 °C (standard sensor: Nickel sensor with Kapton coating, various sensor sizes); Measuring range 0.005 to 500 W/(m·K); measurement time 1 to 2560 s |

## 2.3 Gas chromatography – mass spectrometry method to detect gas phase composition of polyurethane foam

### 2.3.1 Introduction

Not much attention has been paid to the gas content measurement of PU foams. The reason for that is the complexity of the gas chromatography - mass spectrometry (GC-MS) measurement of atmospheric gases. In the seventies and eighties there were two categories of cell gas analysis methods: the chemical analysis and those one based on physical principles. The chemical analysis was based on the dissolving of cell gases and performing a titration. The physical analysis consisted of infrared spectroscopy, gas chromatography and mass spectrometry.[1,2] In the nineties and in the 21st century gas chromatography was considered as the main method for testing the gas content, the only difference was in sampling methods. In du Cauze de Nazelle's[1] and other[3] studies a gas sampling is performed right from the foam by a syringe in a desiccator filled with gas that is not used in foams and does not interfere with the other gaseous components in the chromatographic analysis. In other research works the foam cylindrical samples are drilled out of foam, rotated and pressed together[4-7] or grinded[7,8], specific instrument collects escaping gases into GC injection port.

In methods where the foam is compressed during sampling[4-6] one of the drawbacks is a high applied pressure and due to this fact the increased amount of blowing agents may dissolve in the solid polymer. In order to eliminate this risk, the "grinder" method[7,8] was developed, where the pressure is not affected during sampling. Beside this, for some foams it was found that if the pressure of flushing gas (that is used in order to remove all oxygen and nitrogen in the gas phase surrounding the sample) is too high, this gas can diffuse into the foam and a too high cell gas pressure might be calculated. It is necessary to note that the sampling does not lead to the rise in temperature, because the last one can increase the amount of hydrocarbons in the gas phase due to higher vapor pressure and lower solubility in a matrix polymer. For example, in sampling grinding methods, temperature rise can't be measured. However, high density foams are difficult to grind and the procedure takes a long time that leads to a rise in temperature. Additionally, both grinding and compressing-crushing methods require a special setup beside the syringe and GC chromatograph.[4-8]

The method with direct penetrating of the foam is simple in implementation and fast, there is no change in partial pressure of cell gases and temperature during sampling. However, there are possible disadvantages. The first one is dealing with the variable quantity of desiccator gas surrounding the foam sample sucked into the syringe when taking out the gases from the cells. The second one can be the gas losses and air contamination when bringing the filled gas sampling syringe from the desiccator to the gas chromatograph injection port.[1,3] The approach followed herein eliminates both risks. In order to eliminate the first risk, the argon gas that is inside desiccator and that one which was sucked into syringe during foam penetrating is measured and calculated. The set of experiments proved that there is no influence of this factor on the final result of foam gas content. In order to eliminate the second risk, the needle of syringe was subjected to a cleaning procedure before sampling and injecting.

In the present work, the new fast and simple GC-MS method for separation of $N_2$, $O_2$, $CO_2$, $C_5H_{10}$ and Ar is described. For this method a PU foam is located inside filled with Ar gas desiccator, where the gas specimen is taken right from the foam manually with a syringe. In research works where the foam is compressed during sampling, the partial pressures of every cell gas derived from the weight of the original foam cylindrical sample, the foam density and closed cell content are calculated and used in determination of cell gas composition, which is given in weight percentage or partial pressures. In the present work where foam is manually puncturing, the partial pressure of cell gases does not change during sampling. Therefore resulted areas under the peak are used for calculation of concentration of every cell gas, given in percentage (volume or mole). Based on this information, it is assumed that the total pressure of cell gases must be calculated in research works with crushing method in order to analyze the cell gas concentrations, because in these methods the original volume of cell gas is changed. Meanwhile, in the present work with syringe penetrating method, there is no change of cell gas volume and the peak area is recalculated to molar fraction of gas that is used in Wassiljewa equation[9,10] for calculation of theoretical thermal conductivity of cell gas mixture. At constant temperature the partial pressure does not change. Even if during penetrating of foam there is a channel, nothing except argon gas will diffuse inside the cell, that means that total pressure may vary, but partial pressures of cell gases will not change.[11,12]

### 2.3.2 GC-MS test parameters

Cell gas content was determined by gas chromatograph-mass spectrometer. Temperature of the column was adjusted to 35 °C. Flow rate of the carrier gas (He) was 146.6 ml/min for split ratio 170 and sample volume 10 µl. SIM mode with 5 mass fragments (m/z = 28; 32; 40; 44; 55) was selected. Sample injections were conducted manually by syringe (SGE Syringe, Trajan Scientific Australia Pty Ltd, Australia).

### 2.3.3 Sampling

**Figure 2-1** Foam gas sampling

A rectangular sample (50 mm x 50 mm x 20 mm) is cut from the foam with a saw. Attention is paid to cutting the skin from all sample sides, because foam skin provides a greater barrier to diffusion than core foam.[13] Then the sample is located in a desiccator, which is blown subsequently with argon gas for removing all air gases around the foam. Argon was selected because it is not applied in PU foams and does not interfere with other gases in the GC analysis. The cell gases of the foam are released by syringe needle penetrating the foam inside desiccator (Figure 2-1). The gas-tight syringe with gas sample is entered the GC column. Afterwards, the gas sample is injected into GC column. The chromatographic analysis is performed.

Much attention has been paid to accurate sampling. For instance, the needle of syringe was cleaned before sampling (by keeping in desiccator before penetrating the foam in order to replace air gases to argon gas on needle surface) and before injecting (by 1 minute keeping inside GC column port and blowing by flow carrier helium gas). Care is taken to the accurate work of needle push-pull valve, in order to avoid the leakage of the gas sample from the syringe during blowing procedure.

Additionally it is highly important to select a suitable syringe for avoiding of contamination the foam gas specimen with surrounding air. Sample storage and sample transportation ability is the main criteria for selecting the manually operated syringe. For this purpose the syringe with push-pull valve with replaceable needle was selected. Such valves allow gas to be stored and transported in the syringe without contamination. Removable needle is recommended for polyurethane foam application, because the utilizer can select the main needle parameters, such as length, gauge as well as a point style. In case of PU foam application the conical needle with side port, so called point style 5, is suggested. This allows achieving efficient foam penetration with minimized needle coring or blocking.

### 2.3.4 Calibration

For finding out the absolute value of unidentified gas concentration, it is necessary to recalculate the obtained relative value of unidentified gas concentration according to the calibrated values of the identified gas concentration. For this purpose, two calibration procedures were developed. The first one is based on measurement of air sample and calibration gas mixture with known concentrations; it should be performed before every experiment on foams. The second one is based on measurement of every examined gas of the whole range of concentrations, this has to be done once and checked on a regular basis. All procedures consist of measuring the areas under the peak depending on gas concentration. The area of the chromatographic peak corresponds to volume percentage of gas in the gas mixture. In the first procedure samples of different known concentrations were injected into GC port by a syringe. In the second procedure instead of injection of gas samples of different concentrations, the change of split ratio was used as a dilution apparatus. That means, injected gas sample volume was fixed and equal to 3 µl, but split ratio was changed in the range of 10-200 and, therefore, the concentration was changed from 100 % to 5 %. Calibration curves show linear behavior of ratio between gas concentration and the area under the peak.

**Table 2-3** Calibration procedure - air sample

| Gas type | Content, vol% |
|---|---|
| Nitrogen | 78.09 |
| Oxygen | 20.95 |
| Carbon dioxide | 0.03 |
| Argon | 0.93 |

A 10 µl volume air sample was injected into GC column. Each measurement was repeated 2 times.

**Table 2-4** Calibration procedure - gas mixture sample (Linde Gas GmbH)

| Gas type | Content, vol% | Content, ppm |
|---|---|---|
| Nitrogen | 98.96 | 989600 |
| Carbon dioxide | 0.041 | 410 |
| Cyclopentane | 1 | 10000 |

A 10 µl volume Linde gas mixture sample was injected into GC column. Each measurement was repeated 2 times.

### 2.3.5 PU foam cell gas composition

The quantitative determination of the gas phase in PU foam mainly consists of sampling and GC analysis. The sampling is procedure is more challenging in comparison with the GC analysis. The major problem was how to obtain a representative specimen of the cell gas without contamination by surrounding air gases. This problem was successfully solved. The gas composition was calculated accurately with input data obtained from measurement of ratio of each peak area on the chromatograms (Figure 2-2; 2-3).

The entire cell gas sampling procedure took place at the room temperature in order not to disturb the equilibrium between gas phase, condensed phase and cell gases dissolved in the polymer. This was of particular interest for cyclopentane.

A clear separation of $N_2$, $O_2$, $CO_2$, $C_5H_{10}$ and Ar from the gas mixture was performed by a SIM mode with 5 mass fragments (m/z = 28; 32; 40; 44; 55) within a short retention time (5 minutes). Each experiment was repeated 5 times in order to obtain an average value of each peak area and careful calibration of the injected gases was very important for having accurate results. Figure 2-2 shows a typical gas chromatogram of the gas mixture of foam sample. Five different peaks were successfully obtained. Overlapping of $N_2$, $O_2$, $CO_2$ and Ar peaks does not make any difficulty in separation and identification of a peak because a SIM mode was used. Each peak was assigned from its retention time and molar mass.

**Figure 2-2** GC-MS chromatogram of 5 foam cell gases, retention time for $N_2$, $O_2$ and Ar is 2.95 min; for $CO_2$ - 2.96 min; for $C_5H_{10}$ – 3.71 min. (X axe: retention time in minutes. Y axe: intensity)

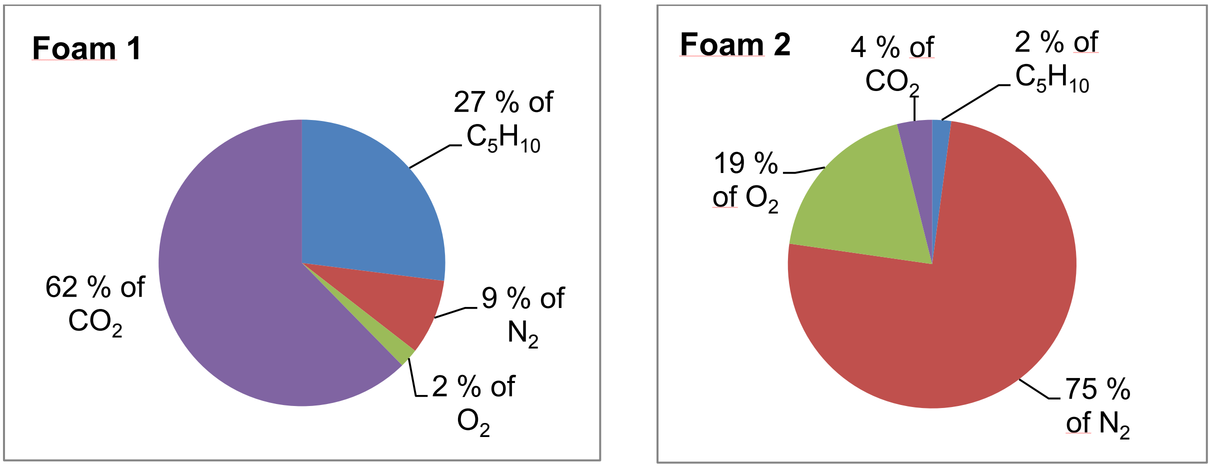

**Figure 2-3** Example of cell gas content of two PU foam samples

### 2.3.6 Prediction of thermal conductivity of gas phase of PU foam

Prediction of thermal conductivity of gas phase of PU foam is an example of potential application of the described in this work gas content method. If one has a cell gas composition, it is possible theoretically to derive the thermal conductivity of the cell gas mixture by Wassiljewa equation.[10]

$$\lambda_g = \sum_{b=1}^{n} \frac{y_b \lambda_c}{\sum_{c=1}^{n} y_b A_{bc}}$$

(1)

Where $\lambda_g$ is the thermal conductivity of the gas mixture, $\lambda_b$ is the thermal conductivity of a pure constituent element i, ($y_b$,$y_c$) are the mole fractions of constituent elements *b* and *c* and $A_{bc}$ is a function of the binary system (A = 1).

For calculations I have used 27 °C thermal conductivities of nitrogen (25.67 $mW \cdot m^{-1} \cdot K^{-1}$)[14,15], oxygen (26.49 $mW \cdot m^{-1} \cdot K^{-1}$)[14,15], carbon dioxide (16.69 $mW \cdot m^{-1} \cdot K^{-1}$)[14,15] and cyclopentane (13.00 $mW \cdot m^{-1} \cdot K^{-1}$)[16].

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# Chapter 3
# 3-carboxyphenyl-azosulphonate sodium

The scientific approach of this PhD thesis is to incorporate a polar additive (azo polyol) into the PU foam and thus to slow down the permeation mechanism. For implementation of polarity approach the polar material 3-carboxyphenyl-azosulphonate was selected among others for chemical coupling to standard polyol. In this chapter the synthesis of 3-carboxyphenyl-azosulphonate sodium is described.

## 3.1 Introduction

### 3.1.1 General information

3-carboxyphenyl-azosulphonate sodium belongs to the class of azo compounds (Figure 3-1 (a.3)). Azo compounds are characterized by the functional group diazenyl R-N=N-R', in which R and R' can be either aryl or alkyl, the N=N group is called an azo group.

For the first time azosulphonates were mentioned in literature in 1869.[1] Back then analysis of compounds was carried out by elemental analysis and distinguished the formation of two isomers (stable trans-isomer and very instable cis-isomer) with different properties. After the 1950's Dijkstra and de Jonge[2] and Lewis and Suhr[3] determined the equilibrium of the reaction together with rates of the separate reaction steps and the pH dependence. They found out that the formation of the primary reaction product (cis-isomer) is very fast and they continued to study in detail the isomerization to the secondary reaction product (trans-isomer). Later in the 1960's the reaction of diazonium salts with sulfite ions and especially the photo-isomerization of the reaction products were studied intensively by Van Beek et al.[4-7]

The application of azosulphonates in PU foams has not been considered in the published literature yet. This azo compound, indeed, has a range of special properties, for instance it is polar, water-soluble, surface-active, light sensitive and non-toxic. The most important characteristics of azo compounds are the color, photo lability and solubility behavior. Azo compounds are often used in polymer chemistry as initiator functions for free radical polymerization. Polymers containing azo group are attractive for high technology applications due to the UV-induced cis-trans isomerism of thermally stable azobenzene derivatives. Depending on the application, a wide range of azo functional groups with different photo and thermal stability has been used in the past in polymer chemistry including azobenzene derivatives, arylalkyl and dialkyl azo compounds, azophosphonates etc.[7]

### 3.1.2 Methodology of synthesis

The described in this work 3-carboxyphenyl-azosulphonate sodium was synthesized in such a way to react with a hydroxyl group from the polyol afterwards. For this purpose, a carboxylic acid was chosen as the functional group of azo compound, since it can be esterified with a polyol hydroxyl group. Therefore, an azosulfonate with a carboxyl group on the aromatic ring was prepared by diazotization followed by coupling with sulfite (see scheme of synthesis on Figure 3-1). Two main organic reactions of this synthesis – diazotization and sulphonation are described below in detail.

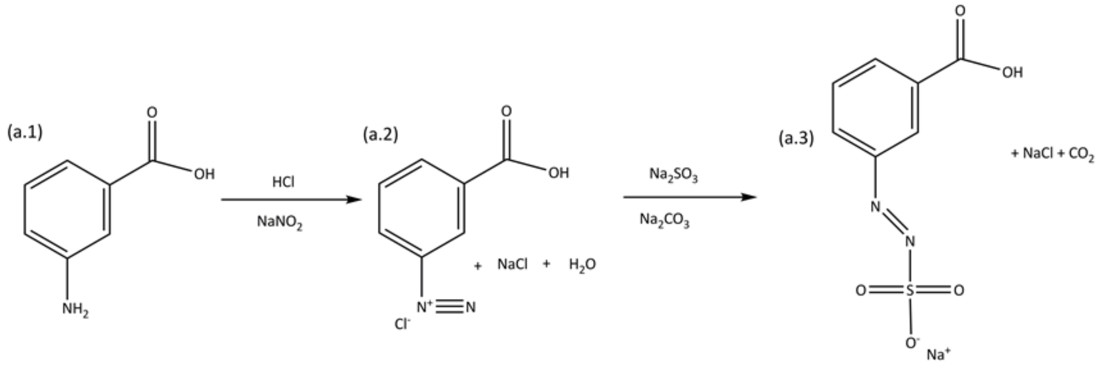
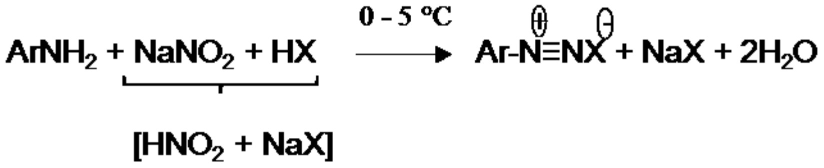


**Figure 3-1** Scheme of synthesis of 3-carboxyphenyl-azosulphonate sodium

## *Diazotization of amino acid*

3-carboxyphenyl-azosulphonate sodium belongs to the class of aryldiazonium salts. Aryldiazonium salts due to their high reactivity and commercial availability are widely used for synthesis of other classes of organic compounds, in the synthesis of chemo-pharmaceutical substances, in industry for production of azo dyes of different colors and tints, therefore aromatic diazo compounds belong to the one of the most important and well-investigated class of organic chemistry.[8]

The main method for the preparation of aryldiazonium salts is a treatment of primary aromatic amines with nitrous acid. The nitrous acid is usually generated by acidification of aqueous solutions sodium nitrite with a mineral acid. This reaction is called “diazotation”, “diazoniatation”, or “diazotization” (Figure 3-2) and it was firstly reported by Peter Griess in 1858.



$$ArNH_2 + \underbrace{NaNO_2 + HX}_{[HNO_2 + NaX]} \xrightarrow{0-5\ °C} Ar\text{-}\overset{\oplus}{N}\equiv N\overset{\ominus}{X} + NaX + 2H_2O$$

**Figure 3-2** Diazotization reaction

For successful diazotation reaction the implementation of well-defined conditions is required. Among them there is the temperature control, acidity of medium and accurate mole ratio of reagents:

1) Temperature control

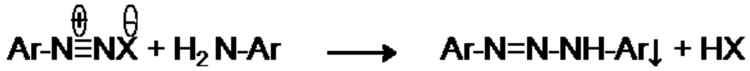
Diazotization is an exothermic reaction following with evolution of huge amount of heat, meantime diazonium salts are thermally not stable (decomposition with gas evolution), therefore the reaction is performed in cooling bath 0 – 5 °C. Careful continuous stirring is required for avoiding of local warming. The reaction is correct, if the solution is transparent and there is no foaming (evolution of nitrogen) as a result of $HNO_2$ decomposition.

2) Acidity of medium

Acidity of medium plays a great role in the diazotization. Hydrochloric acid should be used in more than 3 mol in accordance with 1 mol of amine. The pH value of reaction mixture should be less than 2, 10 minutes after addition of the whole amount of sodium nitrite solution to amine solution. The excess of nitrous acid is required for:

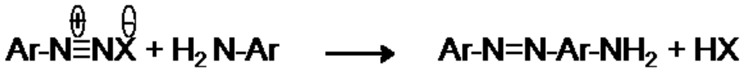
- transferring of amine into soluble salt
- extraction of nitrous acid from its salt
- generation of active diazotizing particle
- stabilization of product (diazonium salt)
- avoiding of byproducts

High acidity is required for avoiding of two undesirable reactions with participation of initial amine and diazonium salt (Ar = aryl):



$$\mathrm{Ar\text{-}\overset{\oplus}{N}{\equiv}N\overset{\ominus}{X} + H_2N\text{-}Ar \longrightarrow Ar\text{-}N{=}N\text{-}NH\text{-}Ar\downarrow + HX}$$

**Diazoamino compound**
**(triazen)**



$$\mathrm{Ar\text{-}\overset{\oplus}{N}{\equiv}N\overset{\ominus}{X} + H_2N\text{-}Ar \longrightarrow Ar\text{-}N{=}N\text{-}Ar\text{-}NH_2 + HX}$$

**Aminoazo compound**

3) Control of nitrous acid amount

Amine and sodium nitrite are used in equal mole ratio. The amount of $NaNO_2$ should be taken with high accuracy, because its excess leads to not stable forms of diazonium compounds, oxidation and resin formation. The presence of nitrous acid is controlled by potassium iodide test paper. At correct reaction process, the paper does not change its original grey-light blue color. By excess of nitrous acid in the reaction mixture the test paper becomes intensive blue due to formation of Iodine:

$$2HNO_2 + 2KI + 2HCl \longrightarrow I_2 + 2NO + 2KCl + 2H_2O$$

Excess of nitrous acid is reduced by addition of urea until evolution of all gases stops:

$$2HNO_2 + H_2N\text{-}CO\text{-}NH_2 \longrightarrow CO_2\uparrow + 2N_2\uparrow + 3H_2O$$

Diazotation reaction goes in time, therefore the control by potassium iodide test paper is performed in 10-15 minutes after addition of the whole amount of sodium nitrite.

4) Nitrite solution should be added drop wise to amine solution by means of dropping funnel during 15-60 minutes depending on the amount of the solution.[8]

### *Sulphonation of aryldiazonium salt*

Azosulphonates can be obtained from azo coupling reaction of aryldiazonium salt and alkali sulfite.[9-13] Sodium sulfite is the most commonly used sulfite for such reaction. It is very important to control the pH of the reaction medium during the coupling reaction. One has to work at pH 7, because the hydrogen sulfite ion ($HSO^{3-}$) is not suitable for the coupling reaction. Higher basicity of the reaction media leads to decomposition products of dark color. In strong acids the azosulfonate is considered only as an intermediate product, meantime the reaction product is phenylhydrazine. Generally for azosulfonate synthesis, sodium acetate or sodium carbonate is added to the aqueous sulfite solution to buffer the reaction, and the diazonium salt solution is added very quickly to the sulfite solution at temperatures below 10 °C. Usually, the resulting solution becomes yellow or orange immediately indicating the formation of the product, however, it is recommended to keep stirring for at least one hour for completion of the isomerization of the cis-isomer to the trans-isomer. The dry cis-isomer has a tendency to explode, that's why it has never been isolated as dried substance and characterized in detail. Most of the low molar mass trans-azosulfonates slowly precipitate from the reaction medium. Trans-azosulphonates can be purified by recrystallization from water, but this process reduces the yield significantly. Due to the very polar character of azosulfonates, purification by other solvents is always difficult. The solubility of almost all azosulfonates is limited to water, mixtures of water with methanol or ethanol and dimethyl sulfoxide (DMSO). The color of the solid, crystalline trans-isomer products varies from light yellow to orange, depending on the substituents on the aromatic ring. These trans-isomer products can be stored in the dark for several years without decomposition. The most common impurities are reaction products of the instable cis-isomer, which can decompose under the formation of diazonium salts before the isomerization process is completed. The diazonium salts can react with other components to deeply colored azo dyes or decompose further to aryl derivatives. A large variety of low molar mass azosulphonates has been synthesized and described in the literature, with 3-carboxyphenyl-azosulfonate-sodium among them.[14,15] The 3-carboxyphenyl-azosulfonate-sodium was obtained as solid, yellow colored compound with high yield, this compound is thermally very stable with decomposition temperature 240 °C and can be dissolved in water.[7]

## 3.2 Experimental part

The described in this work 3-carboxyphenyl-azosulphonate sodium was prepared by diazotization followed by coupling with sulfite (see scheme of synthesis on Figure 3-1). The methodology of this synthesis was described in detail in the introduction to this chapter (see paragraph 3.1.2). The quantity of reagents and conditions of synthesis will be described in detail below.

### 3.2.1 Synthesis of 3-carboxyphenyl-azosulphonate sodium

*Quantity of reagents*

3-aminobenzoic acid in HCl solution (solution A)

1. m (3-aminobenzoic acid, 98%) = 13.7 g
2. V (hydrochloric acid, 37% solution in water) = 27 ml
3. V ($H_2O$) = 73 ml

Sodium nitrite solution (solution B)

1. m (sodium nitrite) = 6.9 g
2. V ($H_2O$) = 100 ml

Sodium carbonate and sodium sulphite solution (solution C)

1. m (sodium sulphite) = 12.6 g
2. m (sodium carbonate) = 15.9 g
3. V ($H_2O$) = 100 ml

*Preparation of solution A*

3-Aminobenzoic acid (13.7 g, 100 mmol) was portion wise dissolved in 100 mL aqueous HCl solution. The mixture was stirred with a magnetic stirrer for 15 minutes at RT to allow good dissolution of 3-aminobenzoic acid. Afterwards, solution A was placed into refrigerator for cooling up to 0 °C.

*Preparation of solution B*

Sodium nitrite (6.9 g, 100 mmol) was dissolved in 100 ml deionized water and stirred with a magnetic stirrer for 15 minutes at RT to allow good dissolution of sodium nitrite. Afterwards, solution B was placed into refrigerator for cooling up to 0 °C.

*Preparation of solution C*

Sodium carbonate (15.9 g, 150 mmol) and sodium sulphite (12.6 g, 100 mmol) were portion wise dissolved in 100 ml deionized water and stirred with a magnetic stirrer for 15 minutes at RT to allow good dissolution of both salts. Afterwards, solution C was placed into refrigerator for cooling to 0 °C.

### *Diazotization of 3-amino benzoic acid. Formation of aryldiazonium salt*

The pre-chilled sodium nitrite solution (solution B) was added drop wise to the pre-chilled amino acid solution (solution A) in the cooling bath during 15-30 minutes. By the end of addition a change in aggregate state and in color was observed (the view of reaction mixture was changing from white slurry to orange transparent liquid, see Figure 3-4). During addition there was almost no foam except some bubbles on the surface of mixture, and no orange color vapor. The reaction mixture was stirred with a magnetic stirrer at 0 °C for 30 minutes for diazotization process following by control of a pH value of 1.

**Figure 3-4** Diazotization of 3-amino benzoic acid, formation of aryldiazonium salt

### *Sulphonation of aryldiazonium salt*

Aryldiazonium salt solution was quickly poured into 100 ml of a pre-chilled sodium sulphite and sodium carbonate solution (12.6 g 100 mmol / 15.9 g 150 mmol) (solution C) at 0 °C with continuous stirring. Care should be taken due to a great foaming (evolution of carbon dioxide). A color of reaction mixture was changed rapidly from orange into light orange. After 40 minutes of stirring it was kept overnight in refrigerator at 4 °C.

### *Protonation, isolation*

After 24 hours of cooling the color of reaction mixture remained the same – light orange. For easier handling the reaction mixture was poured from the glass into a one-liter conic flask. Prior to the protonation step the pH value of 7.5 of reaction mixture was controlled. The reaction mixture was acidified to a pH of 2 by the dropwise addition of hydrochloric acid (37% concentrated, around 10 ml) in the cooling bath with continuous stirring. This led to the precipitation of the product.

Note: During 20 minutes addition of hydrochloric acid to the reaction mixture a slightly foaming and formation of precipitate was observed. At the moment when pH value was changing from 7.5 to 5, the mixture color was changing from light orange to dark yellow. When the pH value reached 2, the color of solution became light yellow (Figure 3-5).

**Figure 3-5** Protonation, isolation

As soon as the pH value of 2 was reached, the resulting yellow mixture was kept overnight at 4 °C to increase the amount of precipitate in the solution, which was filtered through a filter paper. After filtration the precipitate was dried and grounded into fine powder (Figure 3-6). When the product is dried at room temperature, the slides of water are detected by FTIR, therefore drying in the oven at around 40 °C for 18 h is recommended. After filtration the filtrate was discarded. The product of light yellow color in the amount of 25.5 g was obtained. Yield of the reaction: 100 % from theoretically calculated, product was not purified.

