

University of Pardubice

Faculty of Chemical Technology

**Recycling of Polyurethane Foams**  
*Theses of the Doctoral Dissertation*

**Rudolf Beran**



**Pardubice 2021**

**UNIVERSITY OF PARDUBICE**  
**FACULTY OF CHEMICAL TECHNOLOGY**  
Institute of Chemistry and Technology of Macromolecular Materials

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Supervisor: **prof. Ing. Petr Kalenda, CSc.**

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## References

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## Abstract

Polyurethane foams are widely used materials in many fields of applications. PU foams are crosslinked polymers and this fact excludes common recycling ways employing the polymer melting, extrusion, blowing etc. Typical recycling of rigid foams consists of the foam grinding and using this powder like filler in PU systems. Flexible foams can be crumbled to flakes for rebound foam manufacturing. Chemical recycling (chemolysis) is not commercially used with a few exceptions, due to its high energy demands and formation of useless waste products.

The author's dissertation describes and explains the novel methods for recycling of both, rigid and flexible PU foams and uses the recycled products in adhesives formulations. Rigid foams were micro-milled to the form of reactive filler useful for preparation of PU adhesives. For flexible foams an innovative method of chemical partial depolymerization was discovered producing polyol and thermoplastic resin; both usable in adhesive formulation and rigid foam manufacturing.

## Abstrakt

Polyuretanové pěny jsou široce používanými materiály v mnoha oblastech použití. PU pěny jsou zesítené polymery a tato skutečnost vylučuje běžné způsoby recyklace využívající tavení, vytlačování, vyfukování polymerů atd. Typická recyklace tvrdých pěn spočívá v jejich mletí a použití tohoto prášku jako plniva v PU systémech. Měkké pěny lze drtit na vločky pro výrobu tzv. pojenky. Chemická recyklace (chemolýza) se až na několik výjimek komerčně nepoužívá pro vysokou energetickou náročnost a tvorbu nevyužitelných odpadních produktů.

Disertační práce popisuje a vysvětluje nové metody recyklace tvrdých i měkkých PU pěn a použití recyklovaných produktů ve formulacích lepidel. Tvrdé pěny byly zpracovány mikromletým do podoby reaktivního plniva použitelného pro přípravu PU lepidel. U pružných pěn byla zpracována inovativní metoda chemické parciální depolymerace, při níž se vyrábí polyol a termoplastická pryskyřice; oba produkty jsou použitelné ve formulaci lepidla nebo při výrobě tvrdé pěny.

## Keywords

Polyurethane foam, recycling, milling, filler, depolymerization, adhesive

## Klíčová slova

Polyurethanová pěna, recyklace, mletí, plnivo, depolymerizace, lepidlo

## Table of contents

Introduction and analysis of the current state of the art.....	6
Definition of goals of the dissertation.....	8
Methods.....	9
Milling methods .....	9
Adhesive formulation for testing of active micro-milled PUR powder .....	11
Determination of particle size of micro-milled rigid foam.....	11
Determination of amine number .....	11
Determination of hydroxyl number .....	12
Viscosity .....	12
Mechanical testing .....	12
Scanning electron microscope (SEM) .....	12
Preparation of flexible PUR foam samples for depolymerisation .....	13
Process of partial depolymerisation.....	13
Preparation of adhesives from depolymerised PUR foam.....	14
Results.....	15
Result of micro-milling the rigid PUR foam .....	16
Reactivity of the micro-milled rigid PUR foam and its addition to PUR adhesive..	18
Result of partial depolymerisation of the flexible PUR foam .....	20
Elemental analysis of the PUR foam and resinous phase.....	22
Usage of the depolymerised products in 1C and 2C PUR adhesives .....	23
Possible use of resinous phase of PUR depolymerisation .....	23
Benefits and novel approach; conclusions.....	24
List of references.....	26
15. Silva, A.L., Bordado, J.C., 2004. Recent developments in polyurethane catalysis: catalytic mechanisms review. Catal. Rev. 46, 31–51 .....	26
List of author publications .....	28

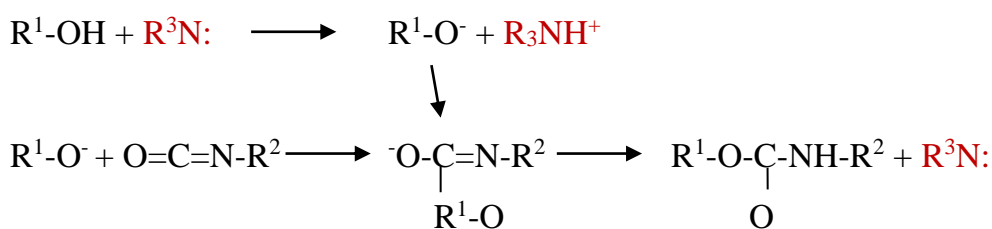
## Introduction and analysis of the current state of the art

Polyurethanes are polyaddition polymers discovered by Otto Bayer in 1937 and introduced in wide industrial use in Sixties of 20<sup>th</sup> Century. Majority of produced volumes are sold in form of foams.

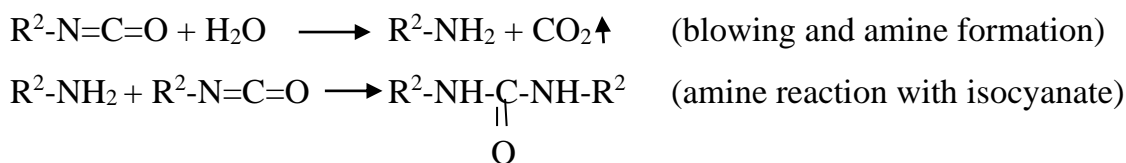
Rigid polyurethane foams are used as heat and acoustic insulation materials in construction, building industry, home appliances and vehicle industry. They are usually synthesised with 4,4,-difenyldimethanediisocyanate (MDI) and short-molecular polyols with functionality 3, 5 or more. On the contrary, flexible PUR foams exhibit their benefits for mattresses, upholstery, car seats, washing sponges and textile industry. Compared to rigid foams, they are not so dense crosslinked. Flexible foams are produced using 2,4-toluene diisocyanate (TDI) and long-molecular diols or triols. Basic polyurethane reactions are stated on Fig. 1.

Chemistry of polyurethane foams is relatively complicated because diisocyanates are enormously reactive substances able to react with “active hydrogen” in amines, alcohols, water, acids, amides, substituted ureas etc. Due to nitrogen content and crosslinked thermosetting character it is not possible to recycle these polymers by common methods of melting, extrusion and similar. Incineration of foam wastes leads to forming poisonous gases (nitrogen oxides, hydrogen cyanide, and free diisocyanates). Biodegradation of rigid polyurethane foam is extremely slow; it means polyurethanes do not belong in compostable plastics [23].

a) *Catalysed polyaddition (gelling reaction):*



b) *Reaction of isocyanate with water (blowing) and polyurea formation:*



c) *Example of crosslinking: reaction of isocyanate with urethane resulting allophanate:*

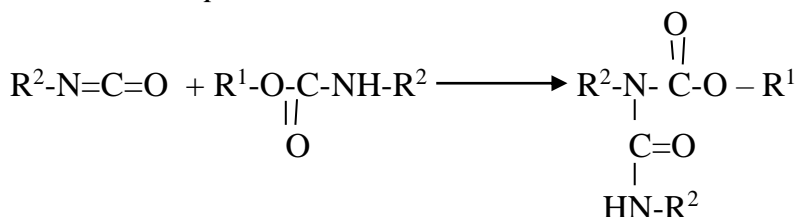


Fig. 1: Scheme of PUR reactions [23]

**Rigid polyurethanes** feature with high glass transition temperature. It means, the foam is brittle enough for milling process. Milling or crumbling (grinding) is one of common way how to recycle rigid PUR foams. Rigid foam wastes can be milled to the form of fine powder and used as adhesive fillers or as spillage absorbent [1, 2]. In the dissertation the possible chemical reactivity of the micro-milled rigid PUR foam was studied. It was observed that very fine particles under 100  $\mu\text{m}$  exhibit measurable chemical reactivity and such recycled material may be used in polyurethane chemistry as partial replacement of polyols [22].