**Figure 3-6** 3-Carboxyphenyl-azosulphonate sodium

Note: Synthesis is performed correctly, if obtained powder is of yellow color. If the synthesis is not performed correctly, the product will have a brown or orange color, it depends on the trans/cis isomerism of product (Figure 3-7). To the typical mistakes that lead to formation of cis and not trans-isomer of product refer: inefficient cooling during the whole synthesis, incorrect speed of addition of solutions to each other, dealing with pH value of reaction medium.

**Figure 3-7** 3-carboxyphenyl-azosulphonate sodium of different colors

### 3.2.2 Dissolution of 3-carboxyphenyl-azosulphonate sodium in polyol

The solubility of azosulphonate in the standard polyol was one of the requirements for the selection of the modified system. For that purpose 0.3 g of azosulphonate was added to 3 ml of standard polyol and left for a certain time at RT for dissolution. Visual monitoring was performed daily. After 20 days the whole amount of azo crystals was dissolved in standard polyol. Concurrently to this experiment the dissolution of azosulphonate in cold water was tested. The results showed partial dissolution of azo crystals in water at RT after 20 days.

## 3.3 Results and discussion

For the modification of standard polyol, the polar 3-carboxyphenyl-azosulphonate sodium was selected among other compounds. Carboxylic acid was chosen as the functional group of azo compound, since it can be esterified with a hydroxyl group of standard polyol. The product of light yellow color was synthesized according to the well-known literature source.[14] The azo product was not purified in this work. The identification of synthesized compound was done using FTIR, NMR and UV-VIS techniques.

### *Determination of structure by NMR*

For identification of synthesized compound, 3-carboxyphenyl-azosulphonate sodium was dissolved in deuterated water ($D_2O$) followed by $^1H$ and $^{13}C$ NMR measurements. The spectra for azosulphonate are presented in Figure 3-8. Every peak is color marked in accordance with the corresponding atom of chemical structure.

Analysis of $^{13}C$ and $^{1}H$ NMR spectra showed that all signals could be assigned to the structure of 3-carboxyphenyl-azosulphonate sodium, the signals have a good intensity and compound is of high purity.

$^{1}H$ NMR spectrum shows peaks at 8.3, 8.1, 8.0 and 7.6 ppm, which are assigned to the protons of the aromatic ring. The additional peak at 4.6 ppm is attributed to impurities of deuterated water (Figure 3-8 a).

$^{13}C$ NMR spectrum demonstrates a strong signal of the carboxylic moiety at 169 ppm as well as the Ar-N=N-$SO_3^-$ shift at 150 ppm. The position of carbon atoms of the aromatic ring is in the range of 134 to 125 ppm (Figure 3-8 b).

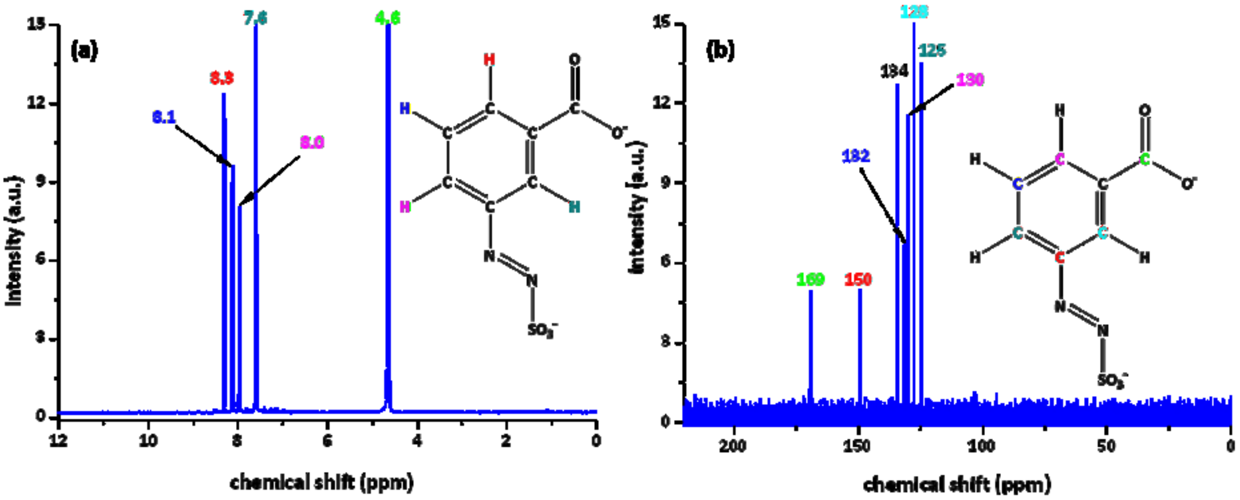


**Figure 3-8** $^{1}H$ (a) and $^{13}C$ (b) NMR spectra of 3-carboxyphenyl-azosulphonate sodium in deuterated water

## *Determination of structure by FTIR*

For identification of synthesized compound, 3-carboxyphenyl-azosulphonate sodium was measured by FTIR spectroscopy. Transmission spectra were recorded in a wavenumber range of 4000-635 $cm^{-1}$, with emphasis on the aryl carboxylic, azo and sulphonic absorption bands (Figure 3-9, Table 3-1).

The FTIR spectrum of azosulphonate shows a strong signal of the aryl carboxylic moiety at 1680 $cm^{-1}$. The observed two bands of small intensity at 1604 and 1590 $cm^{-1}$ could be assigned to primary aromatic amine group (N-H) or/and to aromatic ring group (C=C) or/and to aromatic carboxylate group (Ar-$COO^-$). If one of them or both peaks belong to a primary aromatic amine group, this is a byproduct of diazotization step, when the diazonium salt reacts with the rest of amine. If one of them or both peaks belong to aromatic carboxylate group, it is resulted by the precipitation step, hence a large part of the carboxylic moieties is protonated, while a residue of carboxylates is left.

The observed small peak at 1508 $cm^{-1}$ is assigned to aromatic ring C=C band. The weak absorption of the aromatic azo compound occurs at 1450 and 1424 $cm^{-1}$ (N=N).

Primary aromatic amine absorption of strong intensity occurs at 1325 and 1290 $cm^{-1}$ (=C-N).

The detected strong peak with shoulders at 1229 and 1241 $cm^{-1}$ belongs to covalent sulphonate group $R\text{-}SO_2\text{-}OR'$ ($SO_2$) or/and sulphonic acid salt $SO_3^-H^+$ ($SO_3$).

FTIR test also helped to control the drying process of 3-carboxyphenyl-azosulphonate sodium, for instance to detect the crystallized water that exists in the azosulphonate dried at room conditions. The presence of two hydroxyl bands with strong signal at 3406 $cm^{-1}$ and medium signal at 1637 $cm^{-1}$ (O-H) of azosulphonate dried at room temperature was observed (Figure 3-10). Meantime, the spectrum belonging to the azosulphonate dried in the oven at 40 °C for 18 hours does not contain such signals (Figure 3-9).

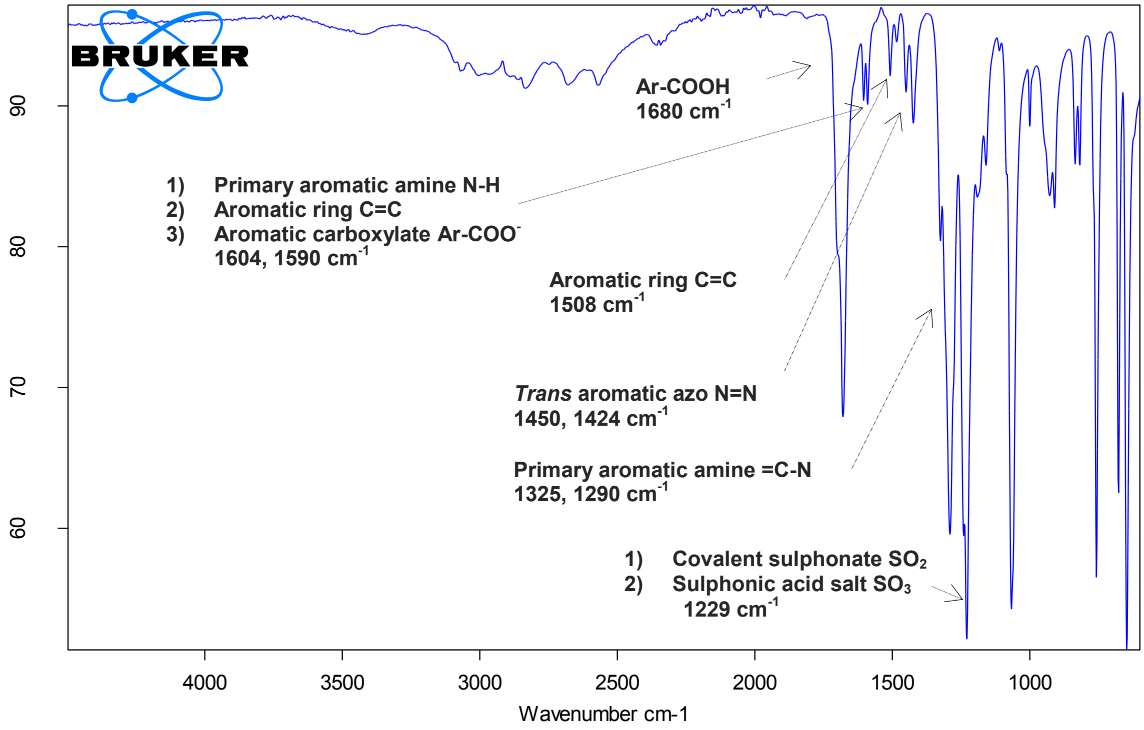


**Figure 3-9** FTIR spectrum of azosulphonate dried in the oven at 40 °C for 18 h

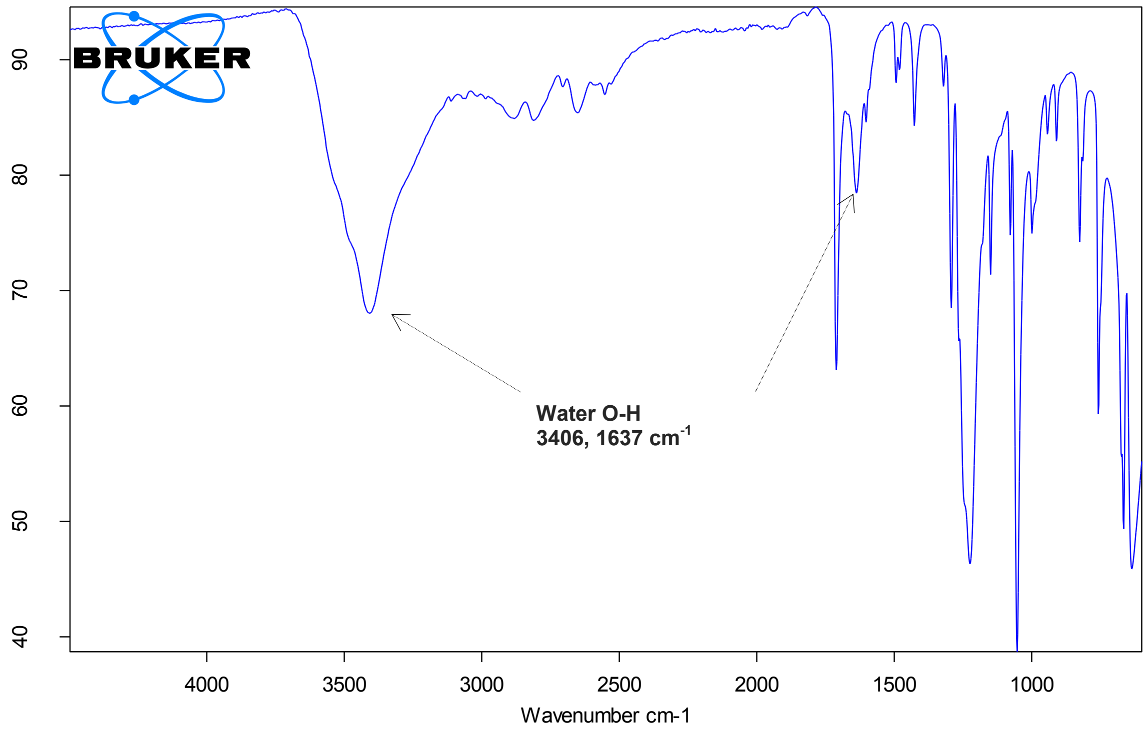


**Figure 3-10** FTIR spectrum of azosulphonate dried at room temperature for 7 days detecting the presence of O-H bands. All characteristic peaks belonging to 3-carboxyphenyl-azosulphonate sodium are described on Figure 3-9.

**Table 3-1** Characteristic absorptions of 3-carboxyphenyl-azosulphonate sodium

| Functional groups | FTIR signal, $cm^{-1}$ | Bands, region ($cm^{-1}$) |
|---|---|---|
| Hydroxyl | 3406, 1637 | O-H str vib, 3600-3100, 1630-1600 |
| Aryl carboxylic acid | 1680 | C=O sym str, 1710-1660 |
| Primary aromatic amine | 1604, 1590 | N-H def vib, 1615-1580 |
| Aromatic ring | 1604, 1590, 1508 | C=C str vib, two or three bands, 1625-1430 |
| Aromatic carboxylate | 1604, 1590 | Ar-$COO^-$ vib, 1610-1550 |
| Aromatic azo compound | 1450, 1424 | N=N str, trans form, 1465-1380 |
| Primary aromatic amine | 1325, 1290 | =C-N str vib, 1360-1250 |
| Covalent sulphonate R-$SO_2$-OR' | 1229, 1241 | $SO_2$ str, 1420-1330, 1235-1145 |
| Sulphonic acid salt | 1229, 1241 | $SO_3$ str, 1250-1140 |

### *Determination of structure by UV-VIS*

The structure of 3-carboxyphenyl-azosulphonate sodium was analyzed also by UV-VIS spectroscopy. The UV-VIS analysis of diluted aqueous solution of azosulphonate in a wavenumber range of 200-700 nm was conducted to investigate the salt composition, with the emphasis on aromatic and azosulphonate groups (Figure 3-11). For this purpose two aqueous azosulphonate solutions were prepared, one - with a high concentration, another - with the low concentration. For preparation of the high concentrated solution, 0.5 g of azosulphonate was dissolved in 10 mL of deionized water. 1 mL of this solution was diluted with 10 mL of deionized water and used as a low concentrated solution. All measurements were performed at room temperature.

The spectrum of low and high concentrated solutions of 3-carboxyphenyl-azosulphonate sodium demonstrates two absorption peaks. A strong signal at 220 nm is assigned to the aromatic system. The second signal of smaller intensity at 285 nm (ε = 11400 l/mol·cm) is assigned to π-π* transition of the chromophore azosulphonate group. The n-π* transition of the chromophore azosulphonate group should occur around a wavelength of 410 - 420 nm (ε = 171 l/mol·cm), but due to the small absorption coefficient it is not discernible. To detect the signal at around 410 - 420 nm, the aqueous azosulphonate solution with concentration of 5 x $10^{-3}$ mol/l should be prepared and diluted 1:100. The UV-VIS spectrum of prepared high concentrated solution shows a cut of absorption peak at 220 nm, therefore the low concentrated solution to analyse the azosulphonate structure is preferable.

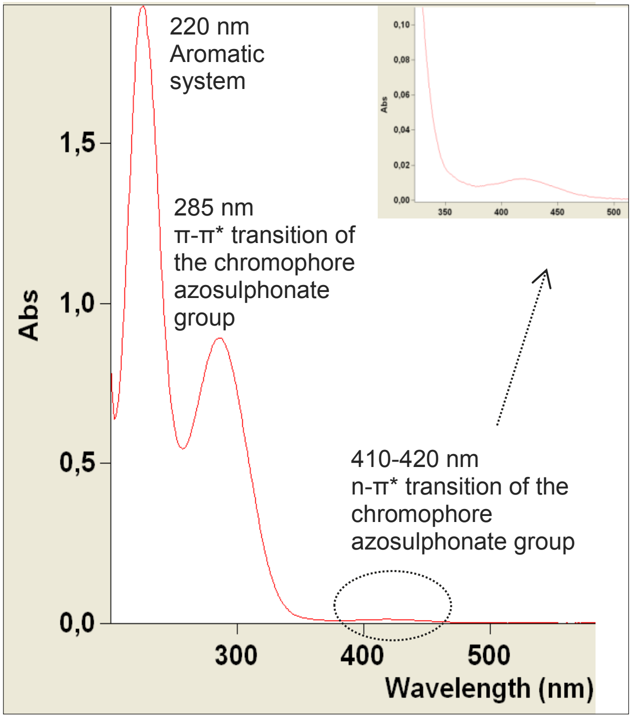


**Figure 3-11** UV-VIS spectrum of 3-carboxyphenyl azosulphonate sodium; aqueous solution

## 3.4 Conclusion

Aryl azosulphonate with carboxylic moieties attached to the aromatic ring has been synthesized. The identification of product was performed using 3 analytical techniques: FTIR, NMR and UV-VIS. The structural analysis showed all the characteristic groups of the synthesized azo compound. The yellow color product was not purified in this work, because all possible impurities can be vanished during the synthesis of azo polyol (during the purification step), thus, it will not influence on the manufacturing of new PU foam. That means the synthesized azo compound can be applied for the modification of standard polyol in laboratory conditions.

## 3.5 References

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# Chapter 4

# Polyol modified with 3-carboxyphenyl-azosulphonate sodium

A branched polyether polyol, one of the main components for manufacturing of PU foam, was selected for functionalization with an azosulphonate group. The branched polyether polyol, commercially utilized product (see Table 2-1), will be denoted in this work as the standard polyol, meantime the modified version of this polyol will be denoted as azo polyol. Thus, azo polyol is a polar additive, which will be premixed to the standard polyol prior to manufacturing of new PU foam. The modified system is an azosulphonate (a component used for the synthesis of an additive). The modification of polyol with 3-carboxyphenyl-azosulphonate sodium is described in this chapter. The synthesis of the azosulfonate component has been described in chapter 3.

## 4.1 Introduction

### *Polyols in PU foam manufacturing*

Polyol is one of the main components for manufacturing of polyurethane foam. Each application of PU foams has individual performance criteria, so there are many types of polyol structures depending on the required combination of foam properties and processing conditions. Therefore, the polyol composition varies from supplier to supplier.

Polyol is an organic compound containing multiple hydroxyl groups. The polyol is not a ‘pure’ compound, it is often a mixture of similar molecules with different molecular weights and molecules containing different number of hydroxyl groups. The polyols used in the polyol mixture can contain additional isocyanate-reactive groups and have functionality in the range of 2 to 8.[1,2] Polyols used to make rigid polyurethane foams have low molecular weights in the range of hundreds, while those used to make flexible polyurethane foams have high molecular weights from 2000 up to 10000 or more.

Depending on the properties of foam product, polyols are generally divided into two groups, there are polyether and polyester polyols. Polyether polyols are more frequently utilized polymers, the reason for this is because they are cheaper, easier in implementation, more resistant to hydrolysis than polyester polyols. Polyether polyol is a copolymer of ethylene and propylene oxides, it is made by the reaction of epoxides with compounds containing active hydrogen. Polyester polyol is made by the polycondensation reaction of multifunctional carboxylic acids and polyhydroxy compounds. The polyol variables mostly used in adjustment of foam product properties are functionality, oxypropylene/oxyethylene ratio, placement of oxyethylene in the backbone and end capping of the chains.[2, 3]

Functionality, hydroxyl number and equivalent weight are three key parameters of polyol material used in making of polyurethane foam. Functionality is the number of polyol reactive sites on a molecule. An average functionality is generally used. Hydroxyl Number (OH Number) is determined as the number of milligrams of potassium hydroxide necessary for neutralization of the acetic acid which is prepared to acetylate 1 gram of a chemical substance with free OH groups.

### *Polyol modified with 3-carboxyphenyl-azosulphonate*

Each modification of polyol has individual criteria, so there are many types of polyol modification depending on the required foam properties and processing. The selection of the modified system in this work was based on the following requirements. Firstly, an additive must be polar. Secondly, an additive must be a liquid or solid and soluble in polyol, because any inhomogeneity in the foam structure leads to deterioration of its insulation properties. Thirdly, it should be chemically bonded to a polyol chain for better compatibility. Finally, the additive should not react with isocyanate in order to avoid change of commercial PU foam formulation.

Thus, 3-carboxyphenyl-azosulphonate sodium was selected among others for the modification of standard polyol. The 3-carboxyphenyl-azosulphonate is a powder and it is soluble in standard polyol, its synthesis has been described in chapter 3. For chemical bonding, the azo component was subsequently esterified with the standard polyol, the scheme of the reaction is presented in Figure 4-1. In order to avoid the change of the polyurethane foaming reaction and to keep the standard commercial formulation, the development of azo polyol additive was focused on substitution of all hydroxyl groups which could react with isocyanate.

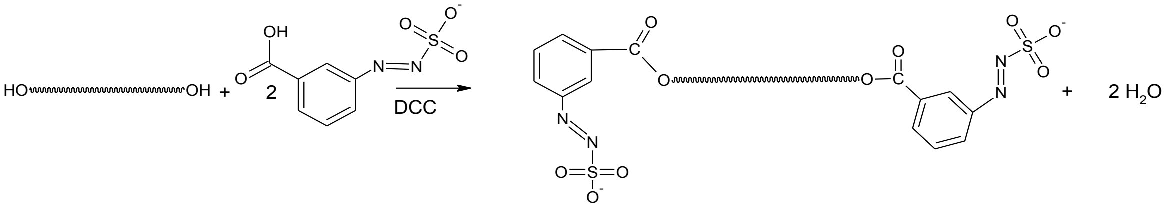

**Figure 4-1** Scheme of the esterification of polyol with 3-carboxyphenyl-azosulphonate

A Steglich esterification was selected as a background for the modification of standard polyol. The Steglich esterification is a reaction that was first described by W. Steglich in 1978.[4] According to this reaction a range of alcohols can be esterified using a carboxylic acid in the presence of coupling reagent - dicyclohexylcarbodiimide (DCC) and a catalyst - 4-Dimethylaminopyridine (DMAP). This reaction typically takes place at room temperature. Dichloromethane ($CH_2Cl_2$) is the solvent for reagents. The reaction mechanism is the following (Figure 4-2).

The reaction proceeds with amines without problems to the corresponding amides because of nucleophilicity of amines. If the esterification goes slow, it leads to the side reaction, reducing the final yield or making the product purification complicated.

Therefore, DCC together with carboxylic acid forms an O-acylisourea intermediate, which has reactivity similar to the corresponding carboxylic acid anhydride. This side-reaction is a rearrangement of the O-acylisourea intermediate into a N-acylurea, which does not further react with the alcohol. The alcohol added to the activated carboxylic acid forms a stable DCU and an ester. DCC is a dehydrating agent, it hydrates with the generated water in the reaction, forming the urea compound dicyclohexylurea (DCU) which is almost insoluble in many organic solvents and totally insoluble in water. Filtration may help to remove DCU, but the last traces are not easy to remove from non-polar products. The addition of DMAP accelerates the DCC-activated esterification of carboxylic acids with alcohols in accordance with Steglich.[4-9]

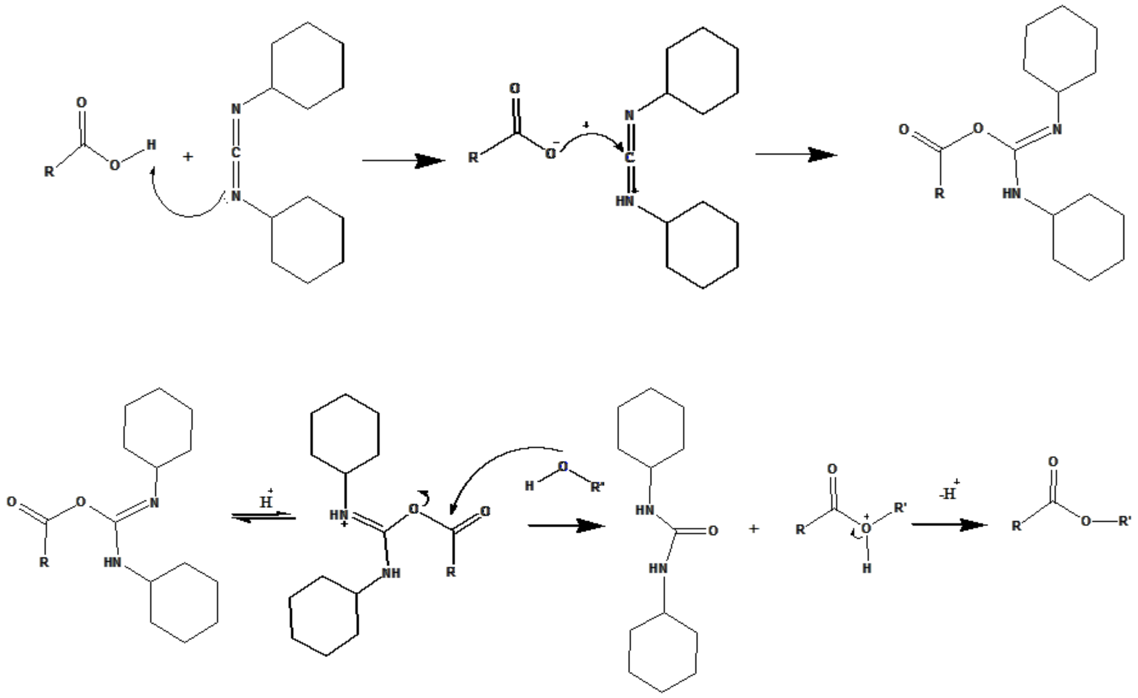

**Figure 4-2** Mechanism of Steglich reaction

DMAP is a derivative of pyridine, colorless solid, it is an effective nucleophilic catalyst for many reactions, especially for esterification with anhydrides. DMAP is relatively toxic and can be absorbed through the skin.

DCC is a white crystalloid substance (at standard conditions) and has a typical sweet, heavy odor. It is highly soluble in $CH_2Cl_2$, tetrahydrofuran (THF), acetonitrile and dimethylformamide (DFM), but insoluble in water.

$CH_2Cl_2$ helps to dissolve reagents of the reaction mixture. It boils at 38 °C, therefore the synthesis cannot be done at high temperature. It is a transparent, volatile liquid, low toxic, in industry it is used in foaming of PU. It is removed from the final product by evaporation.

Acetic acid is a colorless organic liquid with a sour taste and pungent smell. It is used for quenching of rest amount of DCC in the reaction mixture.

## 4.2 Experimental part

For the synthesis of azo polyol additive, 3-carboxyphenyl-azosulphonate was chemically bonded to the standard polyol in such a way in order not to react with isocyanate during PU foam manufacturing.

### 4.2.1 Determination of standard polyol structure

The standard polyol utilized in this work was provided by the company partner. It is necessary to mention that the exact chemical composition as well as the average molecular weight and functionality of standard polyol was not provided to us due to confidential material data from the side of supplier of the company partner. Calculations used for the synthesis of azo polyol additive were based on information from the safety data sheet and internal research.

Prior to the development of azo polyol synthesis, the structure of standard polyol was analyzed. Determination of functionality, average molecular weight and chemical composition was of particular importance.

According to the safety data sheet the standard polyol is identified as Elastopor* H 2130/88/OT and it is a commercial product of BASF Polyurethanes GmbH. This product has a pH value of 6-8 (at 20°C), density 1.06 g/cm$^3$ (at 20°C) and partially solubility in water. This product is a polyol blend with the following chemical composition:

1. cyclohexyldimethylamine (content w/w: ≥0.1% - <0.9%)

   Cyclohexyldimethylamine (CAS number: 98-94-2) is a tertiary amine catalyst used for manufacturing of polyurethane foam.

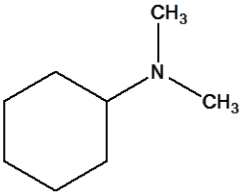

**Figure 4-3** Chemical scheme of cyclohexyldimethylamine

2. 1, 1’, 1’’, 1’’’-ethylendinitrilotetrapropan-2-ol (content w/w: <10%)

   1, 1’, 1’’, 1’’’-ethylendinitrilotetrapropan-2-ol (CAS number: 102-60-3) is a tertiary amine cross-linking agent and catalyst used for manufacturing of polyurethane foam.

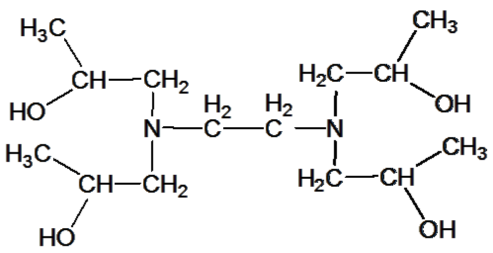

**Figure 4-4** Chemical scheme of 1, 1’, 1’’, 1’’’-ethylendinitrilotetrapropan-2-ol

3. bis(2-dimethyl-amino-ethyl)(methyl)amine (content w/w: ≥0.1% - <0.9%)

   Bis(2-dimethyl-amino-ethyl)(methyl)amine (CAS number: 3030-47-5) is a tertiary amine catalyst used for manufacturing of polyurethane foam.

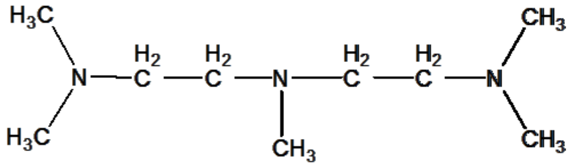

**Figure 4-5** Chemical scheme of bis(2-dimethyl-amino-ethyl)(methyl)amine

4. branched polyether polyol (content w/w: <25%);

   Branched polyether polyol (CAS number: 9082-00-2). In some editions there are several materials with this CAS number. But generally, it is a glycerin-initiated polyether polyol with a functionality of three. Some of them have an average molecular weight of 6000 (hydroxyl number = 28 mg KOH/g). Other types have an average molecular weight of 5000 (hydroxyl number = 34 mg KOH/g). According to another source, the polyether polyol with such CAS number is a propylene glycol 2000 (hydroxyl number = 56.1 ± 1.4 mg KOH/g).

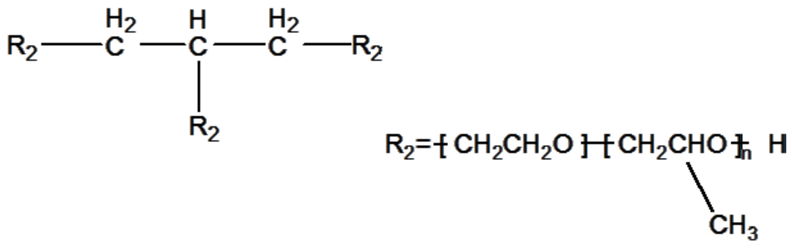

**Figure 4-6** Chemical scheme of branched polyether polyol

5. polyether polyol based on amines (content w/w: ≥25%)

   Polyether polyol based on amines (CAS number: 67800-94-6). There are many products with this CAS number commercially available. Mainly they belong to the family of triol polyether polyols - toluenediamine propoxylated/ethoxylated polyols that react with isocyanates to produce pour-in-place polyurethane foam used for insulation and packaging. For this family of products the hydroxyl number, molecular weight and other main properties vary widely. The benefit of these polyols is that due to the active amine initiator, when blended with other polyols, they require less additional catalyst for reaction.

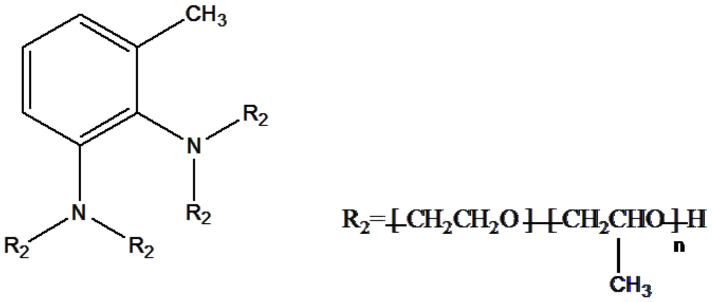

**Figure 4-7** Chemical scheme of polyether polyol based on amines

## *Determination of functionality, hydroxyl number, average molecular weight of standard polyol*

Considering that data safety sheet of standard polyol did not contain information about the average molecular weight, functionality and hydroxyl number, these three parameters were determined.

### *Calculation of hydroxyl number of standard polyol*

From the foam standard formulation it is known that the polyol : isocyanate weight ratio is 100:158. In the isocyanate datasheet, one can find the wt% NCO content (31%) of the given product. Using the molar mass of NCO (42 g/mol) group one can calculate the amount of moles of NCO group per 158 g of isocyanate. In case of polyols, one deals with a hydroxyl OH number, from which the OH wt% is recalculated. Using the molar mass of the OH group one can calculate the mol/g concentration of the OH group.[10,11]

$$\mathrm{n\ (NCO)} = \frac{31.1}{42} = 0.74\ (\mathrm{mol\ per\ 100\ g\ of\ isocyanate})$$

$$\mathrm{n\ (NCO)} = \frac{0.74 \times 158}{100} = 1.17\ (\mathrm{mol\ per\ 158\ g\ of\ isocynate})$$

For the given formulation of PU foam, one needs 1.17 mol of NCO group and the same amount of OH group, therefore n (OH) = 1.17 mol.

Based on the amount of OH groups and molar mass of one OH group (17 g/mol), one can calculate the wt% OH groups used in the given PU foam formulation:

$$\mathrm{m\ (OH)} = 1.17 \times 17 = 19.8\ (\mathrm{g\ or\ wt\%})$$

Based on wt% OH group, one can calculate the hydroxyl number of polyol according to the following equation:

$$\text{Hydroxyl (OH)number} = \frac{\text{OHwt\%} \times 56100}{17 \times 100} = 655$$

*Determination of functionality and average molecular weight of polyol*

Determination of average molecular weight was done by calculation and estimation. Estimation of average molecular weight of standard polyol was based on the performance of produced polyurethane foam and weight ratio of foam reagents. On the one hand, polyurethane foam produced from the standard polyol is classified as rigid one and has density in the range of 40-70 g/cm$^3$, it was assumed that its polyol average molecular weight is below 1000-2000. On the other hand, from the foam formulation it is known that the polyol : isocyanate weight ratio is 100:158 and according to the data safety sheet the polyol has functionality of 2 and/or 3 and/or 4 and isocyanate PMDI has most likely the functionality of 2, that means average molecular weight of polyol is 200 or 300 or 400.

From the calculated polyol hydroxyl number and estimated functionality of 2, one can calculate the average molecular weight of polyol according to the following equation:[10,11]

$$\text{Mw} = \frac{56100 \times (2 \times 1000)}{655} = 171 \; (\frac{\text{g}}{\text{mol}})$$

Taking into account that utilized polyol is a mixture of different polyols and functionality used in calculations was an estimated value, the calculated value 171 is an average molecular weight of polyol mixture. The calculated value 171 is comparable with estimated value 200 for functionality 2.

### 4.2.2 Azo modified polyol: synthesis and optimization

A Steglich esterification was selected as a background for the synthesis of azo modified polyol.[4-8] The optimization of synthesis and purification procedure was performed in accordance with the used raw materials and desirable structure of a final product.

#### 4.2.2.1 Materials

Reagents DCC, DMAP, $CH_2Cl_2$ and Acetic acid were used as the received ones from the commercial suppliers. 3-carboxyphenyl-azosulphonate sodium was synthesized in MUL laboratory (Chapter 3.2.1). Standard polyol was supplied by the company partner (Chapter 4.2.1).

#### 4.2.2.2 Synthesis procedure

For chemical bonding, the 3-carboxyphenylazosulphonate sodium was subsequently esterified with the standard polyol. The molar ratio of reagents was adopted according to our internal research, meantime the conditions of synthesis were kept as in the literature source[7]. The new molar ratio of reagents was estimated in such a way in order firstly to replace all free hydroxyl groups of standard polyol (in order a new additive did not react with isocyanate during foam manufacturing) and secondly to avoid the equilibrium of esterification reaction. Thus, azosulphonate component was used in excess in order to substitute all hydroxyl functional groups of standard polyol. Theoretical molar ratio between reagents was the following - 1 (polyol) : 1.46 (azosulphonate) : 1.66 (DMAP) : 1.66 (DCC). Reaction molar ratios were recalculated in accordance with 0.0115 mole of polyol taken from literature source[7]. In accordance with the synthesis source[7], DCC was added portion wise to a stirred solution of azosulphonate, polyol and DMAP in $CH_2Cl_2$ at 0 °C, the temperature of the reaction mixture was allowed to rise to ambient and mixture was left for stirring 24 h (Figure 4-8). At the end of 24 h stirring period, a precipitate was filtered-off, following by concentration of the filtrate by means of evaporating the $CH_2Cl_2$ (atmospheric pressure, T water = 52 °C) by the rotor vapor (Figure 4-9; 4-10). The identification of both compounds was done using FTIR. The FTIR identified the precipitate compound as an urea and it was decided to discard the precipitate, and to continue investigation of evaporated oily filtrate product. The further investigation of oily product was focused on purification, as three undesirable substances, such as water (as a result of esterification reaction), DCU (as a result of reaction between water and DCC) and DCC (rest from reaction process) were detected by FTIR. The described synthesis procedure was noted C3 (azosulphonate component from batch B1).

Further investigation of product C3 was focused on purification, the summary of this investigation is presented below, in paragraph 4.2.2.3 (C4, C5, C6, C7, C9 procedures). As a result, C7 procedure was selected among others as the most appropriate one. Therefore, all next manufacturing batches of an additive was based on C7 procedure, this means C10.0 (azosulphonate from batch B2.1), C10.1 (azosulphonate from batch B2.2), C10.3 (azosulphonate from batch B3), C10.4 (azosulphonate from batch B3), C10.5 (azosulphonate from batch B3), C10.6 (azosulphonate from batch B4) and C10.7 (azosulphonate from batch B7).

Considering that the yield of a product C7 (=C10.7) was not satisfied, the investigation of the product C7 (=C10.7) was continued. For this purpose, the molar ratio of DMAP was decreased and the procedure for addition of reagents was slightly changed according to the literature source[4,8] and our internal research, meantime the conditions of synthesis were kept the same. This synthesis procedure was noted C10.8 (azosulphonate from batch B7). The identification of the product was done using FTIR. For the further optimization of the product yield, the purification procedure was improved.

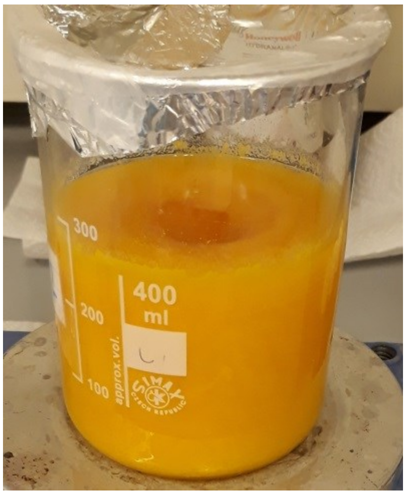

**Figure 4-8** Synthesis C10.8, step – mixing of reaction mixture after addition of all reagents

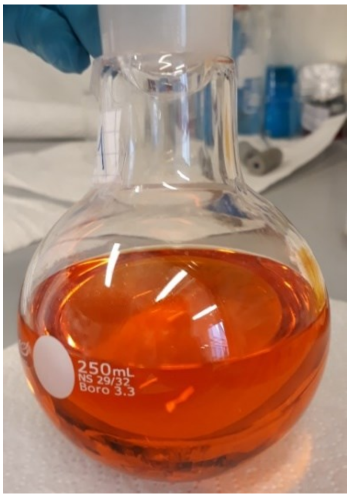

**Figure 4-9** Synthesis C10.8, step – after filtration, filtrate

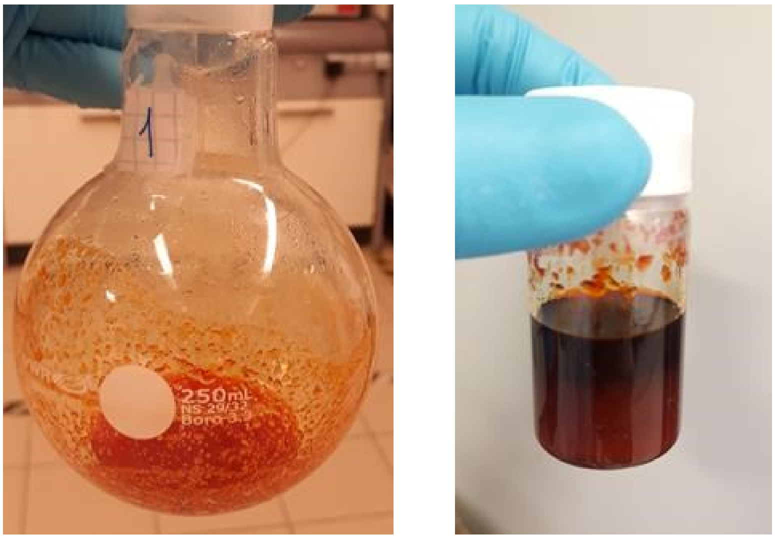

**Figure 4-10** Synthesis C10.8, step – after evaporation by rotor vapor, water temperature 50 °C, atmospheric pressure, 1h.

#### 4.2.2.3 Purification procedure

It is well known that if one doesn't quench the rest amount of DCC after the reaction completed, it will always slowly hydrolyze towards DCU and make problems. Several purification methods were tested until the best suitable method was found. The overview of the purification procedure development is presented below.

##### *Addition of water*

The first ideas were based on addition of a calculated amount of water to the reaction mixture after 24 h stirring for reacting with the rest amount of DCC and stirring for 3 – 24 hours prior to filtration and evaporation. The scheme of DCC hydrolysis is presented in Figure 4-11.

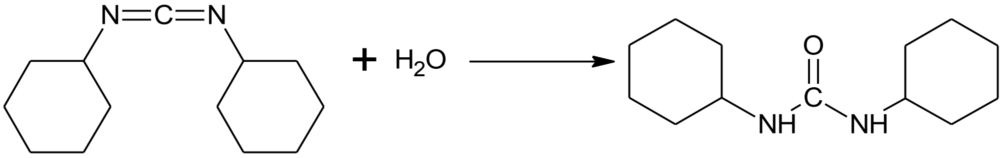

**Figure 4-11** Scheme of DCC hydrolysis (formation of dicyclohexylurea (DCU))

By this procedure, it was expected to transfer the rest of DCC into DCU and to have it precipitated from the reaction mixture, but as a result a similar intensity of DCC and higher intensity of DCU was detected by FTIR in the final product after precipitation and evaporation. The experiments were noted C4, C5 (azosulphonate from batch B1).

##### *Addition of acetic acid, $NaHCO_3$, $Na_2SO_4$*

Another method was based on washing of reagents mixture after 24 h of stirring with cold 10% acetic acid, following by washing with $NaHCO_3$ and absorption by $Na_2SO_4$. This method did not show any positive changes in the composition of a final product. The experiment was noted C9 (azosulphonate from batch B2.1).

##### *Addition of acetic acid solution*

Another idea was based on the addition of different concentrations (3%, 5%) of acetic acid solution (ratio of acetic acid to water was 1:1) to quench unreacted DCC and cooling for 24 h at -20 °C prior to filtration and evaporation. After the addition of acetic solution into the reaction mixture and stirring for 1-3 hours, two phases appeared, one of them was oily transparent liquid, another one was white "flake" precipitate. This method was selected as the most suitable for purification of a desirable product. The experiments were noted C6 and C7 (azosulphonate from batch B1).

The optimization of this purification method was done by the following evaporation in the vacuum oven at 50 °C during 18h.

### 4.2.3 Summary of selected azo modified polyol formulations

**Table 4-1** Summary of the selected azo modified polyol formulations

| Synthesis index | Stoichiometric ratio | | | | Procedure | Yield |
|---|---|---|---|---|---|---|
| | polyol | azo | DMAP | DCC | | |
| C3 | 1 | 1.46 | 1.66 | 1.66 | 1. DCC (3.95 g, 19.12 mmol) was added portion wise to a stirred solution of azo (4.24 g, 16.83 mmol), polyol (2.03 g, 11.5 mmol) and DMAP (2.34 g, 19.12 mmol) in $CH_2Cl_2$ (130 ml) at 0 °C. 2. Stirring at RT for 24 h. Quantities of all reagents were reduced twice.<br>3. Filtration.<br>4. Evaporation by rotor vapor<br>(atm. pressure, T water = 52 °C, 1h) of $CH_2Cl_2$ from filtrate. | - |
| C10.0 | 1 | 1.46 | 1.66 | 1.66 | 1. DCC (3.95 g, 19.12 mmol) was added portion wise to a stirred solution of azo (4.24 g, 16.83 mmol), polyol (2.03 g, 11.5 mmol) and DMAP (2.34 g, 19.12 mmol) in $CH_2Cl_2$ (130 ml) at 0 °C. 2. Stirring at RT for 24 h.<br>3. Addition of 5% AcOH:$H_20$ (3.2ml : 3.2ml) solution.<br>4. Stirring at RT for 3 h.<br>5. Cooling at 0°C for 24 h.<br>6. Filtration.<br>7. Evaporation by rotor vapor<br>(atm. pressure, T water = 52 °C, 1h) of $CH_2Cl_2$ from filtrate. | 9.24 g, >100% from theoretical |
| C10.8 | 1 | 1.46 | 0.15 | 1.66 | 1. Azo (4.24 g, 16.83 mmol) was stirred 20 min in $CH_2Cl_2$ (130 ml) and cooled till 0 °C. This | 6.98 g<br>(or 13.97g- |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | was followed by the addition of DMAP (0.21 g, 1.68 mmol), mixture was stirred 15 min at 0 °C. The last was followed by the addition of polyol (2.03 g, 11.5 mmol), mixture was stirred 15 min at 0 °C. DCC (3.95 g, 19.12 mmol) was dissolved in $CH_2Cl_2$ (19 ml), cooled and added to the reaction mixture by dropping funnel. These quantities of all reagents were increased twice.<br>2. Stirring at RT for 24 h.<br>3. Addition of 5% AcOH:$H_20$ (6.5ml : 6.5ml) solution.<br>4. Stirring at RT for 3 h.<br>5. Cooling at 0°C for 24 h.<br>6. Filtration.<br>7. Evaporation by rotor vapor<br>(atm. pressure, T water = 52 °C) of $CH_2Cl_2$ from filtrate. | in double portion),<br>95%<br>From theoretical |
| C10.8* | 1 | 2.2 | 0.2 | 2.5 | Continue of C10.8 procedure:<br>8. Evaporation in vacuum oven at 50 °C for 15 h. | 5.55 g<br>(or 11.09 g-in double portion),<br>75%<br>From theoretical |

*Note*

C3: synthesis without purification
C10.0: synthesis with purification by acetic acid solution and evaporation by rotor vapor
C10.8: synthesis with purification by acetic acid solution and evaporation by rotor vapor, but 11 times decreased amount of DMAP
C10.8*: additional purification for C10.8 that means evaporation in the vacuum oven at 50 °C for 15 h.

### *Calculation of theoretical yield of reaction*

Prior to calculation of theoretical yield of the reaction, the average molecular weight of the azo polyol product is calculated. Thus, based on the molar mass of 3-carboxyphenyl-azosulphonate (252 g/mol) and average molecular weight of standard (177 g/mol and functionality = 2), the average molecular weight of azo polyol is equal to 516 g/mol.

The theoretical yield calculation starts with the chemical reaction equation, takes into account the molar amounts of reactants and products (Chapter 4.2.2.2). Thus, the molar amount of azo polyol product is equal to 0.00765 mol. To determine the theoretical yield, the number of moles of the product is multiplied by the average molecular weight of the product:

$$\mathrm{m}\ (\text{azo polyol product}) = 0.00765 \times 516 = 3.92(\mathrm{g})$$

## 4.3 Results and discussion

For the manufacturing of an additive for PU foam the 3-carboxyphenyl-azosulphonate was subsequently esterified with the standard polyol in the presence of DCC and a catalytic amount of DMAP. A Steglich esterification was selected as a background for the modification of standard polyol.[4,7,8] The molar ratio of reagents was adopted according to our internal research, meantime the conditions of synthesis were kept as in the articles[4,7,8]. Additionally the purification procedure for the synthesized component was developed. The identification of the synthesized compound was done using FTIR, transmission spectra were recorded in a wavenumber range of 4000-635 $cm^{-1}$.

### *Investigation of product (C3 vs standard polyol)*

For identification of synthesized compound C3, the FTIR spectrum was compared with the spectrum from reference material – standard polyol (Figure 4-12).

Spectrum of standard polyol shows a broad medium peak at 3391$cm^{-1}$, meantime on the spectrum of C3 compound a small peak exists in the same region at 3324 $cm^{-1}$ (O-H str vib). The peak intensity of synthesized compound is much lower in comparison with standard polyol. These peaks could belong to hydroxyl band showing the successful substitution of OH groups of standard polyol.

Both spectra C3 and standard polyol present similar peaks of equal intensities at 2970 and 2870 $cm^{-1}$, which are allocated to C-H. This is explained by the presence of the structure of standard polyol as a part of the chemical structure of the new additive.

A strong peak at 2116 $cm^{-1}$ (aliphatic carbodi-imines) on the spectrum of C3 is assigned to the presence of unreacted DCC reagent in the product mixture.

Another characteristic peak of medium intensity on the C3 spectrum is located at 1719 $cm^{-1}$ (C=O) belonging to the desired aryl ester.

Besides this, C3 spectrum presents peaks of medium intensity at 1646 $cm^{-1}$ (C=O) and 1524 $cm^{-1}$ (N-H). These two peaks belong to the secondary amides, which could be explained by formation of DCU compound from DCC and water in the reaction mixture.

Two peaks of equal intensities, one at 1450 $cm^{-1}$ (from primary alcohols $CH_2$), the other one at 1372 $cm^{-1}$ (from secondary alcohols O-H or C-O of primary alcohol) present on spectrum of standard polyol.

The absorption of the aromatic azo compound occurs at 1450 $cm^{-1}$ (N=N) on the C3 spectrum.

The spectrum of C3 exhibits two overlapped peaks of medium intensity at 1265 belong to the C-O-C asymmetric stretching vibration of aromatic polyethers and at 1229 $cm^{-1}$ belonging to the sulphonate group ($R-SO_2-OR'$).

The spectrum of C3 exhibits a group of peaks of medium intensity in the region 1101, 1045 and 988 $cm^{-1}$, meantime the spectrum of standard polyol exhibits a strong peak with shoulders in this region. Despite the difficulty with identification coming from absorption of many functional groups in this region, it was assumed that peaks on C3 spectrum are due to C-O-C asymmetric stretching vibration of aliphatic polyethers and maybe from the rest of unreacted 3-carboxyphenyl azosulphonate. Meantime, peaks on spectrum of standard polyol are due to C-O stretching vibration of alcohols.

Two strong peaks on the spectrum of C3 at 732 cm and 701 $cm^{-1}$ (C-Cl) come from $CH_2Cl_2$ solvent.

To sum it up, one can conclude that an additive product of C3 composition contains many unreacted reagents, such as DCC. Therefore, the next investigation of an oily product was focused on purification against DCC.

**Table 4-2** Characteristic absorptions of standard and azo polyols

| Functional groups | FTIR signal, $cm^{-1}$ | | Bands, region ($cm^{-1}$) |
|---|---|---|---|
| | Standard polyol | Azo polyol | |
| Hydroxyl<br>Primary aromatic amine | 3391 | 3324 | O-H str vib, 3600-3100, 1630-1600<br>N-H def vib |
| Aliphatic alkane | 2970, 2870 | 2970, 2870 | C-H str vib, 2975-2950, 2885-2865 |
| Aliphatic Carbodi-imines R-N=C=N-R (DCC) | | 2116 | Asym N=C=N str, 2155-2130 |
| Aryl Ester | | 1719 | C=O str vib, 1740-1705<br>C-O str vib, 1300-1100 |
| Secondary amides (DCU) | | 1646,<br>1524 | C=O str,1680-1630<br>N-H def vib, 1570-1515 |
| Primary alcohols,<br>Secondary alcohols | 1450,<br>1372 | 1450,<br>1372 | $CH_2$ def vib, 1480-1410<br>O-H def vib coupled with CH wag vib, 1430-1370 |

| | | | |
|---|---|---|---|
| Aromatic polyethers | | 1265 | C-O-C asym str vib, 1270-1230 |
| Covalent sulphonate R-$SO_2$-OR’ | | 1229 | $SO_2$ str, 1420-1330, 1235-1145 |
| Sulphonic acid salt | | 1229 | $SO_3$ str, 1250-1140 |
| Aromatic azo compound | | 1450 | N=N str, trans form, 1465-1380 |
| Primary chloroalkanes and dichloroalkanes | | 732, 701 | C-Cl str, 760-505 |

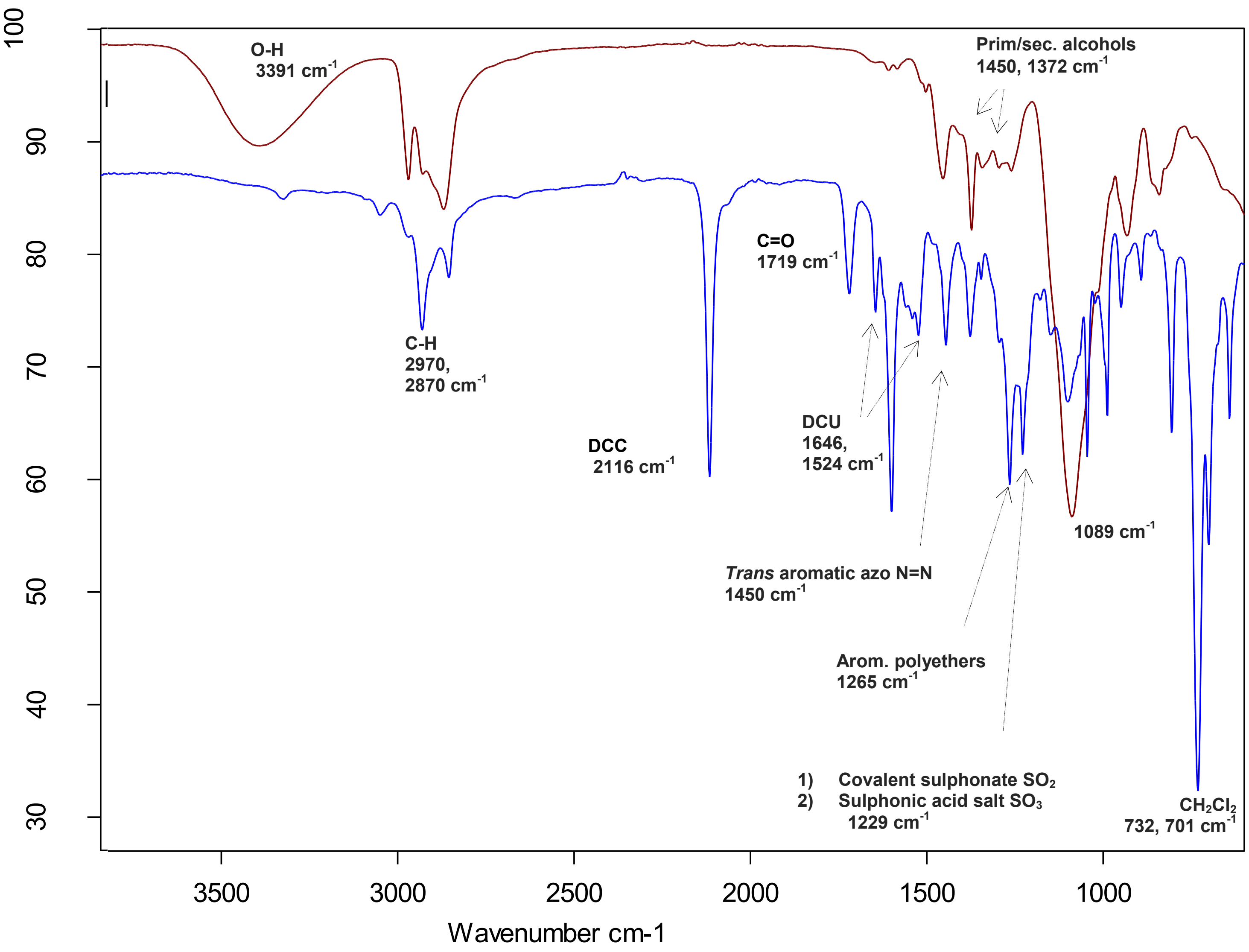

**Figure 4-12** FTIR of synthesized azo polyol C3 (blue) and standard polyol (brown)

### *Purification by acetic acid solution (C3 vs C7/C10.0)*

Taking into account that yield of synthesized product C10.0 was not satisfied (more than 100% from theoretically calculated) and the amount of unreacted DCC catalyst was higher than of an ester product the next investigation of synthesis C3 was continued. For this purpose, the unreacted amount of DCC in the reaction mixture was quenched by different methods. The summary of all methods (C4, C5, C6, C7, C9) is presented in paragraph 4.2.2.3. Procedure C7 based on 5% acetic acid solution was selected among others as the most appropriate. All foam experiments were made with azo polyol additive of this formulation. The identification of the product was done with the help of FTIR, the quantity of reagents in C3 synthesis was twice less than in C7/C10.