On the other hand, rigid PUR foam wastes are not recycled easily by chemical way [3]. Due the highly crosslinked nature of the rigid PUR foams the chemical depolymerisation is very difficult and not so effective for industrial use. High energy input and low yield of the chemical recycling disqualifies this method. Typical product of chemolysis is recycled polyol and the secondary (usually solid) waste polyurea originated from diphenylmethane diisocyanate (MDI) [4]. Also some diamines could be generated by chemolysis, for example diphenyl methane diamine. The product of chemical recycling is difficult to use in next polyurethane synthesis because a lot of side-products is present in the mixture and also due to problematic hygienic properties [2, 5].

**Flexible PUR foams** have glass transition temperature about  $-50^{\circ}\text{C}$  and their milling without cryogenic conditions are practically impossible [23]. In spite of this, the mechanical recycling of the PUR foams is industrially usual process [6]. Flexible foam scraps are used for rebinding of the foam flocks with polyurethane binder. Semi-flexible foam blocks produced by this way are used in mattresses industry and for heat and acoustic insulation purposes.

For possible chemolysis of flexible foams are the same limitations apply as for rigid foams, i.e. the process is characterised by high energy input, long reaction time, raw materials consumption and formation of useless by-products.

The dissertation brings **two novel approaches**. For **rigid PUR** foam it is the addition of powdered material to a binder system in form of an active (reactive) component of the whole system. Thanks to this process the recycled material may be used as a partial replacement of polyol. Such active filler was used and tested in one component PUR wood/wood adhesive [22].

Especially for **flexible PUR** foams the novel method of the chemical decomposition was studied. The essence of common chemolysis is the reversal of a reversible polycondensation reaction to the monomer units from the polymer chains. Generally, chemolysis involves the reaction between polyurethanes and substituents. It results in the formation of simpler compounds like recycled polyol, some secondary solid waste substituted polyurea, and a small amount of diamines [7, 8]. The author dissertation aims to control the depolymerisation process in the way of maximal elimination of these by-products. Currently, there is no method for the recovery of diisocyanate due to its very high reactivity in the conditions of the recycling process with traces of water, glycols, or degraded polyols being found [9]. The typical reaction of diisocyanates with water results in carbon dioxide and diamine (Fig.2). The reaction provides the principal source of gas for the foam blowing and the heat power for the expansion of the polyurethane [23]. Additionally, the free isocyanate takes part in

other reactions due to its high reactivity. For example, the isocyanate together with a diamine gives substituted urea [10, 11].

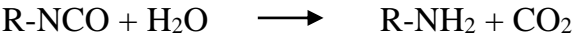


Fig. 2: Blowing reaction of isocyanate with water

### Definition of goals of the dissertation

The dissertation proceeded in steps described in figure 3.