For evaluation of the purification results, the FTIR spectrum of not purified C3 product was compared with spectrum of purified C7/C10.0 product (Figure 4-13). The purification results showed that peak at 2116 $cm^{-1}$ (belonging to DCC) has been disappeared from spectrum C7/C10.

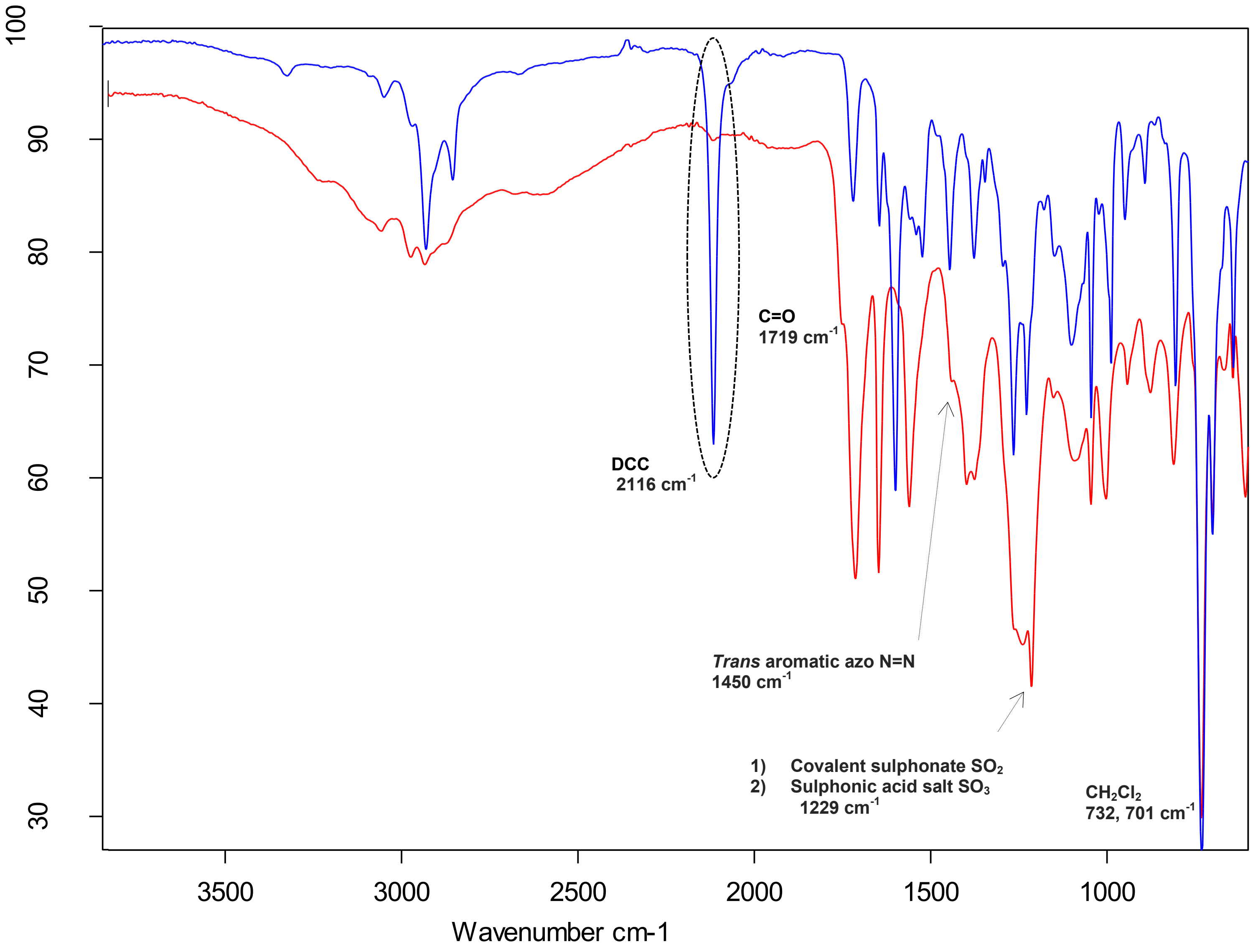

**Figure 4-13** FTIR of azo polyol C3 (blue, not purified) and C10.0 (red, purified against DCC)

### *Optimization of synthesis and purification (C10.8, C10.8*)*

Taking into account that yield of product C10.0 (/C7) was not satisfied (more than 100% from theoretically calculated), the optimization of synthesis and purification procedures of product C10.0 (/C7) was performed. For this purpose, the molar ratio of DMAP catalyst was decreased and procedure for addition of reagents was slightly changed according to the literature source[4,8], meantime the conditions of synthesis were kept the same. Purification was optimized by means of evaporation of highly volatile liquids from reaction mixture in the vacuum oven at 50 °C and 100 mbar for 10h. The optimized synthesis procedure was noted C10.8, the optimized purification procedure was noted C10.8*. The identification of the product was done with the help of FTIR, the quantity of reagents in C10 synthesis was twice less than in C10.8.

The analysis of optimization of additive synthesis has shown the improvement of the reaction yield, by means of decreasing the DMAP reagent until minimum required amount. The yield of the reaction was equal to 95% from theoretical calculated. Here attention must be paid to the calculated yield of the reaction, because 95% is a theoretical yield of product together with DCU byproduct. The analysis of FTIR spectra of C10.0 and C10.8 has shown a significant reduction of peak intensities at 1650 $cm^{-1}$ (C=O str) and 1560 $cm^{-1}$ (N-H def) belonging to the secondary amides, which could be explained by the reduction of DCU component in the reaction mixture (this could be effected by the addition of less water from DMAP or DMAP itself that could lead to formation of DCU) (Figure 4-14).

The analysis of optimization of purification has shown the improvement of the reaction yield, by means of evaporation of highly volatile liquids from reaction mixture in the vacuum oven at 50 °C and 100 mbar during 10h. The yield of the reaction was equal to 75% from theoretical calculated. Here attention also must be paid to the calculated yield of the reaction, because 75% is a theoretical yield of product together with DCU byproduct. The analysis of FTIR spectra of C10.8 and C10.8* has shown the disappearance of two sharp peaks at 735 and 701 $cm^{-1}$ (C-Cl) and appearance of a small sharp peak at 757 $cm^{-1}$ (C-Cl) belonging to the primary chloroalkanes and dichloroalkanes, which could be explained by complete/more efficient evaporation of $CH_2Cl_2$ solvent (Figure 4-15).

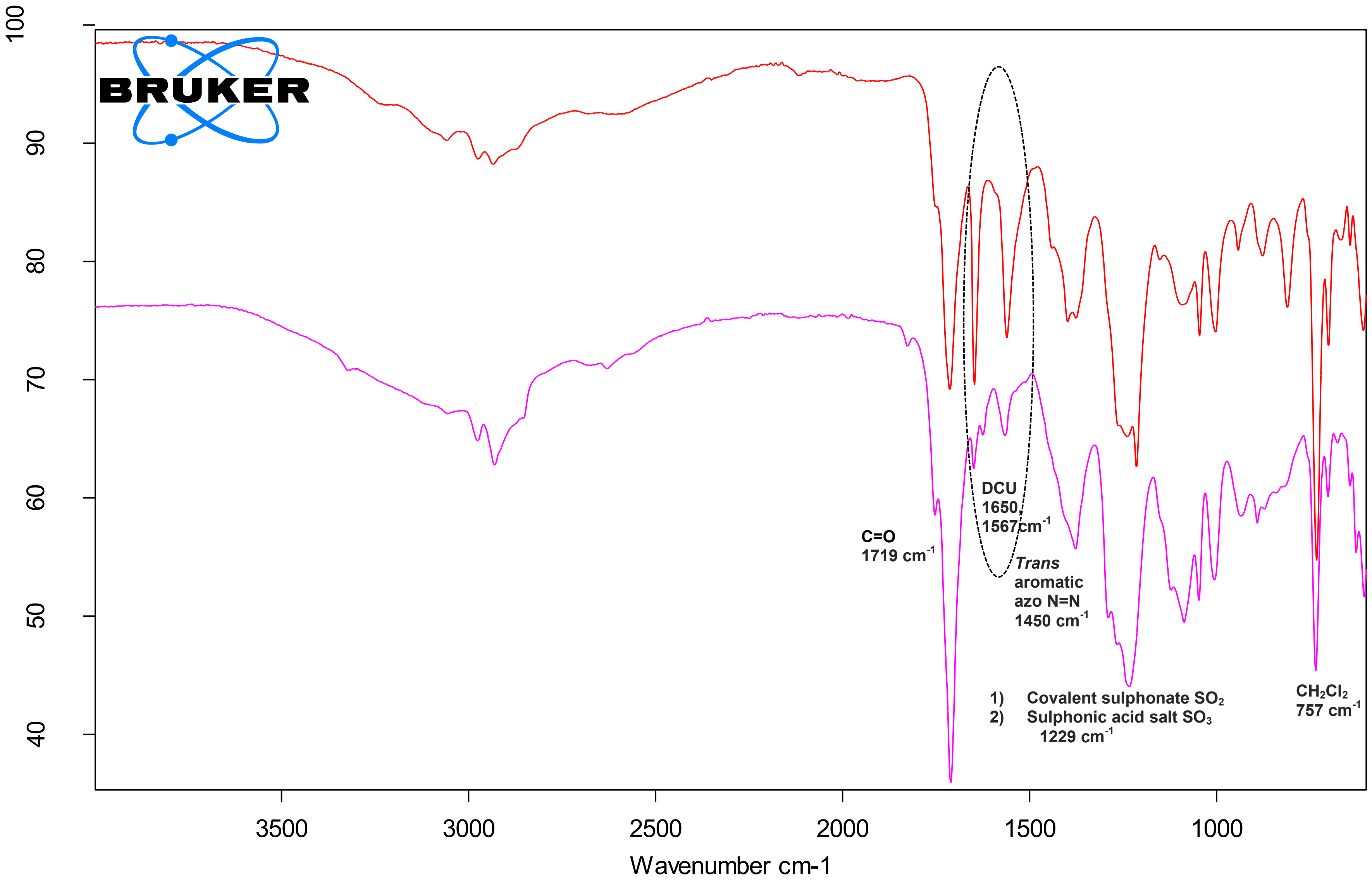

**Figure 4-14** FTIR of azo polyol C10.0 (red, not optimized); C10.8 (rose, DMAP optimized)

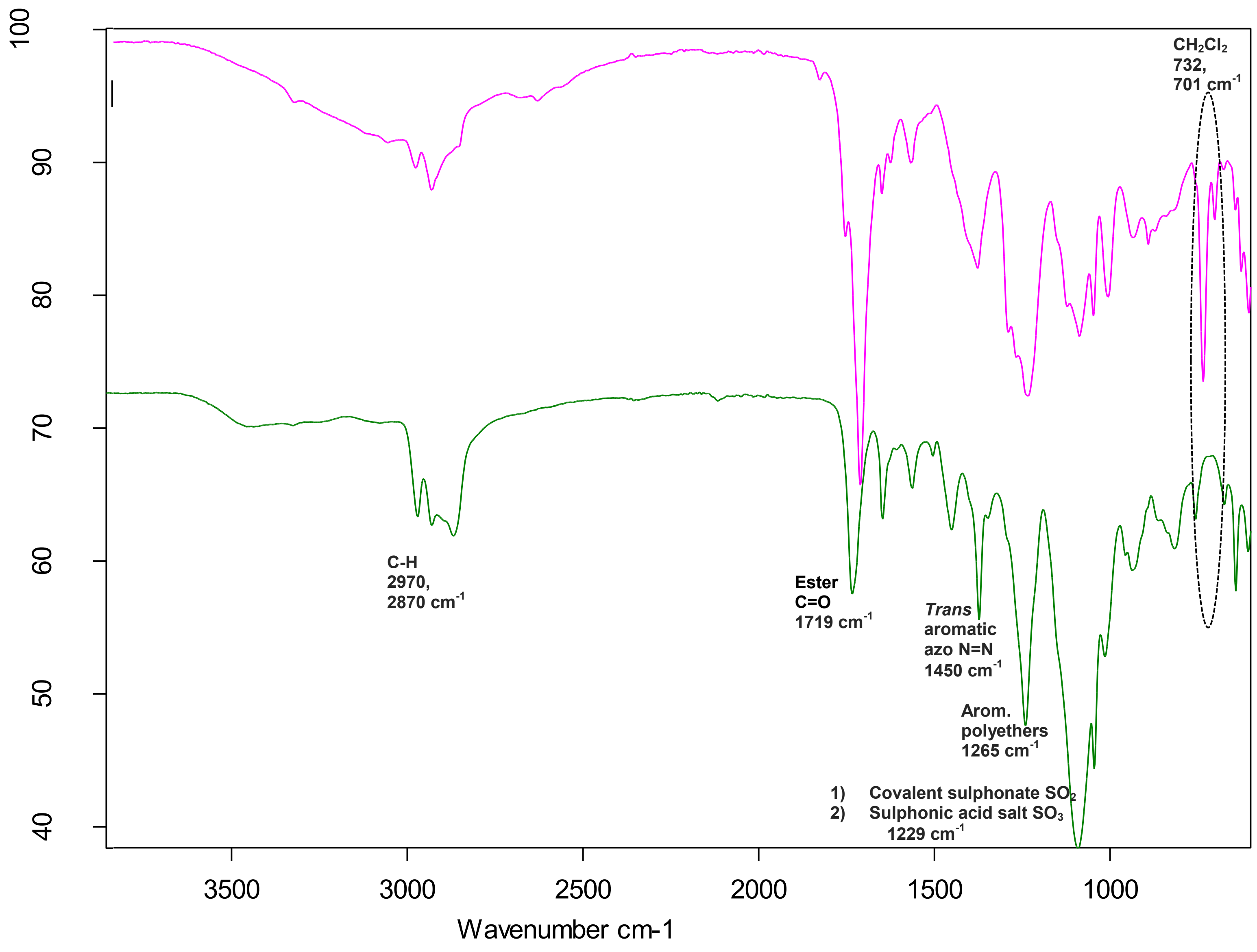

**Figure 4-15** FTIR of azo polyol C10.8 (rose); C10.8* (green, $CH_2Cl_2$ optimized purification)

## 4.4 Conclusion

An azo polyol additive for manufacturing of new foam was developed. The synthesized compound has oily state, orange color and yield of 75% is a theoretical yield of product together with DCU byproduct. It is soluble in dichloromethane ($CH_2Cl_2$), acetone, ethanol and acetonitrile. Azo polyol shows a good mixing ability with standard polyol. Purification against DCC, water and $CH_2Cl_2$ was performed.

Results presented in this work showed that:

- The rest amount of DCC was removed from the final product mixture by quenching with acetic solution.
- Most of the free hydroxyl groups were substituted in the synthesized additive according to the results form FTIR, taking into account that exact chemical composition of standard polyol was not provided and Mw together with functionality were calculated and estimated internally.
- Synthesized component had a yield of 75% and consisted of azo polyol liquid product with DCU crystalloid byproduct. DCU was formed from the reaction of water and DCC during the synthesis.
- Synthesized additive had another viscosity than standard polyol. Viscosity of azo polyol from batch C10.0 was much lower than from batch C10.8* due to residue of dichloromethane solvent.
- Prior to manufacturing of new foams, synthesized component (C10.0 batch) was premixed to the standard polyol in a range of concentrations (0.5; 3; 5; 10; 20 wt%) by automatic VM-200 Vortex mixer resulting in homogeneous mixing.

## 4.5 References

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# Chapter 5

# Polyurethane foam with a polar azo polyol

Polyurethane foams functionalized with a polar surface-active component that have other morphological and thermal properties than conventional PU foams are described in this chapter. The novel PU foams were produced with different concentration of additive and tested for thermal properties. The effect of additive incorporation and mixing parameters on foam kinetics, cellular structure, foam gas phase and the overall foam thermal conductivity was also investigated.

## 5.1 Introduction

### 5.1.1 Preparation of rigid PU foam

Polyol, blowing agent, isocyanate, surfactants, stabilizers and catalysts generally belong to the components of PU foam. Stabilizers and catalysts are added to the PU reagent mixture in order to achieve the desired foam structure. Regarding the blowing agents (BA) they are divided into physical (cyclopentane) and chemical (water) ones. There are two main reactions in the formation of polyurethane foams: blow reaction (gas formation) and polyaddition reaction. Balancing the rates of these two reactions, one may vary the foam morphology influencing the physical properties, for instance the thermal conductivity. If the polyaddition reaction goes very quickly, a tight close-cell structure can be obtained. If the blow reaction goes very quickly, the cells may open before the polymer has enough strength to maintain the cell structure, an open-cell structure can be obtained.

### *Cyclopentane and carbon dioxide gas formation reactions*

Liquid cyclopentane is evaporated due to heat generated from the reaction of polyol with isocyanate. Then gaseous cyclopentane diffuses into existing cells already nucleated in the reaction mixture causing growing of cells (expansion of foam).

Carbon dioxide gas formation reaction: the reaction of water with isocyanate is a two-step process, firstly a thermally unstable carbamic acid is generated, which exothermically decomposes till carbon dioxide and amine. Thus, carbon dioxide gas diffuses into existing cells already nucleated in the reaction mixture causing growing of cells (expansion of foam). Additionally, heat generated will also play a role in expanding the gas in the liquid reaction mixture.

For comparison of both blowing agents, it can be mentioned that $CO_2$ has a higher value of thermal conductivity and diffuses faster out of foam cells, meantime the $C_5H_{10}$ has a lower value of thermal conductivity and diffuses more slowly from foam cells.

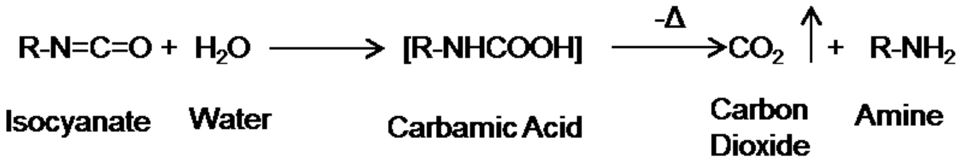


**Figure 5-1** Scheme of the 1st step of the blow reaction

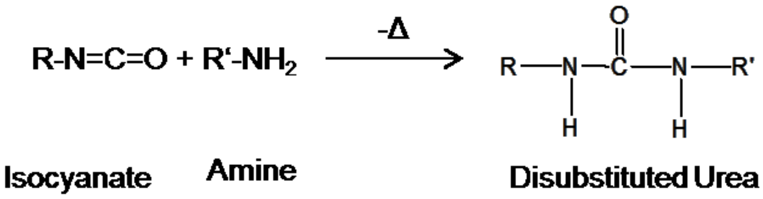


**Figure 5-2** Scheme of the 2nd step of the blow reaction

A blowing agent plays one of the main roles in making a foam material. For the formation of polyol/cyclopentane solution only a soluble amount of liquid cyclopentane should be premixed to the polyol. If the concentration of cyclopentane in polyol is too high, it can lead to some processing problems, such as cavities in a final product.[1,2] If the concentration of added cyclopentane is too low, it can also affect the product quality, by increase in density, for example. The solubility of blowing agent in polyol determines the viscosity reduction and maximum foam expansion ratio too. The solubility limit usually depends on the polymer, BA, temperature and pressure.[1,3] One of the key parameters for solubility of $C_5H_{10}$ in the polyol is a diffusion coefficient.[1,4] Diffusion coefficient is different for all blowing agents and depends on the temperature. Generally, the blowing agent with lower molecular weight has a higher diffusion coefficient at the same temperature and pressure.

## *Polyaddition reaction*

A polyaddition reaction is an exothermic reaction between polyol and isocyanate resulting in polyurethane linkage.

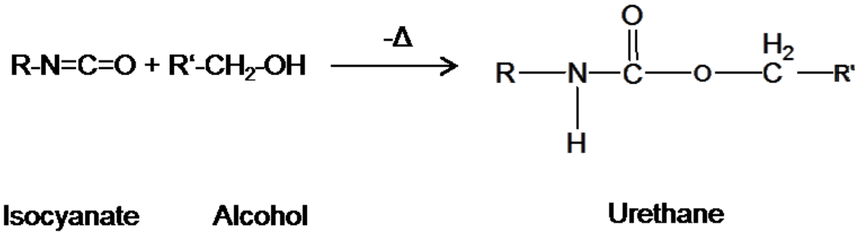


**Figure 5-3** Polyaddition reaction

### Cell nucleation and growth

Cell nucleation happens, when the surrounding conditions change, during exothermic reaction of polyol with isocyanate, this allows the phase separation through diffusion and vaporization.[1,4] Afterwards, the cells continue to grow by diffusion of gaseous cyclopentane or/and carbon dioxide into them. Cells grow until its stabilization, that means hardening by cooling, or rupturing if overstretching occurs.

### Characteristic times

The kinetic of foam reaction is described by four characteristic times that is cream time, gel time, rise time and cure or tack-free time. Cream time is defined at the start of bubble rise, at this moment the color of mixture is changed from transparent dark brown to creamy like due to formation of bubbles. Gel time starts at formation of stable polymer network, this can be noticed visually as the start of foam rising. Rise time is the time when the foam stops to grow. Cure or tack-free time is determined when foam is not sticky any more (completion of urethane curing reaction).

## 5.1.2 Foam structure

In the following, the structural parameters of polyurethane foams are described.

### Cell gas

The cell gas mixture of fresh PU foam contains cyclopentane (30-40 vol%), carbon dioxide (50-70 vol%), air (a few vol%). Initially the foam cells contain a high amount of insulating gases $C_5H_{10}$ and $CO_2$, but if the foam is not diffusion-tight covered, the insulating gases will continually leave the foam until after many years the cells are completely filled with air. It is known that carbon dioxide diffuses faster than oxygen and nitrogen, while cyclopentane is the slowest diffusing gas.[5-10] For the most new PU foams the oxygen/nitrogen ratio of the cell gas mixture is typically higher than of the air. After foam manufacturing, isocyanate reactions are still not complete what gives rise to a gradually increasing amount of carbon dioxide during the first weeks or months after production. It was reported that at room temperature foam cells may contain cyclopentane as a condensed liquid up to 40% of the total added amount of cyclopentane to the foam. Despite, around half of the total amount of cyclopentane added to the foam is dissolved in the polyurethane matrix.[11]

### Matrix

The matrix is the solid polyurethane material in the foam that encloses the gas filled cells. The matrix is made up of cell windows and struts. Cell windows separate two cells, meantime struts are places where three cells meet. The cell windows are much thinner (<1 μm) in comparison with struts (about 30 μm).[5,12]

### *Foam categories*

PU foams are categorized by cell size, expansion ratio and open/close cells. The categories are independent of the processing technology and the polymers used, and they reflect different applications and different physical properties of the foams.

*Cell size*

The foams are categorized by conventional with an average cell size above 100 μm, fine-celled foams between 20 and 100 μm and microcellular foams with an average cell size below 20 μm.[1,13]

*Expansion ratio*

Expansion ratio is defined as the ratio of polymer density to foam density. High-density foams have been used in structural applications where mechanical properties are important, while low-density foams have been used in insulation and packaging applications, where energy absorption is important.[1,14]

*Open/close cells*

Open-cell foams have been used as sound insulation materials and filters, while closed-cell foams are suitable for packaging, cushioning and heat insulation applications.[1,4]

*Density*

There are rigid and flexible PU foams. Rigid foams have density around 30-86 g/m$^3$, while flexible foams have density in the range of 5-40 g/m$^3$. The present-day foam research is going in the direction of lower density foams with smaller cells. The low density of the foam may decrease the heat conduction through the matrix, but meantime may increase the heat transfer by radiation. The latter mechanism can be reduced by making the cell size smaller.[5]

### 5.1.3 Foam thermal conductivity

Standard PU foam consists of 92 - 98 % of gas by volume. This gas is a gas mixture consisting of $C_5H_{10}$ and $CO_2$ blowing agents and $N_2$ with $O_2$ atmospheric gases.[15,16] Therefore, one of the main applications of such material is a thermal insulation with the main property – thermal conductivity.[17]

The thermal conductivity of a substance λ ($W \cdot m^{-1} \cdot K^{-1}$) characterizes the amount of the heat flow q ($W \cdot m^{-2}$) through the substance for a specific temperature gradient T (K) through the substance. Therefore, the thermal conductivity of the insulation material should be as low as possible.

There are four modes of heat transfer in the foams: conduction along the solid phase ($\lambda_s$), conduction through the gas phase ($\lambda_g$) and thermal radiation ($\lambda_r$). The fourth mode - convection inside the cells ($\lambda_c$) can be neglected when the cells' size is small (lower than 2 mm).[18,19] The total thermal conductivity of polyurethane foam is a sum of all contributions. All heat transfer modes are temperature dependent. For an ordinary polyurethane foam, the total initial thermal conductivity increases with the temperature from about 23 to around 39 mW·m$^{-1}$·K$^{-1}$ in the 10-120 °C temperature interval.[5]

As solid materials conduct heat much better than gases, the minimum amount of solid material in the foam insulation is preferable. The thermal conductivity of solid polyurethane is around one order of magnitude larger (210 mW·m$^{-1}$·K$^{-1}$)[20] than of most gases (10-30 mW·m$^{-1}$·K$^{-1}$, at room temperature*)*. For further reduction of foam thermal conductivity, the foam cell gases with thermal conductivity lower than the air should be selected. If the cell gas composition is defined, it is possible to theoretically derive the thermal conductivity of the cell gas mixture by Wassiljewa equation.[18,19] Since the void vol. fraction of the foam is very high, the conduction through the gas phase is around 68% of the total thermal conductivity of the foam.[5,15,21,22]

Conduction through the polyurethane matrix and radiation generally represents 20-40% of the total thermal conductivity of the foam.[23] Heat conduction through the PU polymer matrix depends on the thermal conductivity of the PU polymer, as well as on the amount and distribution of the material.

The heat transfer by radiation depends on the number of cells, the more cells exist in the foam the more layers the radiation has to pass.

Permeability coefficient, temperature and thickness are three factors that influence the heat transport resistance of the material.[5] Besides this, cell anisotropy and orientation also influence the heat conduction: the more solid exists in the surface perpendicular to the heat flow direction, the lower the heat conduction (this is typical for free-rise foams with elongated cells that show strongly anisotropy effect) is.[24,25,26] Additionally, the thickness of a cell wall and variation in cell size play a role: thinner cell walls reduce solid conduction but increase radiation conduction; the broader the cell size range is, the more quickly happens the deterioration of thermal conductivity happens.[26]

## 5.2 Experimental part

### 5.2.1 Foam preparation: Background

Two different PU foam systems were studied: the standard material (with no additive, used as a reference material) and that containing azo polyol additive in a different range of concentrations.

#### *Materials*

Main components from commercial formulation: isocyanate, polyol, cyclopentane were used to produce the standard polyurethane foams. Additive - azo polyol (synthesis is described in Chapter 4) was added to the main formulation for manufacturing of new PU foams.

### *Preparation equipment*

For the manufacturing of foam in laboratory conditions, the automatic mixer was used. This mixer is a biaxial centrifuge VM-200 Vortex mixer (Figure 5-1). It was used for the mixing of components of reagent mixture, achieving a good mixing effect in a short period of time (sec).

However, there are limitations of such equipment. The limitations deal with the maximum size of the produced foam sample because the mixing process takes place in a closed system, in a special container of fixed volume (diameter = 8.2 cm, height = 6 cm) and scrolled cap (Figure 5-2). Taking into account that foaming reaction can go in a short period of time (some seconds) care should be taken with the estimation of expected expansion of foam. Therefore, it is highly recommended to carry out experiments starting from small reagents' mixture amount and visual observation of foaming behavior of every individual foam composition. If the foaming takes longer period of time (more than 70 sec), than after finishing of mixing and removing of container from the mixer and opening the cap, the mixture can be pureed from the mixer container into any other container of preferable geometry.

For the manufacturing of foam, two mixer parameters – speed and time – were used. Here attention should be paid to adjustment of a speed parameter. Thus, the speed is not linear, preliminary adjustment of the required speed should be done (Table 5-1).

**Table 5-1** Adjustment of speed parameter of Vortex mixer VM-200

| Adjusted rotation speed, % | Real rotation speed, % | Real rotation speed, rpm |
|---|---|---|
| 100 | 100 | 2000 |
| 50 | 80 | 1600 |
| 40 | 60 | 1200 |
| 30 | 40 | 800 |

**Figure 5-1** Vortex mixer VM-200 used for manufacturing of PU foam in laboratory

**Figure 5-2** Container and cap for mixing of reagents by Vortex mixer VM-200

**Figure 5-3** Preparation of foam specimens

The manufacturing of PU foam in MUL laboratory was different from typical large-scale factory's practice, for instance the way of components addition to each other, mixing process, raw components storage conditions. These technical differences influence the cellular structure of the produced foam, for instance the cell size and foam density.

### 5.2.2 Preparation of standard PU foam

Prior to making of new foams and evaluation of their barrier properties, the processing behavior of standard foam was investigated. Taking into account that reference standard foams should have very similar cell size and density to new foams, a set of reference foam samples was produced (Table 5-3).

The manufacturing of standard PU foam was based on the commercial formulation using three components: isocyanate, polyol and cyclopentane. The original formulation comprises 100 g of polyol, 4% (that is 4.17 g) of cyclopentane and 158 g of isocyanate (Table 5-2). Homogeneous mixing of components was performed by Vortex mixer (see paragraph 5.2.1). Firstly 4.17 g of cyclopentane was premixed to 100 g of polyol in a plastic container, using an auto mixer, at 1600 rpm for 10 sec. Then 158 g of isocyanate was added and mixed at 800 rpm for a different period of time. The mixed liquids were not poured into another container, but left for foaming and curing in the mixer container due to very short (in a range of sec) foaming time. During the manufacturing process the characteristic times (Cream, Gel, Rise and Tack-free) of PU foams were recorded.

For the development of standard foam structure, the formation of set of foams with a different cell size was based on varying of total amount of reagent mixture together with mixing parameters individually for every foaming experiment by keeping the ratio between reagents at the same level. For understanding and predicting of a foam cellular structure, it was decided to fix one processing parameter – speed of rotation and to vary just mixing time at the moment when isocyanate is premixed to polyol and cyclopentane blend. Taking into account, that foaming process lasts in the range from some seconds to some minutes, some special attention was paid to searching for a balance between foam quality and auto mixing parameters. After some trials, the correlation was found between time of mixing and foam cellular structure which could help in formation of some groups of foam structures. Information about cell growth comes from either theoretical modelling or from direct observation of cell growth. In this work the second approach was applied.

After foaming, the samples were left in open mixer container for one day at RT and then foam samples were cut for characterization (Figure 3).

**Table 5-2** Standard PU foam formulation

| Component | Mass, g |
|---|---|
| Polyol | 100 |
| Isocyanate | 158 |
| Cyclopentane | 4.17 |

**Table 5-3** Processing procedure for selected reference foam samples

| Foam Index | Mass of components, g | | | | Mixing parameters | |
|---|---|---|---|---|---|---|
| | polyol | $C_5H_{10}$ | isocyanate | total | Polyol + cyclopentane | Isocyanate + (polyol, $C_5H_{10}$) blend |
| F-St5 | 12.5 | 0.5 | 19.8 | 32.8 | 1600 rpm, 10s | 800 rpm, 5s |
| F-St10 | | | | | | 800 rpm, 10s |
| F-St20 | | | | | | 800 rpm, 20s |
| F-St40 | | | | | | 800 rpm, 40s |

### 5.2.3 Preparation of PU foam with azo polyol additive

Modified PU foam was obtained in a way that classical polyurethane foam components – isocyanate, polyol and cyclopentane were added together with azo polyol component. The azo polyol was synthesized in such a way that it did not contain hydroxyl groups, that's why this component did not react with the monomers of polyurethane mixture. Considering that PU foams with different chemical structure react in processing conditions and geometric constraints in a different way, the new foam with azo polyol showed different processing behavior than the standard foam did. Therefore, firstly the processing behavior of the new foam with azo polyol was investigated. Afterwards, a set of new foams with a cellular structure similar to standard foams was produced, what was necessary for evaluation of the new foam thermal properties (Table 5-5).

The manufacturing of new PU foam was based on the standard formulation using isocyanate, polyol and cyclopentane with addition of azo polyol additive. Therefore, the new formulation comprises 100 g of polyol, 4% (that is 4.17 g) of cyclopentane, 158 g of isocyanate and a calculated amount of an additive depending on preferable concentration (Table 5-4). Mixing of components was performed by Vortex mixer (see paragraph 5.2.1). Firstly, the calculated amount of azo polyol was premixed to 100 g of standard polyol in a plastic container, using an auto mixer at 1600 rpm for 60 sec. Secondly, the 4.17 g of cyclopentane was premixed to new polyol blend and mixed at 1600 rpm for 10 sec. Then 158 g of isocyanate was added and mixed at different speed and period of time. During the manufacturing process the characteristic times (Cream, Gel, Rise and Tack-free) of PU foams were recorded. The mixed liquids were not poured into another container, but left for foaming and curing in the open mixer container (due to a very short period of foaming time) for one day at RT and then foam samples were cut for characterization (Figure 3).

The development of manufacturing procedure was based on two approaches. The first one dealt with the testing of influence of additive different concentrations on foaming reaction. This was of particular interest for evaluation and comparison of the new foam thermal properties. Starting from 0.5 wt%, the concentration of azo polyol in the new foam formulation was varied up to 20 wt% in order to analyze how the new additive influences the structure of the foam. The second one was based on the development of foaming process in every azo polyol concentration group depending on different mixing speed and time for searching for a balance between foam quality, structure and auto mixing parameters. Mixing parameters were varied just at the moment when isocyanate was premixed to polyol and cyclopentane blend. The total amount of reagent mixture was varied individually for every foaming experiment, but the ratio between polyol, isocyanate and cyclopentane was kept at the same level. Information about cell growth comes from either theoretical modelling or from the direct observation of cell growth. In this work the second approach was applied.

**Table 5-4** New PU foam formulation

| Component | Mass, g |
|---|---|
| Standard polyol | 100 |
| Azo polyol | 0.5 / 3 / 5 / 10 / 20 |
| Isocyanate | 158 |
| Cyclopentane | 4.17 |

**Table 5-5** Manufacturing procedure for selected new foam samples

| Foam index | Mass of components, g | | | | | Mixing parameters | | |
|---|---|---|---|---|---|---|---|---|
| | polyol | azo polyol | $C_5H_{10}$ | isocyanate | total | Polyol + Azo polyol | (Polyol, azo polyol) blend + cyclopentane | Isocyanate + (polyol, azo polyol, $C_5H_{10}$) blend |
| F-0.5 | 6.67 | 0.03 | 0.28 | 10.53 | 17.54 | 1600 rpm, | 1600 rpm, | 800 rpm, 30s |
| F-3 | 10.00 | 0.30 | 0.42 | 15.80 | 26.50 | | | 800 rpm,10s |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| F-5 | 11.11 | 0.55 | 0.46 | 17.55 | 29.70 | 60s | 10s | 800 rpm,10s |
| F-10 | 10.00 | 1.00 | 0.42 | 15.80 | 27.20 | | | 800 rpm,5s |
| F-20 | 4.00 | 0.80 | 0.17 | 6.32 | 11.23 | | | 1600 rpm,5s |

### 5.2.4 Characterization of PU foams

#### *Structure*

To determine a cell size, cell shape and number of cells the foam was examined by SEM. For this purpose, cured foams were cut into 0.5 x 0.5 x 0.5 $cm^3$ samples to provide a smooth surface, which was coated under vacuum with gold for obtaining of conductivity. The measurements were carried out at voltage 5 kV and magnification 40x. If the analyzed foam sample has cells of an asymmetrical shape in parallel and perpendicular direction to foam rise, some attention should be paid to the position of sample cutting. Quantitative image analysis was performed using ImageJ software.

To determine close/open - cell content, the helium gas pycnometer is generally used. In this work the foam samples were examined by gas pycnometer (Quantachrome, Ultrapycnometer 1000), but the results could not be obtained. Several foam sample sizes and foam types have been tested, but it did not give a result. It was assumed that for measuring of PU foams not every type of helium gas pycnometer is suitable, and some attention should be paid to the usage of the helium pycnometer with chamber volume bigger than 1.7 $cm^3$.

#### *Physical parameters*

To detect density, a sample of 5 x 5 x 1.5 $cm^3$ geometry was cut out of foam. The weight and volume of the sample were included in the calculation of foam density. Three measurements were used for obtaining the average value of weight.

To determine height, the sample was not cut, the whole length was examined by a caliper.

To detect expansion ratio, the general average density of solid polyurethane (1086 $kg/m^3$) was divided by the determined foam density.

#### *Foam thermal conductivity*

For determination of total foam thermal conductivity, the samples were measured by Hot Disk System. For this purpose, cured foams were cut into two equal 2.5 x 2.5 x 1.5 $cm^3$ samples to provide a smooth surface. 40 minutes prior to measurement the samples were stored in the laboratory of a thermal conductivity device for conditioning. The test was performed at RT, time of one measurement was 40 sec and power - 0.004 W. If the analyzed foam sample has cells of an asymmetrical shape in a parallel and perpendicular direction to foam rise, some attention should be paid to the position of cutting and testing. The measurement was repeated minimum 3 times for results' accuracy.

### *Polyol properties*

Taking into account that changes in the formulation of new foam were based on modified azo polyol, the viscosity and water content of standard and modified polyol were determined.

To determine of viscosity, the standard and azo polyol were investigated by Modular Compact Rheometer. The test was run at 25 °C and four different share rates 5.0; 10.0; 15.0 and 20.0 (1/sec) with two measurement points for results' accuracy. Cone/plate spindle (2°) was used.

To determine of water content, the standard and azo polyol were tested by Carl Fischer Coulometer with normal titration medium at RT. The measurement was repeated 2 times for results' accuracy.

### *Foam Cell Gas Content*

To determine foam cell gas content and calculate foam cell gas thermal conductivity, the foam samples were measured by GCMS. The gas sampling method was especially developed for this work. The detailed information about sample preparation and testing procedure is described in chapter 2.3.

## 5.3. Results and discussion

### 5.3.1. Characterization of standard PU foam

The polyurethane foams described in this paragraph were produced with the same formulation (from three components: polyol, isocyanate and cyclopentane), but different mixing time. Standard foam F-St5 was mixed for 5sec, foam F-St10 - 10sec, foam F-St20 - 20sec and foam F-St40 - 40sec. The difference in mixing time had led to variation in PU foam morphology. Considering that the formation of polyurethane foam consists of two main reactions, such as blow reaction (gas formation) and gelation (crosslinking) reaction and difference in mixing times between four foam samples, the viscosity of the reaction mixture as well as the temperature distribution changes during the foam processing in every sample individually.[1] Although, neither viscosity, nor temperature of the reaction mixture was measured in this study, the influence of different mixing time on foam morphology and thermal properties of standard PU foam was analyzed and will be described below.

### *Morphological characterization*

#### *Cell size, cell shape, number of cells*

Table 5-7 shows the reduction of foam cell size and increase in cell number when the mixing time is increased. The cell size reduction is significant, from 1120 μm for

F-St5 to 160 μm for F-St40. The reason for the observed cell size reduction is related to the rheological properties of polymer and polymer-BA mixtures. The rheological properties determine the distributions of fluid pressure and velocity in the processing system, and influence the cell growth during the foam manufacturing process. The main factors of resistance to fluid flow are fluid velocity and fluid viscosity. The frictional forces, caused by the resistance to flow, act in fluid as it flows through the tube. If the rate of frictional forces is increased, the free energy to form cells will decrease, the cell nucleation rate will increase, and the average cell size will decrease accordingly.[1] Therefore, when the time of mixing the PU blend by static mixer is increased, the average cell size of the foam is decreased.

Figure 5-4 shows SEM images of the cellular structure of foams F-St5, F-St10, F-St20 and F-St40. All samples presented regular polyhedral mostly closed-cell structures with pentagonal or hexagonal faces.

*Foam density, foam height, expansion ratio, open /close-cell*

During 5 sec mixing blowing agent cyclopentane dissolves in the mixture reducing its viscosity and polyol starts to react with isocyanate producing heat. The generated heat causes evaporation of liquid cyclopentane, which diffuses from fluid into the cell, that’s why at this moment cells start to grow. From the first view the cells should be small at short mixing time, but due to low viscoelastic behavior of mixture during foaming reaction, small cells are combined into large one or shrinkage of foam happens resulting in large cells. A short mixing time, 5 sec, of mixture has led to a poor and slow reaction between polyol and isocyanate, resulting in low expansion ratio (19.11 for F-St5), low foam height (9.16 cm for F-St5) and long rise time ( 132 sec for F-St5) (Table 5-6).

When the mixing time is increased from 5 sec to 10 - 20 sec, the prolonged time for reaction between polyol and isocyanate results in higher rate of crosslinking and blowing reactions. Thus, higher amount of gas diffuses into the cells resulting in the higher expansion ratio (19.69 for F-St10; 19.92 for F-St20) and more polyurethane linkages form resulting in faster growing (125 sec for F-St10; 121 sec for F-St20) and larger height (9.97 cm for F-St10; 10.3 cm for F-St20) of the foam. At better mixing, the mixture has sufficient viscosity together with strain to break, cells grow at reasonable rate without rupturing, resulting in closed-cell low density foams (56.8 kg/m$^3$ for F-St5; 55.2 kg/m$^3$ for F-St10; 54.5 kg/m$^3$ for F-St20) (Table 5-6; 5-7).

When the mixing time is increased to 40 sec, the acceleration of the reaction between polyol and isocyanate occurs, resulting in the fastest growth of the foam (112 sec for F-St40), highest nucleation rate (740 cells for F-St40). The gas formation goes so quickly that the cells can open before the polymer has enough strength to maintain the cell structure resulting in an open-cell structure visible from F-St40 SEM image (Figure 5-4). Therefore, the expansion ratio (18.68 for F-St40) and foam height (9.8 cm for F-St40) are lower. At this mixing time, the mixture is too stiff to be stretched, therefore small cells are obtained.

*Characteristic times*

The reaction rate of foam samples was measured from the cream time, gel time, rise time and tack-free time.

Table 5-6 shows that cream and gel times for F-St5 and F-St10 stayed mostly unaffected. For F-St20 the cream time and for F-St40 the cream and gel times were not possible to measure due to overlapping with mixing time. It is necessary to note that after finishing of mixing the sample has to stay inside the mixer for around 9 sec due to the security lock system of the mixer. The reduction in rise time and slight differences in tack-free time are connected with the viscosity of the reaction mixture.[1]

**Table 5-6** Foam manufacturing conditions, characteristic times, height and expansion ratio

| Foam index | Mass of mixture, g | Mixing parameters | | Characteristic times | | | | Foam Height, cm | Expansion ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | Speed, rpm | Time, +9 sec inside | Cream time, sec | Gel time, sec | Rise time, sec | Tack free time, sec | | |
| F-St5 | 32.8 | 800 | 5 | 31 | 39 | 132 | 162 | 9.16 | 19.11 |
| F-St10 | | | 10 | 28 | 39 | 125 | 178 | 9.97 | 19.69 |
| F-St20 | | | 20 | <30 | 38 | 121 | 148 | 10.3 | 19.92 |
| F-St40 | | | 40 | <50 | <50 | 112 | 162 | 9.8 | 18.68 |

**Table 5-7** Foam density, cell size and number of cells per area

| Foam index | Density, kg/m$^3$ | Cell size, µm | Number of cells per 25 mm$^2$ |
|---|---|---|---|
| F-St5 | 56.8 ± 0.7 | 1120 ± 200 | 18 |
| F-St10 | 55.2 ± 0.3 | 880 ± 170 | 24 |
| F-St20 | 54.5 ± 0.9 | 500 ± 70 | 50 |
| F-St40 | 58.1 ± 0.7 | 160 ± 40 | 740 |

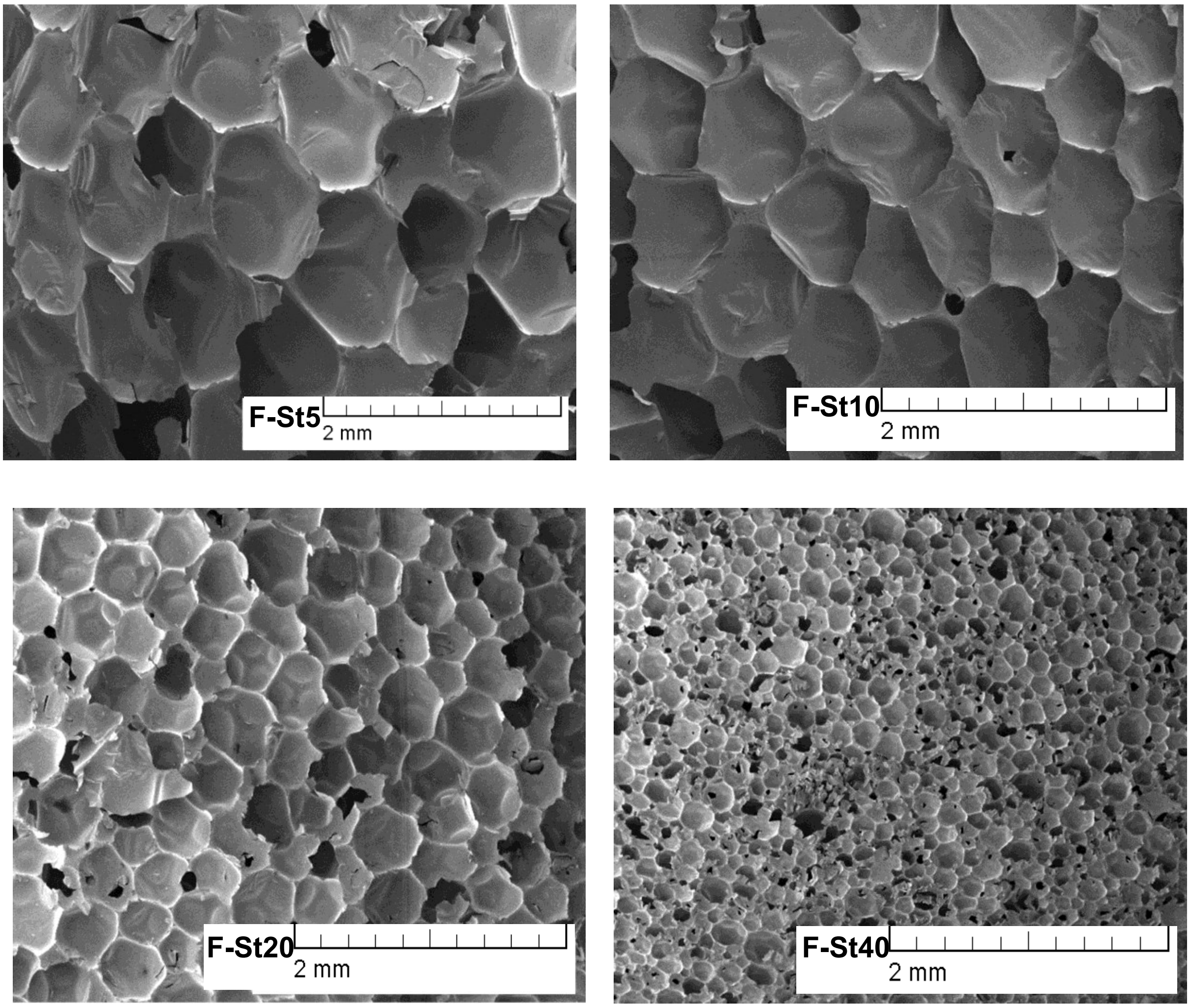


**Figure 5-4** SEM images of cross-sections in perpendicular to the foam rise for F-St5, F-St10, F-St20 and F-St40 at 40x magnification

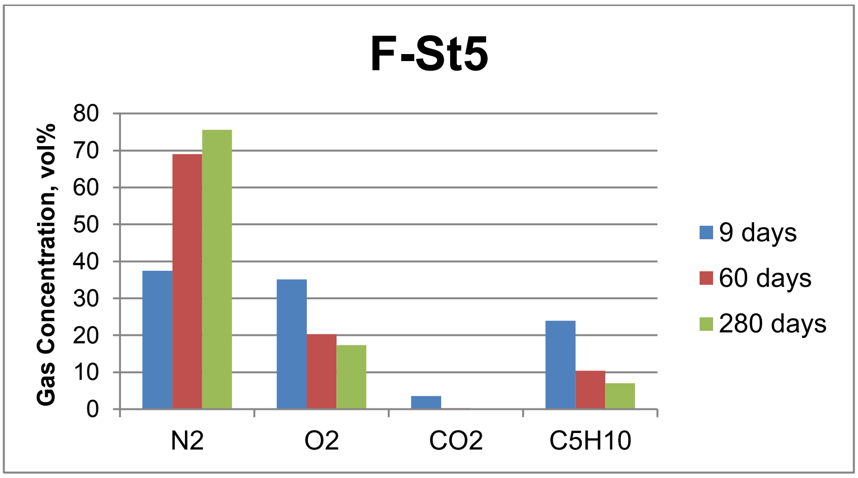
### *PU foam cell gas composition*

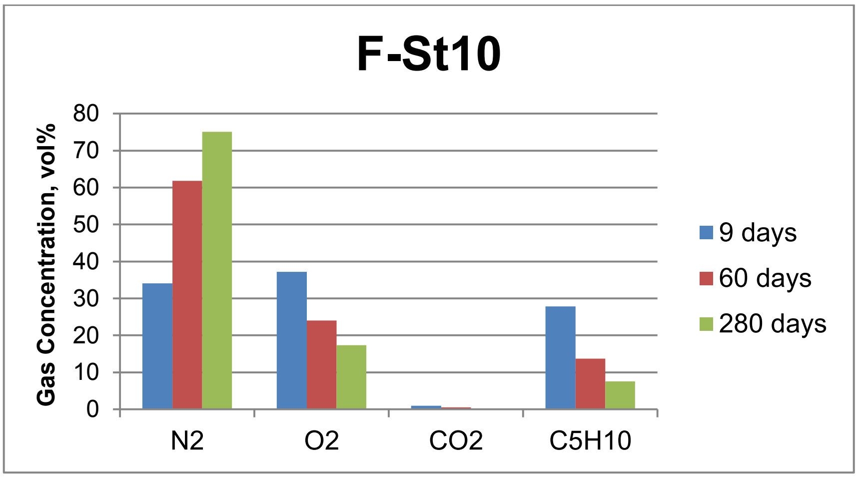
The quantitative determination of the gas phase in PU foam mainly consists of sampling and GC analysis. The sampling is procedure is more challenging in comparison with the GC analysis. The major problem was how to obtain a representative specimen of the cell gas without contamination by surrounding air gases. This problem was successfully solved.

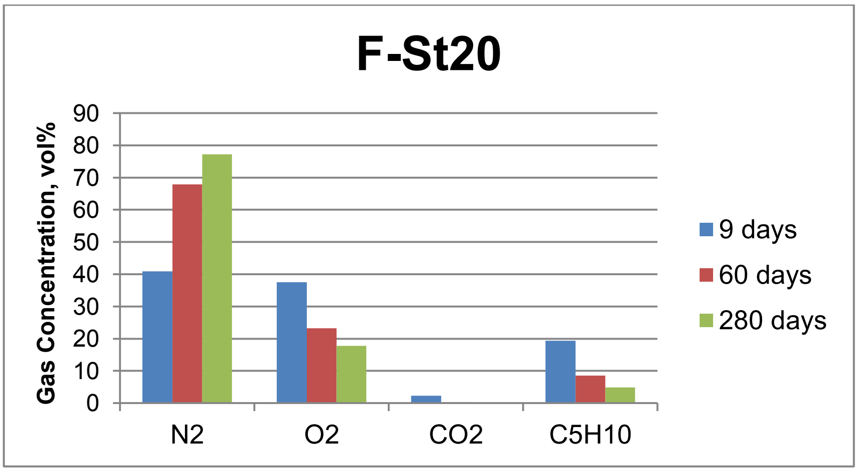
The cell gas composition was calculated with input parameters obtained from measurement of ratio of each peak area on the GC chromatograms. Additionally, areas under the peak were recalculated to molar fraction of gas that was used in Wassiljewa equation[18,19] for calculation of theoretical thermal conductivity of cell gas mixture. Table 5-8 collects foam cell gas composition together with theoretically derived values for the thermal conductivity of foam cell gas mixtures. Although it is recommended to condition a PU foam for 30-40 days for completion of all isocyanate reactions[5,27], the gas content analysis was performed shortly after manufacturing for comparison of initial gas compositions. Additionally GCMS test was performed in the period of the 2nd and 7th month for evaluation of gas diffusion in time between different samples. This test was accomplished with the measurement of foam thermal conductivity (Table 5-9). Figure 5-5 shows the change in cell gas content of standard foams during time.

**Table 5-8** Cell gas content of standard foams together with calculated gas phase thermal conductivity

| Sample index & storage time | Foam cell gas content | | | | $\lambda_{gas\ calcul}$, mW·m$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|---|
| | $N_2$, vol% | $O_2$, vol% | $CO_2$, vol% | $C_5H_{10}$, vol% | |
| **F-St5** | | | | | |
| 9 day | 37.41 | 35.13 | 3.51 | 23.96 | 22.61 |
| 2 month | 69.04 | 20.30 | 0.24 | 10.42 | 24.49 |
| 7 month | 75.61 | 17.31 | 0.057 | 7.02 | 24.92 |
| **F-St10** | | | | | |
| 9 day | 34.05 | 37.21 | 0.92 | 27.82 | 22.37 |
| 2 month | 61.82 | 24.00 | 0.51 | 13.67 | 24.09 |
| 7 month | 75.05 | 17.31 | 0.059 | 7.58 | 24.85 |
| **F-St20** | | | | | |
| 9 day | 40.90 | 37.50 | 2.27 | 19.32 | 23.32 |
| 2 month | 67.86 | 23.26 | 0.34 | 8.54 | 24.75 |
| 7 month | 77.25 | 17.82 | 0.051 | 4.89 | 25.19 |
| **F-St40** | | | | | |
| 9 day | 50.40 | 34.92 | 1.85 | 12.83 | 24.35 |
| 2 month | 72.11 | 22.44 | 0.31 | 5.14 | 25.17 |
| 7 month | 78.96 | 18.09 | 0.050 | 2.90 | 25.45 |


F-St5
Gas Concentration, vol%
0
10
20
30
40
50
60
70
80
N2
O2
CO2
C5H10
9 days
60 days
280 days


F-St10
Gas Concentration, vol%
0
10
20
30
40
50
60
70
80
N2
O2
CO2
C5H10
9 days
60 days
280 days


F-St20
Gas Concentration, vol%
0
10
20
30
40
50
60
70
80
90
N2
O2
CO2
C5H10
9 days
60 days
280 days

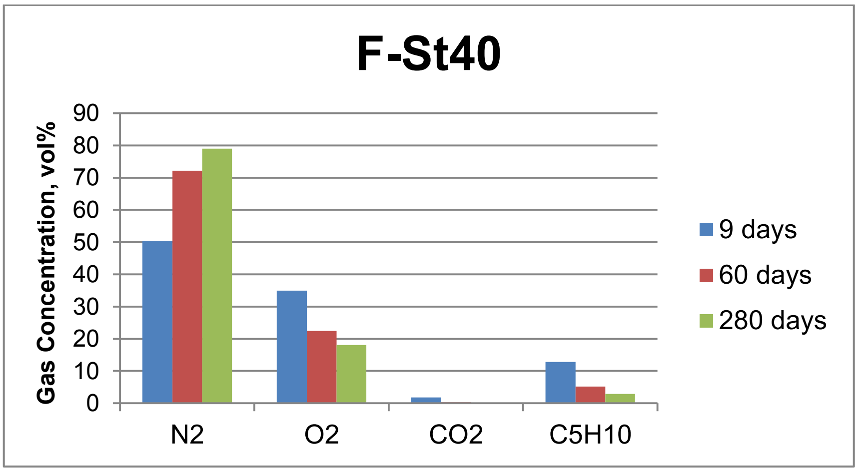


**Figure 5-5** Change in cell gas content of standard foams during time

The analysis of gas composition on the 9th day showed that F-St10 has higher content of $C_5H_{10}$ (27.82%) in comparison with F-St5 (23.96%), this could happen due to the prolonged time for a reaction between polyol and isocyanate resulting in higher rate of crosslinking and blowing reactions, thus higher amount of $C_5H_{10}$ was evaporated and diffused into the cells. With increasing of mixing time up to 20 and 40 sec the content of $C_5H_{10}$ in foam decreases (19.32% for F-St20; 12.83% for F-St40), meantime the content of $N_2$ increases (40.9% for F-St20; 50.4% for F-St40) due to the presence of open cells and supposedly thinner cell walls, which allows $C_5H_{10}$ to escape and $N_2$ from the air to diffuse into the foam. The results showed that the oxygen/nitrogen ratio of the cell gas in all samples is higher than that of the air, which was noted for most new PU foams in Persson.[5] Calculated thermal conductivity of gas mixture is in accordance with cell gas content, where the lowest value (22.37 $mW{\cdot}m^{-1}{\cdot}K^{-1}$) corresponds to the highest $C_5H_{10}$ content (27.82%) for F-St10. In the period of the 2nd and 7th month of foam storage, all samples show similar behavior: decrease in $O_2$ content and increase in $N_2$ content, the $CO_2$ has almost left the foam, $C_5H_{10}$ content decreases gradually. After 7 months F-St10 shows the lowest calculated value of thermal conductivity of cell gas mixture (24.85 $mW{\cdot}m^{-1}{\cdot}K^{-1}$).

### *Measured foam thermal conductivity*

Table 5-9 collects the measured values of foam thermal conductivity. Although it is recommended to condition a PU foam for 30-40 days for completion of all isocyanate reactions[5,27], the measurement of thermal conductivity was performed shortly after manufacturing for comparison the initial values. Additionally thermal conductivity test was performed in the period of the 2nd, 7th, 9th and 10th month for evaluation of deterioration of thermal conductivity in time between different samples. During 10 month of storage, foam samples of 2.5 x 2.5 x 1.5 $cm^3$ geometry were aged at RT. Thermal conductivity was measured at RT and in perpendicular to the foam rise direction. It is well known that foam thermal conductivity is determined by three mechanisms: conduction along the solid phase ($\lambda_s$), conduction through the gas phase ($\lambda_g$) and thermal radiation ($\lambda_r$), the fourth mechanism - convection inside the cells ($\lambda_c$) is not considered for this study, because the cells' size is small (lower than 2 mm).[24] Therefore, the analysis of measured in this study foam thermal conductivity will be done in accordance with the mentioned three mechanisms.

**Table 5-9** Measured foam thermal conductivity

| Ageing time | Measured foam thermal conductivity, mW·$m^{-1}$·$K^{-1}$ | | | | $T_{test}$, °C |
|---|---|---|---|---|---|
| | F-St5 | F-St10 | F-St20 | F-St40 | |
| 9 day | 42.2 ± 0.4 | 40.1 ± 0.5 | 38.5 ± 0.3 | 37.8 ± 0.1 | 24.0 |
| 2 month | 39.4 ± 1.0 | 36.6 ± 0.1 | 36.4 ± 1.6 | 38.8 ± 0.0 | 23.0 |
| 7 month | 39.2 ± 1.3 | 35.6 ± 0.1 | 35.4 ± 0.1 | 38.5 ± 0.5 | 19.2 |
| 9 month | 40.9 ± 0.1 | 37.3 ± 0.1 | 38.9 ± 0.2 | 40.3 ± 0.1 | 18.7 |
| 10 month | 40.7 ± 0.3 | 37.1 ± 0.1 | 38.2 ± 0.8 | 40.1 ± 0.1 | 21.1 |

The results of the measured foam thermal conductivity on the 9th day showed that F-St40 foam has the lowest value (37.8 mW·$m^{-1}$·$K^{-1}$) and F-St5 foam has the highest value (42.2 mW·$m^{-1}$·$K^{-1}$) among others. This could be explained by decrease in cell size (F-St40 has the smallest cell size among others), which increased the extinction coefficient and, consequently, minimized the radiative contribution to the total thermal conductivity. Additionally, thermal conductivity of F-St10 (40.1 mW·$m^{-1}$·$K^{-1}$) and F-St20 (38.5 mW·$m^{-1}$·$K^{-1}$) is lower than of F-St5 due to lower foam density what minimized the solid phase contribution to the total thermal conductivity. Besides this, thermal conductivity of foam F-St10 is lower than F-St5 because it has higher $C_5H_{10}$ content what decreases the gas phase contribution to the total thermal conductivity.

After the 2nd month of ageing at RT three foams F-St5, F-St10 and F-St20 show decrease in thermal conductivity (39.4; 36.6; 36.4 mW·$m^{-1}$·$K^{-1}$ correspondingly), meantime F-St40 show increase (28.8 mW·$m^{-1}$·$K^{-1}$). The improvement in foam thermal conductivity could happen due to the unstabilized foam condition (not complete isocyanate reactions or other mechanism[5,27]), but not due to gas diffusion, because gas content measurements showed deterioration of gas phase conduction. Results showed that F20 is the lowest, and F5 is again the highest.

After the 7th month of ageing at RT all foams show similar trend to the 2nd month or even slightly improvement of total foam thermal conductivity, although gas phase conduction, shown in Table 5-8, continues to deteriorate. Foams F-St10 (35.6 mW·$m^{-1}$·$K^{-1}$) and F-St20 (35.4 mW·$m^{-1}$·$K^{-1}$) show lower values, than F-St5 (39.2 mW·$m^{-1}$·$K^{-1}$) and F-St40 (38.5 mW·$m^{-1}$·$K^{-1}$) do. That means radiative and gas phase contributions play a smaller role, than conduction through the solid phase at this stage.

After the 9th month of ageing at RT all foams show increase in foam thermal conductivity in comparison with the 2nd and 7th month. At this stage foam F-St10 shows the lowest value of thermal conductivity (37.3 $mW \cdot m^{-1} \cdot K^{-1}$) among others. This could be explained by gas phase conduction, although it was not possible to measure it on the 9th month, but according to the trend of gas content measured on the 9th day until 7th month, F-St10 contains more $C_5H_{10}$ and $CO_2$ and less air than other foams.

After the 10th month of ageing at RT all foams show similar trend to the 9th month. Foam F-St10 shows the lowest value of thermal conductivity (37.1 $mW \cdot m^{-1} \cdot K^{-1}$) among others.

It is well known that foams with a smaller cell size and larger number of cells show lower values of foam thermal conductivity. In our study F40 has the smallest cell size and the largest number of cells, but measured thermal conductivity is not the lowest between other samples. Meantime F-St10 has a medium cell size and small number of cells, but, in combination with low density and highest $C_5H_{10}$ and $CO_2$ content and lack of open cells, it shows the lowest measured value of foam thermal conductivity. It means that thermal conductivity is a complex property which is influenced by an individual foam structure. Additionally, the decrease of foam thermal conductivity on the 2nd and 7th month and increase on the 9th month for all samples means that some PU foam samples require more than 10 months of monitoring for evaluation of deterioration of thermal conductivity in time for one sample and comparison between different samples.

### 5.3.2 Characterization of PU foam functionalized with azo polyol

Polyurethane foams described in this paragraph were produced with the same ratio between main components (polyol, isocyanate and cyclopentane), but different concentration of an additive (azo polyol) in order to investigate the effect of the additive on morphological and thermal properties of the foam. The formulation of functionalized foam F-0.5 contained 0.5% of the additive, foam F-3 – 3%, foam F-5 – 5%, foam F-10 – 10% and foam F-20 – 20% correspondingly. During producing the foam in laboratory conditions, the difference in foaming process between foam samples with different concentration of the additive was noticed. One of the reasons for the observed changes in foaming process could deal with difference in viscosity of polyol blend depending on concentration of the premixed additive. Therefore, manufacturing process was developed individually for every foam depending on the concentration of the additive. As a result, a set of foam’s groups was formed, every foam’s group included a functionalized foam with a corresponding additive content and a standard foam of similar morphology (reference material). The effect of the additive on morphological and thermal properties of the polyurethane foam was analyzed and will be described below.

### Foams produced with different concentration of an additive

### 0.5% additive concentration

F-0.5 foam was produced with 0.5% of azo polyol additive. The modified F-0.5 foam and its reference standard F-StA foam were produced with the same mixing speed and similar mass of reagent mixture, but different mixing time in order to reach as much as possible identical morphology between them, for instance foam density and cell size. The analysis of 0.5% additive influence on morphological and thermal properties of a functionalized foam will be described below.

## *Morphological characterization*

#### *Cell size, cell shape, number of cells*

Table 5-12 shows the reduction of a cell size and increase in a cell number of a functionalized foam in comparison with the standard one. The cell size reduction was from 390 ± 110 µm for F-StA to 230 ± 60 for F-0.5. The reason for the observed cell size reduction is related with the rheological properties, for instance the viscosities of pure polyol (standard) and polyol blend (standard polyol with premixed 0.5% of azo polyol) and possible change of cyclopentane solubility in a new reagent mixture, which determine the distributions of pressure and velocity in the processing system, and influence the cell growth during the foam manufacturing process. The results of viscosity measurement showed that azo polyol has a lower value (0.04 Pa·s), than standard polyol (2.00 Pa·s), therefore it reduces the viscosity of 0.5% polyol blend in a new foam reagent mixture (see Table 5-11). The reduced viscosity of azo polyol in comparison with standard polyol is explained by the presence of residue of dichloromethane solvent.

Figure 5-6 shows SEM images of the cellular structure of F-0.5 foam and its reference standard foam F-StA. Both samples presented regular polyhedral structures with pentagonal or hexagonal faces. F-0.5 foam has closed-cell structure, meantime F-StA contains some content of open-cells.

#### *Foam density, foam height, expansion ratio, open / close-cell, characteristic times*

Considering that after addition of 0.5% of an additive to the PU blend an acceleration of the foaming process was noticed, the functionalized foam was mixed during shorter time (30 sec for F-0.5; 40 sec for F-StA), what was followed by the reduction in all characteristic times. The cream time was not possible to measure for both foams due to overlapping with mixing time. One of the reasons for the observed reaction acceleration of the new foam could deal with the measured lower viscosity of the 0.5% polyol blend (see Table 5-11). The accelerated reaction between polyol and isocyanate in the functionalized foam results in higher rate of polyaddition and blowing reactions. Thus, higher amount of gas diffuses into the cells resulting in the higher expansion ratio (17.3 for F-0.5; 16.3 for F-StA) and more polyurethane linkages form resulting in larger amount of blown cells and larger height (4.5 cm for F-0.5; 4 cm for F-StA) of the foam.

When for standard foam the mixing time is increased up to 40 sec, in comparison with the functionalized foam, the high temperature is applied longer time and cells can open before the polymer maintains the cells' structure[28]. This is accomplished with slightly increase in density (66.5 kg/m$^3$ for F-StA) and presence of open cells in F-StA, the open cell structure is visible from F-StA SEM image (Figure 5-6).

**Table 5-10** Foam manufacturing conditions, characteristic times, height and expansion ratio

| Foam index | Mass of mixture, g | Mixing parameters | | Characteristic times | | | | Foam height cm | Expansion ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | Speed, rpm | Time, +9 sec inside | Cream time, sec | Gel time, sec | Rise time, sec | Tack free time, sec | | |
| F-0.5 | 17.54 | 800 | 30 | <40 | 46 | 85 | 190 | 4.5 | 17.3 |
| F-StA | 17.51 | 800 | 40 | <50 | 58 | 106 | 209 | 4 | 16.3 |

**Table 5-11** Viscosity and water content

| Polyol | Viscosity, Pa·s | Water content, % |
|---|---|---|
| Azo polyol | 0.04 | 0.19 |
| Standard polyol | 2.00 | 1.9 |
| 0.5 % polyol blend<br>(0.5% azo polyol premixed to standard polyol) | 1.85 | - |

**Table 5-12** Foam density, cell size, number of cells per area

| Foam index | Density, kg/m$^3$ | Cell size, µm | Number of cells per 25 mm$^2$ |
|---|---|---|---|
| F-0.5 | 62.9 ± 0.3 | 230 ± 60 | 300 |
| F-StA | 66.5 ± 0.2 | 390 ± 110 | 200 |

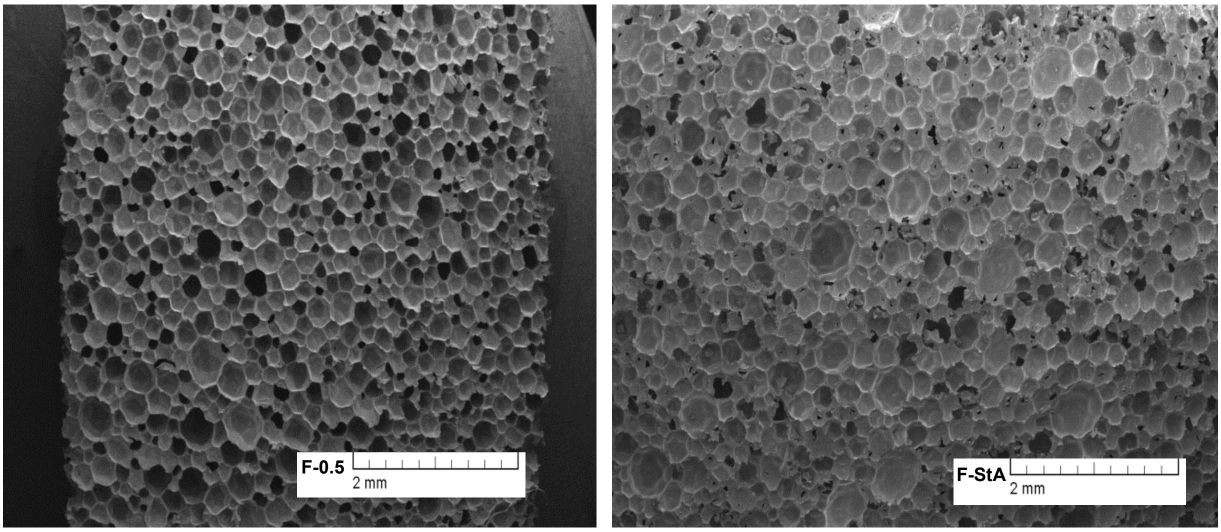


**Figure 5-6** SEM images of cross-sections in perpendicular to the foam rise for F-0.5 foam and its reference standard foam F-StA. MAG: 40x

### *Measured foam thermal conductivity*

Table 5-13 collects the measured values of foam thermal conductivity. Although, it is recommended to condition a PU foam for 30-40 days for completion of all isocyanate reactions[5,27], the measurement of thermal conductivity was performed shortly after manufacturing for comparison of initial values. Additionally, thermal conductivity test was performed on 1st, 2nd and 10th month for evaluation of deterioration of thermal conductivity in time between different samples. During 10 month of storage, foam samples of 2.5 x 2.5 x 1.5 $cm^3$ geometry were aged at RT. Thermal conductivity was measured at RT and in perpendicular to the foam rise direction. As it has been already mentioned in the previous section foam thermal conductivity is determined by three mechanisms: conduction along the solid phase ($\lambda_s$), conduction through the gas phase ($\lambda_g$) and thermal radiation ($\lambda_r$).[24] Therefore, the analysis of measured foam thermal conductivity will be performed in accordance with the mentioned three mechanisms.

**Table 5-13** Measured foam thermal conductivity

| Ageing time | Foam thermal conductivity, $mW \cdot m^{-1} \cdot K^{-1}$ | |
|---|---|---|
| | Modified foam F-0.5 | Standard foam F-StA |
| 8 day | 38.2 ± 0.1 | 38.9 ± 0.0 |
| 1 month | 36.7 ± 0.1 | 38.2 ± 0.1 |
| 2 month | 39.4 ± 0.0 | 40.4 ± 0.1 |
| 10 month | 38.4 ± 0.1 | 38.6 ± 0.1 |

The results of the measured foam thermal conductivity on the 8th day and after 10 months showed that modified F-0.5 foam has slightly lower value (8th day: 38.2 $mW \cdot m^{-1} \cdot K^{-1}$; 10th month: 38.4 $mW \cdot m^{-1} \cdot K^{-1}$) in comparison with standard F-StA foam (8th day: 38.9 $mW \cdot m^{-1} \cdot K^{-1}$; 10th month: 38.6 $mW \cdot m^{-1} \cdot K^{-1}$). On the one hand, this insignificant reduction in foam thermal conductivity could be explained by the presence of 0.5% of an additive in the F-0.5 foam. On the other hand, this could be explained by decrease in cell size, which increased the extinction coefficient and, consequently, minimized the radiative contribution to the total thermal conductivity; and, additionally, by slightly decrease in foam density what minimized the solid phase contribution to the total thermal conductivity. Besides this, standard foam contains open cells which influences on foam gas phase insulation ability. In this case the GCMS analysis could be very helpful, but unfortunately gas content measurement wasn't done on standard foam F-StA.

Both foam samples showed similar trend in deviation of foam thermal conductivity in the 1st and 2nd month of testing. This could happen due to the unstabilized foam condition (not complete isocyanate reactions or other mechanism[5,27]).

Considering that both foams showed slightly differences in morphology, the separation of effect from 0.5% additive and morphological changes on improvement of foam thermal conductivity was not possible.

### 3% additive concentration

The F-3 foam was produced with 3% of azo polyol additive. The modified F-3 foam and its reference standard F-StB foams were produced with the same mixing speed, but different mixing time and mass of reagent mixture in order to reach similar foam morphology between them, for instance foam density and cell size. The analysis of 3% additive influence on morphological and thermal properties of a functionalized foam will be described below.

## *Morphological characterization*

### *Cell size, cell shape, number of cells*

Table 5-16 shows the reduction of a cell size and increase in a cell number of a functionalized foam in comparison with the standard one. The cell size reduction was from 500 ± 70 µm for F-StB to 390 ± 40 for F-3. The reason for the observed cell size reduction is related with the rheological properties, for instance the viscosities of pure polyol (standard) and polyol blend (standard polyol with premixed 3% of azo polyol) and possible change of cyclopentane solubility in new reagent mixture, which determine the distributions of pressure and velocity in the processing system, and influence the cell growth during the foam manufacturing process. The results of viscosity measurement showed that azo polyol has a lower value (0.04 Pa·s), than standard polyol (2.00 Pa·s), therefore it reduces the viscosity of 3% polyol blend in a functionalized foam reagent mixture (see Table 5-15). The reduced viscosity of azo polyol in comparison with standard polyol is explained by the presence of residue of dichloromethane solvent.

Figure 5-7 shows SEM images of the cellular structure of F-3 foam and its reference standard foam F-StB. Both samples presented regular polyhedral structures with pentagonal or hexagonal faces. Both foams have closed-cell structure with some content of open-cells.

*Foam density, foam height, expansion ratio, open / close-cell, characteristic times*

Considering that after addition of 3% of additive to the PU blend an acceleration of the foaming process was noticed, the modified foam was mixed during shorter time (10 sec for F-3; 20 sec for F-StB), what was followed by the reduction in all characteristic times. The cream time was not possible to measure for both foams due to overlapping with mixing time.  One of the reasons for the observed reaction acceleration of the modified foam could deal with the measured lower viscosity of the 3% polyol blend (see Table 5-15). Accelerated reaction between polyol and isocyanate in the new foam results in higher rate of polyaddition and blowing reactions. Thus, higher amount of gas diffuses into the cells resulting in the higher expansion ratio (22.2 for F-3; 19.9 for F-StB and more polyurethane linkages form resulting in a larger amount of blown cells and larger height (4.5 cm for F-0.5; 4 cm for F-StA) of the foam. The height of the new foam sample could be also larger than for standard foam, but considering that mass of reagent mixture for functionalized foam was decreased in comparison with standard one due to acceleration of foaming reaction and limited manufacturing conditions of closed mixer system, the sample height was smaller (8.8 cm for F-3; 10.3 cm for F-StB).

When for a standard foam the mixing time is increased up to 20 sec, in comparison with the functionalized foam, the high temperature is applied longer time and cells may open before the polymer has enough strength to maintain the cellular structure[28]. This is accomplished with slightly increase in density (54.53 kg/m$^3$ for F-StB) and presence of open cells in F-StB, however the open cell structure is visible in both foams from SEM image (Figure 5-7).

**Table 5-14** Foam manufacturing conditions, characteristic times, height and expansion ratio

| Foam index | Mass of mixture, g | Mixing parameters | | Characteristic times | | | | Foam height cm | Expansion ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | Speed, rpm | Time, +9 sec inside | Cream time, sec | Gel time, sec | Rise time, sec | Tack free time, sec | | |
| F-3 | 26.5 | 800 | 10 | <20 | 26 | 75 | 90 | 8.8 | 22.2 |
| F-StB | 32.8 | 800 | 20 | <30 | 38 | 121 | 148 | 10.3 | 19.9 |

**Table 5-15** Viscosity and water content

| Polyol | Viscosity, Pa·s | Water content, % |
|---|---|---|
| Azo polyol | 0.04 | 0.19 |
| Standard polyol | 2.00 | 1.9 |
| 3 % polyol blend<br>(3% azo polyol premixed to standard polyol) | 1.79 | - |

**Table 5-16** Foam density, cell size, number of cells per area

| Foam index | Density, kg/$m^3$ | Cell size, µm | Number of cells per 25 $mm^2$ |
|---|---|---|---|
| F-3 | 49.0 ± 0.1 | 390 ± 40 | 80 |
| F-StB | 54.5 ± 0.9 | 500 ± 70 | 50 |

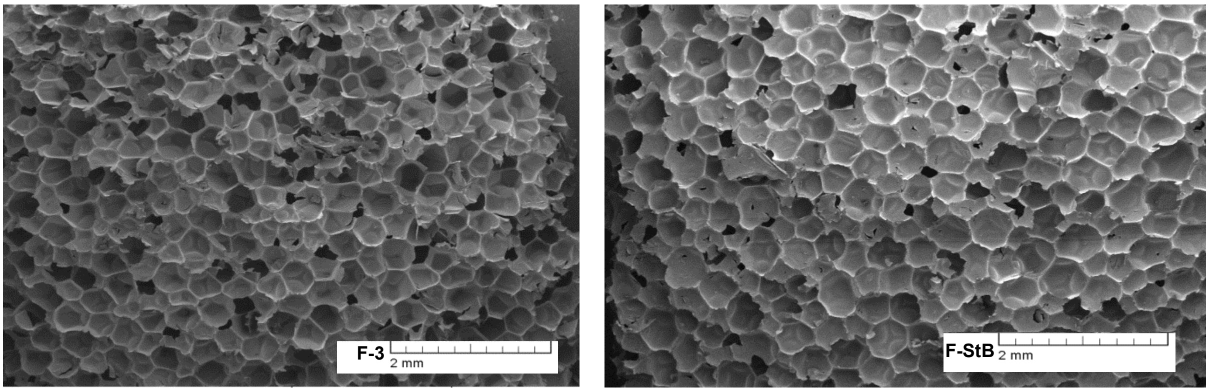


**Figure 5-7** SEM images of cross-sections in perpendicular to the foam rise for F-3 foam and its reference standard foam F-StB. MAG: 40x.

## *Measured foam thermal conductivity*

Table 5-17 collects the measured values of foam thermal conductivity. Although, it is recommended to condition PU foam for 30-40 days for completion of all isocyanate reactions[5,27], the measurement of thermal conductivity was performed shortly after manufacturing to compare the initial values. Additionally thermal conductivity test was performed in the 2nd, 7th, 9th and 10th month for evaluation of deterioration of thermal conductivity in time between different samples (data for the 7th and 9th months exist just for standard sample). During 10 months of storage, foam samples of 2.5 x 2.5 x 1.5 $cm^3$ geometry were aged at RT. Thermal conductivity was measured at RT and in perpendicular to the foam rise direction. As previously mentioned, foam thermal conductivity is determined by three mechanisms (conduction along the solid phase, conduction through the gas phase and thermal radiation).[24] Therefore, the analysis of measured foam thermal conductivity will be accomplished in accordance with the mentioned three mechanisms.

**Table 5-17** Measured foam thermal conductivity

| Ageing time | Foam thermal conductivity, $mW \cdot m^{-1} \cdot K^{-1}$ | |
|---|---|---|
| | Modified foam F-3 | Standard foam F-StB |
| 8 day | 37.9 ± 0.1 | 38.5 ± 0.3 |
| 2 month | 37.1 ± 0.2 | 36.4 ± 1.6 |
| 7 month | - | 35.4 ± 0.1 |
| 9 month | - | 38.9 ± 0.2 |
| 10 month | 38.0 ± 0.1 | 38.2 ± 0.8 |

The results of the measured foam thermal conductivity on the 8th day and after 10 months showed that functionalized F-3 foam has slightly lower values (8th day: 37.9 $mW \cdot m^{-1} \cdot K^{-1}$; 10th month: 38.0 $mW \cdot m^{-1} \cdot K^{-1}$) in comparison with standard F-StB foam (8th day: 38.5 $mW \cdot m^{-1} \cdot K^{-1}$; 10th month: 38.2 $mW \cdot m^{-1} \cdot K^{-1}$). On the one hand, this insignificant reduction in foam thermal conductivity could be explained by the presence of 3% of additive in the F-3 foam. On the other hand, this could be explained by decrease in cell size, which increased the extinction coefficient and, consequently, minimized the radiative contribution to the total thermal conductivity; and, additionally, by slightly decrease in foam density what minimized the solid phase contribution to the total thermal conductivity. Besides this, the gas analysis showed that F-StB contains less cyclopentane (19.32%) on the 9th day of testing (see Table 5-8, sample F-St20), meantime functionalized F-3 foam contains a bit more cyclopentane (21.39%) even on the 12th day of testing (Table 5-28).

Both foam samples showed similar trend in deviation of foam thermal conductivity in the 2nd month of testing. This could happen due to the unstabilized foam condition (not complete isocyanate reactions or other mechanism[5,27]), but not due to gas diffusion, because gas content measurements for functionalized F-3 foam showed deterioration of gas phase thermal conductivity, in particular the significant decrease in cyclopentane content (from 22.3% on the 4th day until 7.8% after one month) and carbon dioxide content (from 25.55% on 4th day until 0.22% after one month) (Table 5-28). At this stage the lower value of the measured thermal conductivity of a standard foam in comparison with a functionalized foam could be explained by gas content measurements, which showed that the standard foam contained more $C_5H_{10}$

(8.54%) and $CO_2$ (0.34%) in the second month (see Table 5-8, sample F-St20), than the functionalized foam after one month (7.8% $C_5H_{10}$; 0.22% $CO_2$ – see Table 5-28).

Considering that both foams showed some differences in morphology, the separation of effect from 3% additive and morphological changes on improvement of foam thermal conductivity was not possible.

**5% additive concentration**

F-5 foam was produced with 5% of azo polyol additive. The modified F-5 foam and its reference standard F-StB foams were produced with the same mixing speed, but different mixing time and mass of reagent mixture in order to reach similar foam morphology, for instance foam density and cell size. Considering that increase of additive concentration in functionalized foam formulation leads to gradually significant decrease in foam density and that most of the standard foams (produced at different mixing times) maintain density in the same range, the reference foam in this set was selected in accordance just with cell size. The analysis of 5% additive influence on morphological and thermal properties of foam will be described below.

## *Morphological characterization*

### *Cell size, cell shape, number of cells*

Table 5-20 shows the reduction of a cell size of the functionalized foam in comparison with the standard one, meantime the cell number is equal in both foams. However, the cell size reduction is not significant, from 500 ± 70 μm for F-StB to 450 ± 70 for F-5. The reason for the observed cell size reduction is related with the rheological properties, for instance the viscosities of pure polyol (standard) and polyol blend (standard polyol with premixed 5% of azo polyol) and possible change of cyclopentane solubility in new reagent mixture, which determine the distributions of pressure and velocity in the processing system, and influence the cell growth during the foam manufacturing process. Results of viscosity measurement showed that azo polyol has a lower value (0.04 Pa·s), than standard polyol (2.00 Pa·s), therefore it reduces the viscosity of 5% polyol blend in modified foam reagent mixture (see Table 5-19). The reduced viscosity of azo polyol in comparison with standard polyol is explained by the presence of residue of dichloromethane solvent.

Figure 5-8 shows SEM images of the cellular structure of F-5 foam and its reference standard foam F-StB. Both samples presented regular polyhedral structures with pentagonal or hexagonal faces. Both foams have closed-cell structure with some content of open-cells.

### *Foam density, foam height, expansion ratio, open / close-cell, characteristic times*

Considering that after addition of 5% of additive to the PU blend an acceleration of the foaming process was noticed, the modified foam was mixed during shorter time (10 sec for F-5; 20 sec for F-StB), what was followed by the reduction in all characteristic times. The cream time was not possible to measure for both foams due to overlapping with mixing time. One of the reasons for the observed reaction acceleration of the new foam could deal with the measured lower viscosity of the 5% polyol blend (see Table 5-19). The accelerated reaction between polyol and isocyanate in the functionalized foam results in a higher rate of polyaddition and blowing reactions. Thus, higher amount of gas diffuses into the cells resulting in the higher expansion ratio (23.5 for F-5; 19.9 for F-StB and more polyurethane linkages. The amount of cells and height of sample are similar for both foams. Increase of additive concentration until 5% in the foam formulation has led to noticeable decrease in the functionalized foam density (46.2 kg/m$^3$), in comparison with the standard foam (54.5 kg/m$^3$).

When for standard foam the mixing time is increased up to 20 sec, in comparison with the modified foam, the high temperature is applied longer time and cells can open before the polymer maintains the cells' structure[28]. The open cell structure is visible in both foams from SEM image (Figure 5-8).

**Table 5-18** Foam manufacturing conditions, characteristic times, height and expansion ratio

| Foam index | Mass of mixture, g | Mixing parameters | | Characteristic times | | | | Foam height cm | Expansion ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | Speed, rpm | Time, +9 sec inside | Cream time, sec | Gel time, sec | Rise time, sec | Tack free time, sec | | |
| F-5 | 29.7 | 800 | 10 | <20 | 22 | 57 | 62 | 10.5 | 23.5 |
| F-StB | 32.8 | 800 | 20 | <30 | 38 | 121 | 148 | 10.3 | 19.9 |

**Table 5-19** Viscosity and water content

| Polyol | Viscosity, Pa·s | Water content, % |
|---|---|---|
| Azo polyol | 0.04 | 0.19 |
| Standard polyol | 2.00 | 1.9 |
| 5 % polyol blend<br>(5% azo polyol premixed to standard polyol) | 1.70 | - |

**Table 5-20** Foam density, cell size, number of cells per area

| Foam index | Density, kg/m$^3$ | Cell size, µm | Number of cells per 25 mm$^2$ |
|---|---|---|---|
| F-5 | 46.2 ± 0.3 | 450 ± 70 | 50 |
| F-StB | 54.5 ± 0.9 | 500 ± 70 | 50 |

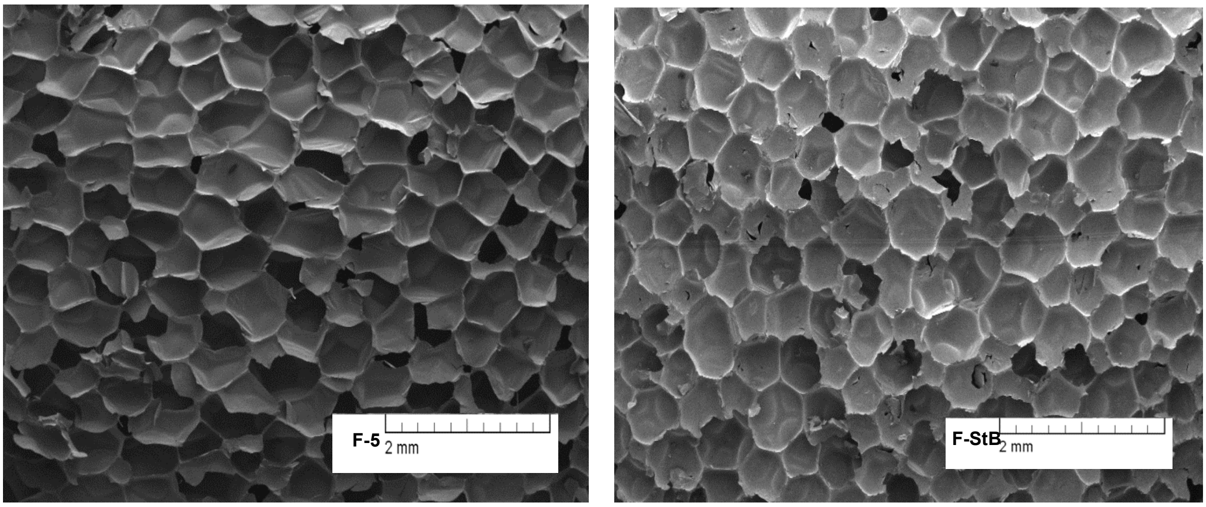


**Figure 5-8** SEM images of cross-sections in perpendicular to the foam rise for F-5 foam and its reference standard foam F-StB. MAG: 40x.

## *Measured foam thermal conductivity*

Table 5-21 collects the measured values of foam thermal conductivity. Although, it is recommended to condition a PU foam for 30-40 days for completion of all isocyanate reactions[5,27], the measurement of thermal conductivity was performed shortly after manufacturing for comparison of initial values. Additionally, thermal conductivity test was performed regularly during 10 months to evaluate deterioration of thermal conductivity in time for functionalized foam and between different samples (data for 4th, 5th and 6.5th months exist just for new foam). During 10 months of storage the foam samples of 2.5 x 2.5 x 1.5 cm$^3$ geometry were aged at RT. Thermal conductivity was measured at RT and in perpendicular to the foam rise direction. As it has been already stated in the previous sections foam thermal conductivity is determined by three mechanisms: conduction along the solid phase ($\lambda_s$), conduction through the gas phase ($\lambda_g$) and thermal radiation ($\lambda_r$).[24] Therefore, the analysis of the measured foam thermal conductivity will be done based on mentioned mechanisms.

**Table 5-21** Measured foam thermal conductivity

| Ageing time | Foam thermal conductivity, mW·m$^{-1}$·K$^{-1}$ | |
|---|---|---|
| | Modified foam F-5 | Standard foam F-StB |
| 8 day | 35.0 ± 0.1 | 38.5 ± 0.3 |
| 2 month | 33.9 ± 0.1 | 36.4 ± 1.6 |
| 4 month | 32.8 ± 0.4 | - |
| 5 month | 32.7 ± 0.1 | - |
| 6.5 month | 32.2 ± 0.1 | - |
| 7 month | 33.6 ± 0.2 | 35.4 ± 0.1 |
| 9 month | 33.7 ± 1.2 | 38.9 ± 0.2 |
| 10 month | 33.2 ± 0.1 | 38.2 ± 0.8 |

The results of the measured foam thermal conductivity on the 8th day and after 10 months showed that modified F-5 foam has much lower values (8th day: 35.0 mW·m$^{-1}$·K$^{-1}$; 10th month: 33.2 mW·m$^{-1}$·K$^{-1}$) in comparison with standard F-StB foam (8th day: 38.5 mW·m$^{-1}$·K$^{-1}$; 10th month: 38.2 mW·m$^{-1}$·K$^{-1}$). On the one hand, this significant reduction in foam thermal conductivity could be explained by the presence of 5% of an additive in the F-5 foam. On the other hand, this could be explained by noticeable decrease in foam density what minimized the solid phase contribution to the total thermal conductivity. The cell size and number of cells in both foams are very similar, therefore its influence on radiative contribution to the total thermal conductivity could be neglected. Besides this, gas analysis of functionalized foam showed that, although cyclopentane content deviates at the beginning (13.6% on 3rd day; 28.5% on 11 day), the carbon dioxide content is high and decreases gradually (42% on 3rd day; 4.9% on 11 day - Table 5-28). Meantime, gas analysis of standard foam on the 9th day showed lower content of cyclopentane and carbon dioxide (9th day: 19.3% $C_5H_{10}$; 2.27% $CO_2$), what decreases the foam gas phase insulation ability (Table 5-8, sample F-St20).

Both foam samples showed similar trend in deviation of foam thermal conductivity on from the 2nd to 10th month of testing. This could occur due to the unstabilized foam condition (not complete isocyanate reactions or other mechanism[5,27]).

Considering that both foams showed noticeable difference in density, the separation of the effect from 5% of an additive and morphological changes on improvement of foam thermal conductivity was not possible.

**10% additive concentration**

F-10 foam was produced with 10% of azo polyol additive. The modified F-10 foam and its reference standard F-StB foams were produced with the same mixing speed, but different mixing time and mass of reagent mixture in order to reach similar foam morphology between them, for instance foam density and cell size. Considering that increase of additive concentration in functionalized foam formulation leads to gradually significant decrease in foam density and that most of the standard foams (produced at different mixing times) maintain density in the same range, the reference foam in this set was selected in accordance just with cell size. The analysis of 10% additive influence on the morphological and thermal properties of the foam will be described below.

## *Morphological characterization*

### *Cell size, cell shape, number of cells*

Table 5-22 shows the reduction of cell size of functionalized foam in comparison with the standard one, meantime the cell number is similar in both foams. However, the cell size reduction is not very significant, from 500 ± 70 µm for F-StB to 430 ± 60 for F-10. The reason for the observed cell size reduction refers to the rheological properties, for instance the viscosities of pure polyol (standard) and polyol blend (standard polyol with premixed 10% of azo polyol) and possible change of cyclopentane solubility in new reagent mixture, which determine the distributions of pressure and velocity in the processing system, and influence the cell growth during the foam manufacturing process. The results of viscosity measurement showed that azo polyol has a lower value (0.04 Pa·s), than standard polyol (2.00 Pa·s), therefore it reduces the viscosity of 10% polyol blend in modified foam reagent mixture (see Table 5-21). The reduced viscosity of azo polyol in comparison with the standard polyol is explained by the presence of residue of dichloromethane solvent.

Figure 5-9 shows SEM images of the cellular structure of F-10 foam and its reference standard foam F-StB. Both samples presented regular polyhedral structures with pentagonal or hexagonal faces. Both foams have closed-cell structure with some content of open-cells.

### *Foam density, foam height, expansion ratio, open / close-cell, characteristic times*

Considering that after addition of 10% of additive to the PU blend a significant acceleration of the foaming process was noticed, the modified foam was mixed at minimum time (5 sec for F-10; 20 sec for F-StB), what was followed by the huge reduction in all characteristic times. The cream and gel times for the modified foam was not possible to measure due to overlapping with mixing time, for standard foam just cream time was not possible to measure. One of the reasons for the observed reaction acceleration of the new foam could deal with the measured lower viscosity of the 10% polyol blend (see Table 5-21). The accelerated reaction between polyol and isocyanate in the new foam results in higher rate of polyaddition and blowing reactions. Thus, higher amount of gas diffuses into the cells resulting in the higher expansion ratio (27.6 for F-10; 19.9 for F-StB) and more polyurethane linkages form resulting in larger height (4.5 cm for F-0.5; 4 cm for F-StA) of the foam, even the mass of mixture was smaller. The number of cells was equal in both foams. Increase of additive concentration until 10% in foam formulation has led to significant decrease in functionalized foam density (39.3 kg/m$^3$), in comparison with the standard foam (54.5 kg/m$^3$).

When for standard foam the mixing time is increased up to 20 sec, in comparison with the modified foam, the high temperature is applied for longer time and cells may open before the polymer has enough strength to maintain the cellular structure[28]. The open cell structure is visible in both foams from SEM image (Figure 5-9).

**Table 5-22** Foam manufacturing conditions, characteristic times, height and expansion ratio

| Foam index | Mass of mixture, g | Mixing parameters | | Characteristic times | | | | Foam height cm | Expansion ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | Speed, rpm | Time, +9 sec inside | Cream time, sec | Gel time, sec | Rise time, sec | Tack free time, sec | | |
| F-10 | 27.2 | 800 | 5 | <15 | <15 | 54 | 54 | 11 | 27.6 |
| F-StB | 32.8 | 800 | 20 | <30 | 38 | 121 | 148 | 10.3 | 19.9 |

**Table 5-21** Viscosity and water content

| Polyol | Viscosity, Pa·s | Water content, % |
|---|---|---|
| Azo polyol | 0.04 | 0.19 |
| Standard polyol | 2.00 | 1.9 |
| 10 % polyol blend<br>(10% azo polyol premixed to standard polyol) | 1.45 | - |

**Table 5-22** Foam density, cell size, number of cells per area

| Foam index | Density, kg/m$^3$ | Cell size, µm | Number of cells per 25 mm$^2$ |
|---|---|---|---|
| F-10 | 39.3 ± 0.2 | 430 ± 60 | 50 |
| F-StB | 54.5 ± 0.9 | 500 ± 70 | 50 |

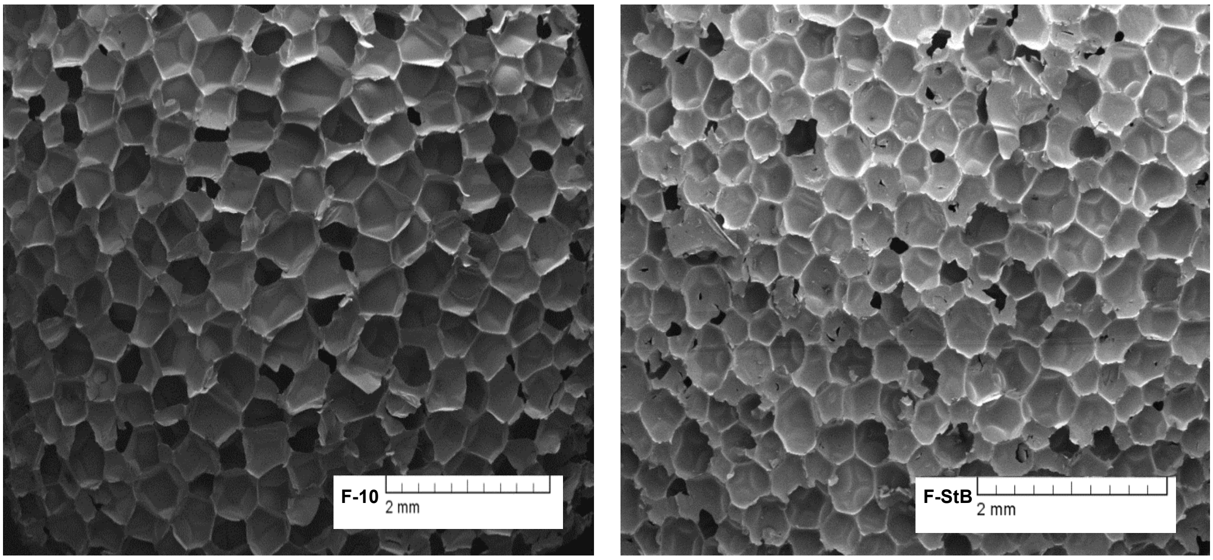


**Figure 5-9** SEM images of cross-sections in perpendicular to the foam rise for F-10 foam and its reference standard foam F-StB. MAG: 40x.

## *Measured foam thermal conductivity*

Table 5-23 collects the measured values of foam thermal conductivity. Although, it is recommended to condition a PU foam for 30-40 days to complete all isocyanate reactions[5,27], the measurement of thermal conductivity was performed shortly after manufacturing to compare initial values. Additionally, thermal conductivity test was performed regularly during 10 months to evaluate deterioration of thermal conductivity in time for functionalized foam and between different samples (data for 4th, 5th and 6.5th months exist just for new foam). During 10 months of storage foam samples of 2.5 x 2.5 x 1.5 cm$^3$ geometry were aged at RT. Thermal conductivity was measured at RT and in perpendicular to the foam rise direction. As indicated previously foam thermal conductivity is determined by three mechanisms (conduction along the solid phase, conduction through the gas phase and thermal radiation).[24] Therefore, the analysis of measured foam thermal conductivity will be done based on three mechanisms.

**Table 5-23** Measured foam thermal conductivity

| Ageing time | Foam thermal conductivity, $mW\cdot m^{-1}\cdot K^{-1}$ | |
|---|---|---|
| | Modified foam F-10 | Standard foam F-StB |
| 8 day | 35.0 ± 0.1 | 38.5 ± 0.3 |
| 2 month | 33.0 ± 0.2 | 36.4 ± 1.6 |
| 4 month | 31.2 ± 0.1 | - |
| 5 month | 31.4 ± 0.1 | - |
| 6.5 month | 32.2 ± 0.1 | - |
| 7 month | 32.2 ± 0.1 | 35.4 ± 0.1 |
| 9 month | 33.0 ± 0.1 | 38.9 ± 0.2 |
| 10 month | 31.6 ± 0.3 | 38.2 ± 0.8 |

The results of the measured foam thermal conductivity on the 8th day and after 10 months showed that F-10 foam has significant lower values (8th day: 35.0 $mW\cdot m^{-1}\cdot K^{-1}$; 10th month: 31.6 $mW\cdot m^{-1}\cdot K^{-1}$) in comparison with standard F-StB foam (8th day: 38.5 $mW\cdot m^{-1}\cdot K^{-1}$; 10th month: 38.2 $mW\cdot m^{-1}\cdot K^{-1}$). On the one hand, this considerable reduction in foam thermal conductivity could be explained by the presence of 10% of an additive in the F-10 foam. On the other hand, this could be explained by serious decrease in foam density what minimized the solid phase contribution to the total thermal conductivity. The cell size and number of cells in both foams are similar, therefore its influence on radiative contribution to the total thermal conductivity could be neglected. Besides this, the gas analysis in the 2nd month showed that gas phase thermal conductivity of functionalized foam is lower, than of standard foam due to higher content of insulation gas $C_5H_{10}$ (9.23% in F-10; 8.54% in F-StB ) (Table 5-8, sample F-St20, Table 5-28).

Both foam samples showed similar trend in deviation of foam thermal conductivity from the 2nd to 10th month of testing. This could happen due to the unstabilized foam condition (not complete isocyanate reactions or other mechanism[5,27]).

Considering that both foams showed significant difference in density, the separation of the effect from 10% of an additive and morphological changes on improvement of foam thermal conductivity was not possible.

### 20% additive concentration

F-20 foam was produced with 20% of azo polyol additive. The modified F-20 foam and its reference standard F-StC foams were produced with different mixing speed, mixing time and mass of reagent mixture in order to reach similar foam structure between them, for instance foam density and cell size. Considering that increase of additive concentration in modified foam formulation leads to gradually significant decrease in foam density and that most of the standard foams (produced at different mixing times) maintain density in the same range, the reference foam in this set was selected in accordance just with cell size. The analysis of 20% additive influence on the morphological and thermal properties of foam will be described below.

## *Morphological characterization*

### *Cell size, cell shape, number of cells*

Table 5-26 shows that both foams have cell size in a similar small range (230 ± 70 µm for F-20; 160 ± 40 for F-StC), but standard foam has much higher number of cells. The reason for the observed cell size refers to the rheological properties, for instance the viscosities of pure polyol (standard) and polyol blend (standard polyol with premixed 20% of azo polyol) and possible change of cyclopentane solubility in new reagent mixture, which determine the distributions of pressure and velocity in the processing system, and influence the cell growth during the foam manufacturing process. The results of viscosity measurement showed that azo polyol has a lower value (0.04 Pa·s), than standard polyol (2.00 Pa·s), therefore it reduces the viscosity of 20% polyol blend in modified foam reagent mixture (see Table 5-25). The reduced viscosity of azo polyol in comparison with the standard polyol is explained by the presence of residue of dichloromethane solvent.

Figure 5-10 shows SEM images of the cellular structure of modified foam F-20 and its reference standard foam F-StC. Both foams have a closed-cell structure. The functionalized foam presented regular polyhedral structure with some amount of large holes. Standard foam presented less regular polyhedral structure with some content of ruptured cells.

### *Foam density, foam height, expansion ratio, open / close-cell, characteristic times*

Considering that after addition of 20% of an additive to the PU blend a significant acceleration of the foaming process was noticed, the modified foam was mixed at minimum time and higher speed (5 sec & 1600 rpm for F-20; 40 sec & 800 rpm for F-StC), what was followed by the huge reduction in all characteristic times. The cream and gel times for both foams were not possible to measure due to overlapping with mixing time. One of the reasons for the observed reaction acceleration of the modified foam could deal with the measured lower viscosity of the 20% polyol blend (see Table 5-25). The accelerated reaction between polyol and isocyanate in the functionalized foam results in higher rate of blowing reaction. Thus, a higher amount of gas diffuses into the cells resulting in the higher expansion ratio (30.9 for F-20; 18.7 for F-StC). The height of new sample could be also higher, but considering that mass of reagent mixture for modified foam was three times lower than for standard one due to acceleration of foaming reaction and limited manufacturing conditions of closed mixer system, the sample height was smaller (4.8 cm for F-20; 9.8 cm for F-

StC). Increase of additive concentration up to 20% in foam formulation has led to almost double decrease in modified foam density (35.2 kg/m$^3$), in comparison with the standard foam (58.1 kg/m$^3$).

When for standard foam the mixing time is increased up to 40 sec, in comparison with the functionalized foam, the high temperature is applied for longer time and cells may open before the polymer has enough strength to maintain the cellular structure[19]. This is accomplished with higher density (58.1 kg/m$^3$ for F-StC), higher amount of blown cells with smaller size (250 cells/25mm$^2$ for F-20; 740 cells/25mm$^2$ for F-StC) and presence of ruptured cells in F-StC visible foams from SEM image (Figure 5-10).

**Table 5-24** Foam manufacturing conditions, characteristic times, height and expansion ratio

| Foam index | Mass of mixture, g | Mixing parameters | | Characteristic times | | | | Foam height cm | Expansion ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | Speed, rpm | Time, +9 sec inside | Cream time, sec | Gel time, sec | Rise time, sec | Tack free time, sec | | |
| F-20 | 11.2 | 1600 | 5 | <15 | <15 | 27 | 27 | 4.8 | 30.9 |
| F-StC | 32.8 | 800 | 40 | <50 | <50 | 112 | 162 | 9.8 | 18.7 |

**Table 5-25** Viscosity and water content

| Polyol | Viscosity | Water content, % |
|---|---|---|
| Azo polyol | 0.04 | 0.19 |
| Standard polyol | 2.00 | 1.9 |
| 20 % polyol blend<br>(20% azo polyol premixed to standard polyol) | 1.13 | - |

**Table 5-26** Foam density, cell size, number of cells per area

| Foam index | Density, kg/m$^3$ | Cell size, μm | Number of cells per 25 mm$^2$ |
|---|---|---|---|
| F-20 | 35.2 ± 0.4 | 230 ± 70 | 250 |
| F-StC | 58.1 ± 0.7 | 160 ± 40 | 740 |

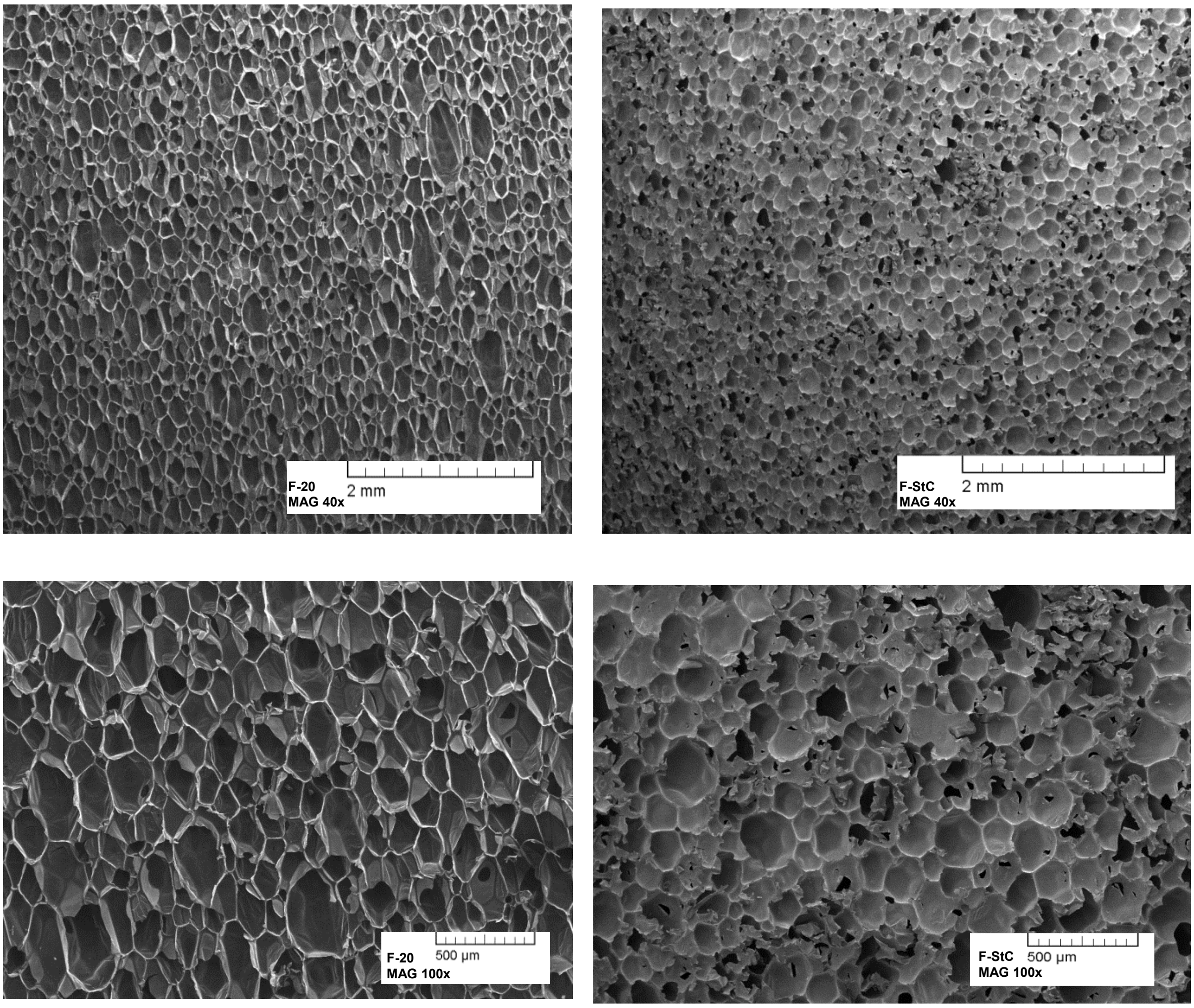


**Figure 5-10** SEM images of cross-sections in perpendicular to the foam rise for F-20 foam and its reference standard foam F-StC. MAG: 40x; 100x.

## *Measured foam thermal conductivity*

Table 5-27 collects the measured values of foam thermal conductivity. Although, it is recommended to condition a PU foam for 30-40 days to complete all isocyanate reactions[5,27], the measurement of thermal conductivity was performed shortly after manufacturing to compare initial values. Additionally, thermal conductivity test was performed regular during 6 months for evaluation of deterioration of thermal conductivity in time for modified foam and between different samples (standard foam contains data until the 10th month). During storage time foam samples of 2.5 x 2.5 x 1.5 $cm^3$ geometry were aged at RT. Thermal conductivity was measured at RT and in perpendicular to the foam rise direction. As mentioned earlier foam thermal conductivity is determined by three mechanisms (conduction along the solid phase, conduction through the gas phase and thermal radiation).[24] Therefore, analysis of measured foam thermal conductivity will be done based on three mechanisms.

**Table 5-27** Measured foam thermal conductivity

| Ageing time | Foam thermal conductivity, mW·m$^{-1}$·K$^{-1}$ | |
|---|---|---|
| | Modified foam F-20 | Standard foam F-StC |
| 8 day | 31.4 ± 0.1 | 37.8 ± 0.1 |
| 1 month | 30.5 ± 0.1 | - |
| 2 month | 33.4 ± 0.1 | 38.8 ± 0.0 |
| 4 month | 30.2 ± 0.1 | - |
| 5 month | 32.1 ± 0.1 | - |
| 6 month | 30.6 ± 0.2 | - |
| 7 month | - | 38.5 ± 0.5 |
| 9 month | - | 40.3 ± 0.1 |
| 10 month | - | 40.1 ± 0.1 |

The results of the measured foam thermal conductivity on the 8th day and after 6 months showed that F-20 foam has significant lower values (8th day: 31.4 mW·m$^{-1}$·K$^{-1}$; 6th month: 30.6 mW·m$^{-1}$·K$^{-1}$) in comparison with standard F-StC foam (8th day: 37.8 mW·m$^{-1}$·K$^{-1}$; 7th month: 38.5 mW·m$^{-1}$·K$^{-1}$). On the one hand, this considerable reduction in foam thermal conductivity could be explained by presence of 20% of additive in F-20 foam. On the other hand, this could be explained by serious decrease in foam density what minimized the solid phase contribution to the total thermal conductivity. Although, the cell size is larger in the modified foam, what could potentially increase the radiative contribution to the total thermal conductivity, but did not do it maybe due to the lower number of cells.

Functionalized foam showed deviation of foam thermal conductivity until the 6th month of testing. This could occur due to the unstabilized foam condition (not complete isocyanate reactions or other mechanism[5,27]).

Considering that both foams showed significant difference in foam density and cellular morphology, the separation of effect from 20% additive and morphological changes on improvement of foam thermal conductivity was not possible.

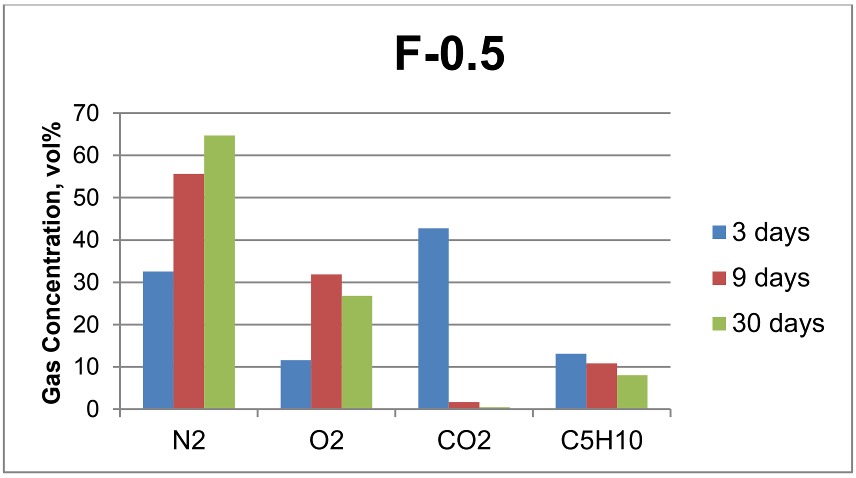
### Results of cell gas analysis of modified foams

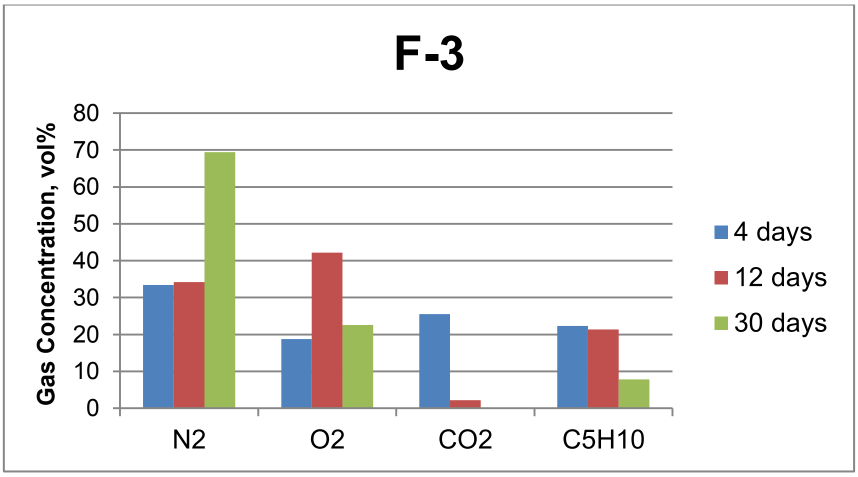
GCMS measurements were performed on the 3rd or 4th day, in the 10th day and on 1st or 2nd month after manufacturing for monitoring of gas diffusion in time. Although, it is recommended to condition a PU foam for 30-40 days to complete all isocyanate reactions[5,27], the measurement of gas content was performed shortly after manufacturing to compare initial gas phases. During 2 month of storage, foam samples of 2.5 x 2.5 x 1.5 $cm^3$ geometry were aged at RT. The cell gas composition was calculated with input parameters obtained from measurement of ratio of each peak area on the GC chromatograms. Table 5-28 collects the values of calculated gas content and theoretically derived thermal conductivity of cell gas mixture by Wassiljewa equation. Gas content measurements were not performed for 20% modified foam sample. Figure 5-11 shows the change in cell gas content of modified foams during time.

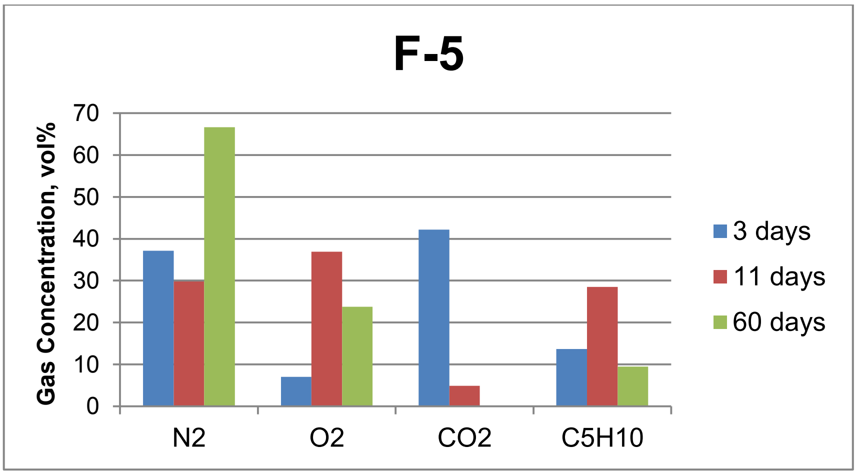
**Table 5-28** Cell gas content of modified foams together with calculated gas phase thermal conductivity

| Sample index & storage time | Foam cell gas content | | | | $\lambda_{gas\ calcul}$, $mW\cdot m^{-1}\cdot K^{-1}$ |
|---|---|---|---|---|---|
| | $N_2$, vol% | $O_2$, vol% | $CO_2$, vol% | $C_5H_{10}$, vol% | |
| **F-0.5** | | | | | |
| 3 day | 32.53 | 11.58 | 42.76 | 13.13 | 20.26 |
| 9 day | 55.67 | 31.84 | 1.66 | 10.83 | 24.56 |
| 1 month | 64.72 | 26.78 | 0.45 | 8.05 | 25.02 |
| **F-3** | | | | | |
| 4 day | 33.39 | 18.75 | 25.55 | 22.3 | 20.81 |
| 12 day | 34.24 | 42.21 | 2.15 | 21.39 | 23.13 |
| 1 month | 69.40 | 22.59 | 0.22 | 7.8 | 24.85 |
| **F-5** | | | | | |
| 3 day | 37.15 | 7.03 | 42.15 | 13.66 | 20.20 |
| 11 day | 29.79 | 36.88 | 4.86 | 28.48 | 21.93 |
| 2 month | 66.65 | 23.75 | 0.17 | 9.44 | 24.66 |
| **F-10** | | | | | |
| 3 day | 31.85 | 5.19 | 47.93 | 15.02 | 19.50 |

| | | | | | |
|---|---|---|---|---|---|
| 10 day | 59.73 | 24.45 | 0.72 | 15.10 | 23.89 |
| 2 month | 60.67 | 29.86 | 0.24 | 9.23 | 24.72 |







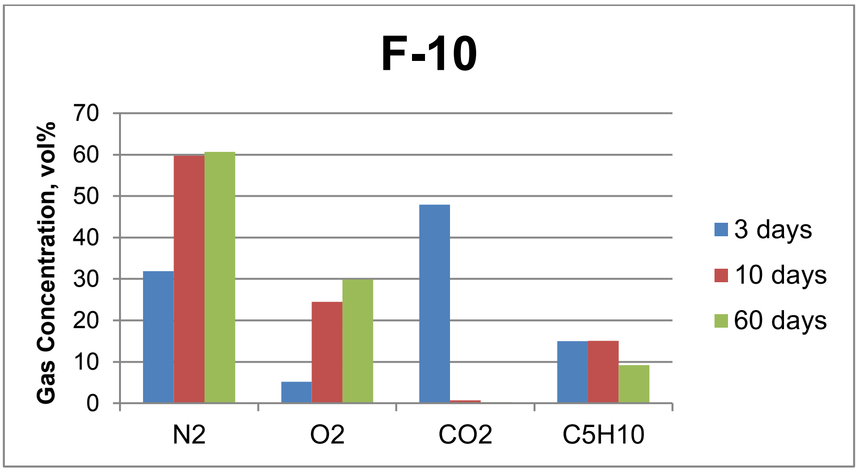


**Figure 5-11** Change in cell gas content of modified foams during time

The discussion in this section covers the general trends of gas diffusion for all modified foam samples and not detailed comparison of gas diffusion between samples due to the following reasons. All the samples had difference in amount of PU reagent mixture and viscosity of polyol blend, what has impacted on the two main PU foam reactions, blowing and polyaddition. In particular, there is a difference in amount of evaporated and diffused into the cells cyclopentane gas and difference in reaction between polyol and isocyanate producing different amount of carbon dioxide.

Gas content measurements of modified foams in 2.5 x 2.5 x 1.5 $cm^3$ geometry showed that $CO_2$ leaves foam after 1-2 month period (from 42% to 0.2%, average value for all samples). The GCMS results demonstrated that nitrogen and oxygen diffuse from the atmosphere into the foam with different speed due to different diffusion coefficients. Besides this, the oxygen/nitrogen ratio of the cell gas in all samples is higher than that of the air, which was noted for most new produced PU foams in Persson[5]. One may notice that the content of nitrogen and oxygen on some measurement days for the individual sample does not change gradually, but deviates, this could be explained by different specimens. Since foams are punctured with needle during sampling, such samples with open channels should be discarded, that's why every next experiment requires a new foam specimen. Regarding the cyclopentane gas, the measurement results indicated that its leaves the foam slowly (from 15% to 8%, average value for all samples). Additionally, cyclopentane quantity may increase during the first months of foam storage due to liquid cyclopentane that was apparently not evaporated fully at the time of foam production.[6]

Considering that diffusion of cyclopentane and carbon dioxide insulation gases out of the foam and diffusion of air gases into the foam is one of the reasons for aging of polyurethane foam thermal insulation, the measurement of foam thermal conductivity itself does not demonstrate the state of gas composition in any particular foam. Therefore, GCMS gas analysis method has shown its benefit as an excellent instrument to determine foam cell gas composition and analysis of gas phase contribution to the total thermal conductivity.

The analysis of general trends in gas diffusion for modified foams is in accordance with standard foam samples. The analysis of gas phase contribution to the total thermal conductivity for standard foam samples is described in section 5.3.1. The analysis of gas phase contribution to the total thermal conductivity for modified foam samples is described in section 5.3.2 separately for every foam set depending on additive concentration.

## 5.4 Conclusion

The concept of this PhD thesis was based on the formation of surfactant barrier layer on the cell wall of the foam for preventing the permeation of the cell gas through the foam in such a way that thermal conductivity of the foam remains constant low. It is well known that nonpolar molecules diffuse faster and easier through the nonpolar polymer, than those which contain polar groups. Considering that PU polymer is nonpolar and such gases as oxygen, nitrogen, carbon dioxide and cyclopentane are also nonpolar, it was decided to incorporate highly polar additive (azo polyol) into the PU foam and thus to slow down the permeation mechanism. Thus, the goal to improve the thermal insulation ability of the PU foam could be reached.

During the work, it was observed that addition of additive has changed the foam reactions during manufacturing and obtained foam morphology, most significantly the foam density. As a result, the thermal conductivity of the functionalized PU foam was 20% lower than of the standard one. Therefore, the aim of the work was reached, but the separation of effect from polar additive and morphological changes on improvement of foam thermal conductivity was not possible. The results obtained in this work are summarized below:

- Incorporation of additive of different concentrations has influenced foaming process in a different way. One of the reasons was dealing with difference in viscosity of new PU blend caused by different concentrations of additive what has led to a different foaming reaction behavior. Another reason could be the action of azosulphonate as accelerator of foaming reaction, maybe it interacts with some catalyst (s) presented in the standard polyol. Besides influence from azosulphonate, maybe the DCU byproduct, presented in azo polyol, interacts with some components from foam reagent mixture.
    - ➢ Adjustment of mixing speed, mixing time and amount of reagent mixture was necessary for obtaining a proper homogeneous foam structure.
    - ➢ The variation of mixing parameters and amount of reagent mixture was used for manufacturing of foam of preferable cell size and density.

- Increase of additive concentration in the PU reagent mixture has led to decrease in foam density, although cell size was possible to vary in wide range by changing the mixing times.
- Reduction of density of modified foam has led to improvement of total foam thermal conductivity due to minimization of the solid phase contribution to the total thermal conductivity.
- Observed improvement in initial thermal conductivity value and in long-term ageing behavior can be explained as by addition of additive, as by decreased foam density. For separation these two factors, it is necessary to develop the manufacturing of functionalized foams for the whole range of additive concentrations keeping the foam density at the same level.
- The complex analysis of functionalized foam density, the presence of open cells, cell size and thermal conductivity of cell gas mixture was uniquely done to contribute to the understanding of the thermal conductivity of PU foam.
- Gas phase thermal conductivity of the foam (theoretically derived from the foam gas content measurements) was in some cases correlated and, in some cases, not with the measured foam thermal conductivity over time. Although, gas phase contribution to the total thermal conductivity is around 75%, there are other mechanisms (such as solid phase, radiative and convection contributions) that play a role.
- Thermal conductivity ($\lambda_{\text{initial}}$, $\lambda_{\text{10 month}}$) of the functionalized foam is 20% lower than of standard one. The reason for the obtained changes in thermal conductivity of functionalized foams could deal with effect from foam density ($\lambda_{\text{solid polyurethane}}$). As it was already mentioned, additive incorporation has strongly influenced on foaming reactions and obtained foam morphology, especially the foam density.

**Table 5-29** Measured thermal conductivity of standard and modified foams

| Time, month | Foam thermal conductivity, mW·m$^{-1}$·K$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | Standard | Modified | | | | |
| | F-St40 | F-0.5 | F-3 | F-5 | F-10 | F-20 |
| 0 | 37.8 | 38.2 | 37.9 | 35.0 | 35.0 | 31.4 |
| 1 | - | 36.7 | - | - | - | 30.5 |
| 2 | 38.8 | 39.4 | 37.1 | 33.9 | 33.0 | 33.4 |
| 4 | - | - | - | 32.8 | 31.2 | 30.2 |
| 5 | - | - | - | 32.7 | 31.4 | 32.1 |
| 6 | - | - | - | 32.2 | 32.2 | 30.6 |
| 7 | 38.5 | - | - | 33.6 | 32.2 | - |
| 9 | 40.3 | - | - | 33.7 | 33.0 | - |
| 10 | 40.1 | 38.4 | 38.0 | 33.2 | 31.6 | - |

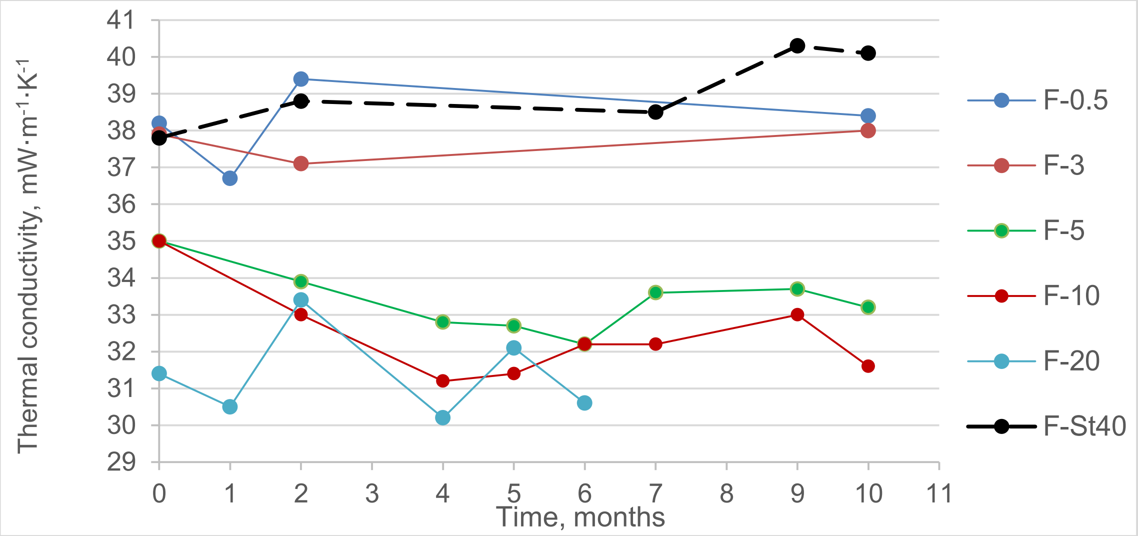


**Figure 5-12** Measured thermal conductivity of modified (F-0.5; F-3; F-5; F-10; F-20) and standard (F-St40) foams

**Table 5-30** Manufacturing parameters, density, measured foam thermal conductivity of modified foams

| concentration | Viscosity "pol+azo pol blend" | mass, g | Mixing time, sec | Characteristic times | | | | H, cm | Density, kg/m$^3$ | $\lambda_{foam\ measur}$, mW·m$^{-1}$·K$^{-1}$ (Fresh / old) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $T_{cream}$,s | $T_{gel}$,s | $T_{rise}$,s | $T_{cure}$,s | | | |
| 0.5 | 2.0 | 17.5 | 30 | <39 | 46 | 85 | 190 | 4.5 | 62.9 | 38.2 / 38.4 |
| 3 | 1.79 | 26.5 | 10 | <20 | 26 | 75 | 90 | 8.8 | 50 | 37.9 / 38.0 |
| 5 | 1.70 | 29.7 | 10 | <20 | 22 | 57 | 62 | 10.5 | 46.2 | 35.0 / 33.2 |
| 10 | 1.44 | 27.2 | 5 | <15 | <15 | 54 | 54 | 11 | 39.3 | 35.0 / 31.6 |
| 20 | 1.13 | 11.2 | 5 | <15 | <15 | 27 | 27 | 4.8 | 35.2 | 31.4 / 30.6 |

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# Chapter 6

## Overall conclusions and final remarks

The work presented in this thesis contributes to the understanding of the thermal properties of closed cell polyurethane (PU) foams, and aims at correlations between foam processing, foam morphology and foam cell gas content. The focus is set on an independent assessment of the two main factors that govern both the initial thermal conductivity of the foam, and the stability of the overall thermal conductivity over time. These factors are the composition of the cell gas, which may change during storage under air, and the cellular structure of the foam.

1) A gas chromatography-mass spectrometry (GC-MS) method for the measurement of the foam cell gas phase was developed, applied and validated. This technique is simple and fast in implementation. One column simultaneously separated five gases including $N_2$, $O_2$, $CO_2$, $C_5H_{10}$ and Ar ($CO_2$ and $C_5H_{10}$ are the blowing agents). In these measurements, there is no change of cell gas volume. The peak area is recalculated to molar fractions of gas components, which are then used in the Wassiljewa equation to theoretically derive a thermal conductivity of the cell gas mixture. The advantage of this gas sampling procedure is that it does not require expensive equipment and there is no change in partial pressure of cell gases and temperature during sampling as in other methods. Moreover, the possible disadvantages dealing with the variable quantity of desiccator gas (surrounding the foam sample) which is sucked into the syringe during taking out the gases from the cells, and gas losses or air contamination of the sample are avoided.

   The results presented in this work show that:

   - GC-MS is a suitable method for the monitoring of changes in gas composition and for comparison of foams with different structures, but it requires a very accurate sample selection and preparation, and also storage conditions have to be considered carefully. For instance, samples have to be produced automatically and not manually, in order to eliminate influences from external factors.

2) A polar additive for the preparation of functionalized PU foam was developed. A 3-carboxyphenyl-azosulphonate component was selected (among others) for the modification of a standard polyether-polyol, considering the following requirements: firstly, the additive must be polar. Secondly, the additive must be a liquid or solid and soluble in polyol, because any inhomogeneity in the foam structure leads to deterioration of its insulation properties. Thirdly, it should be chemically bound to the polyol chain for better compatibility. Finally, the additive should not react with isocyanates in order to avoid any change of the commercial PU foam formulation. A Steglich esterification was selected to achieve the

modification of a standard polyol in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridine (DMAP). By that way, an azosulphonate modified polyol (azo-polyol) was successfully prepared.

The results presented in this work show that:

- Most of the free hydroxyl groups were substituted in the synthesized additive (azo-polyol) according to the results from FTIR spectroscopy, although the exact chemical composition of the employed polyol was not known.
- The synthesized additive was obtained at 75% yield, and consisted of a liquid azo polyol product containing N,N'-dicyclohexylurea (DCU) as byproduct. DCU was formed by the reaction of DCC with water during the synthesis.
- The synthesized additive had another viscosity than the polyol starting compound. The presence of residual dichloromethane (solvent for purification) causes a reduction in viscosity of the azo-polyol from batch C10.0 in comparison with batch C10.8*.
- Prior to manufacturing of functionalized foams, the synthesized azo-polyol (C10.0 batch) was premixed to the standard polyol in a range of concentrations (0.5; 3; 5; 10; 20 wt%) using an automatic VM-200 Vortex mixer. This resulted in homogeneous mixtures.

3) A method for the preparation of conventional PU foams and PU foams functionalized with the azo-polyol additive was developed. For the preparation of foam samples under laboratory conditions, the components of the reagent mixture were subsequently mixed with each other by the automatic VM-200 Vortex mixer. Mixing speed, mixing time and amount of reagent mixture were adjusted in accordance with the desired foam structure. The foams were produced in a free-rising method, with cyclopentane as a blowing agent.

   The results presented in this work show that:

   - The incorporation of the azo-polyol additive at different concentrations influences the foaming process in a different way. One of the reasons is the difference in viscosity of the functionalized PU reaction mixture which is caused by different concentrations of the additive leading to a different foaming behavior. Another reason is that the azosulphonate may act as an accelerator for the foaming reaction, probably by interaction with the polyurethane catalyst(s). Moreover, also the DCU byproduct presented in azo-polyol is expected to interact with some components of the PU reagent mixture.
     - ➢ The adjustment of mixing speed, mixing time and amount of reagent mixture is necessary to obtain a proper homogeneous foam structure.

    - By variation of the mixing parameters and the composition of the reagent mixture foams with different cell size and density can be obtained.

- An increase of additive concentration leads to a decrease in foam density, although the cell size was varied in a wide range by changing mixing times.
- A reduction in density of the modified foam leads to an improvement of overall thermal conductivity, which is related to the minimization of the solid phase contributing to the overall thermal conductivity.
- The observed improvement in initial thermal conductivity value and in long-term stability of thermal conductivity can be explained both by the addition of the additive, and by a decrease in foam density. For a separation of these two factors, it is necessary to develop the manufacturing of functionalized foams for the whole range of additive concentrations keeping the foam density at the same level.
- The complex analysis of the density of the functionalized foam, the presence of open cells, cell size, and thermal conductivity of cell gas mixture was uniquely done to contribute to the understanding of the thermal conductivity of PU foam.
- The thermal conductivity of the gas phase in the foam (theoretically derived from the foam gas content measurements) was in some cases correlated and, in some cases, not correlated with the measured thermal conductivity of the foam. Although the gas phase contributes to the overall thermal conductivity of a foam by approximately 75%, there are other mechanisms that play a role (e.g., the solid phase, radiative and convection contributions to the thermal conductivity).
- The thermal conductivity ($\lambda_{\text{initial}}$, $\lambda_{\text{10 month}}$) of the functionalized PU foam is 20% lower than that of a standard PU foam. The reason for the obtained changes in thermal conductivity of functionalized foams may result from differences in foam density ($\lambda_{\text{solid polyurethane}}$). As it was already mentioned, additive incorporation strongly influences the foaming reactions and the resulting foam morphology, especially the foam density.

Summing up, a polyether-polyol was successfully modified with an azosulphonate unit and was introduced as an additive into a conventional PU foam. The new additive is chemically compatible with and non-reactive towards polyurethane and enables the variation of cell sizes and cell densities in PU foam. However, to consider it on an industrial level, the cost of additive manufacturing must be reduced, which can be achieved by an optimization of the synthetic procedure. Furthermore, the overall thermal conductivity of a foam is a complex property, and the morphology of a PU foam is highly process dependent. Therefore, the impact of the two phases present, solid polyurethane and gas phase, and their contributions to the overall thermal conductivity should be assessed separately in future research.

# Chapter 7

## Publications

In the following, the publications, which resulted from this PhD thesis, are listed.

### *Research articles*

- Galakhova A, Riess G. Fast gas chromatography – mass spectrometry method for the detection of gas phase composition of polyurethane foam and its role in foam thermal conductivity. J Cell Plast **2019**, accepted with minor revision.
- Galakhova A, Santiago-Calvo M, Tirado-Mediavilla J, Villafañe F, Rodríguez-Pérez MA, Riess G. Identification and quantification of cell gas evolution in rigid polyurethane foams by novel GCMS methodology. *Polymers* **2019**, 11(7), 1192; doi:10.3390/polym 11071192.

### *Poster*

Galakhova A, Riess G. Fast gas chromatography – mass spectrometry method for the separation of nitrogen, oxygen, carbon dioxide, cyclopentane and argon and its application in analysis of PU foam aging. *SPE FOAMS* 2017, Bayreuth, Germany.