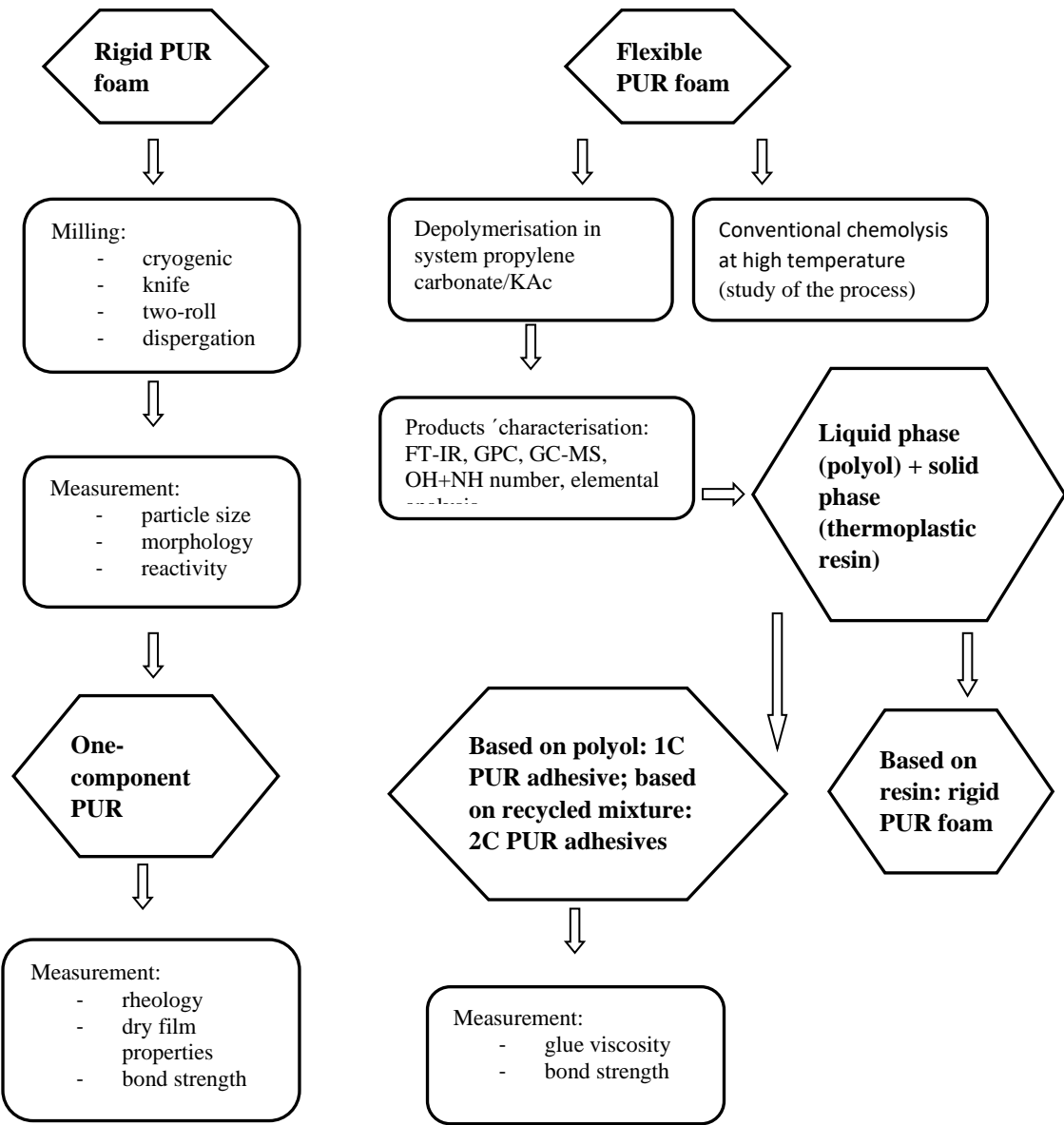


Fig. 3: Goals and process of the dissertation



The dissertation has following goals:

- To develop and validate an innovative method of recycling PUR foams, which are considered as non-recyclable material, in terms of direct reuse.
- To verify the mechanical recycling of polyurethane foams by the micro-milling method, with an emphasis on the processing of rigid PUR foam.
- To characterize micro-milling products and verify their applicability as fillers for PUR chemistry, incl. verification of possible chemical reactivity.
- To find a method of chemical decomposition of PUR foams in order to recover both polyol and diisocyanate and at the same time in order to minimize the consumption of other reagents and prefer this process for flexible PUR foams.
- To characterize the chemical decomposition products of flexible PUR foam using analytical methods FT-IR, GC-MS and GPC and volumetric titration methods such as determination of hydroxyl number and amine number.
- To use prepared recycling products for modification of one-component and two-component PUR binders (adhesives) and evaluate their influence on the user properties of adhesives.
- To outline other possible directions of research in the field of recycling PUR foams.

## Methods

### Milling methods

Rigid PUR foam was processed by milling. Four milling methods were studied.

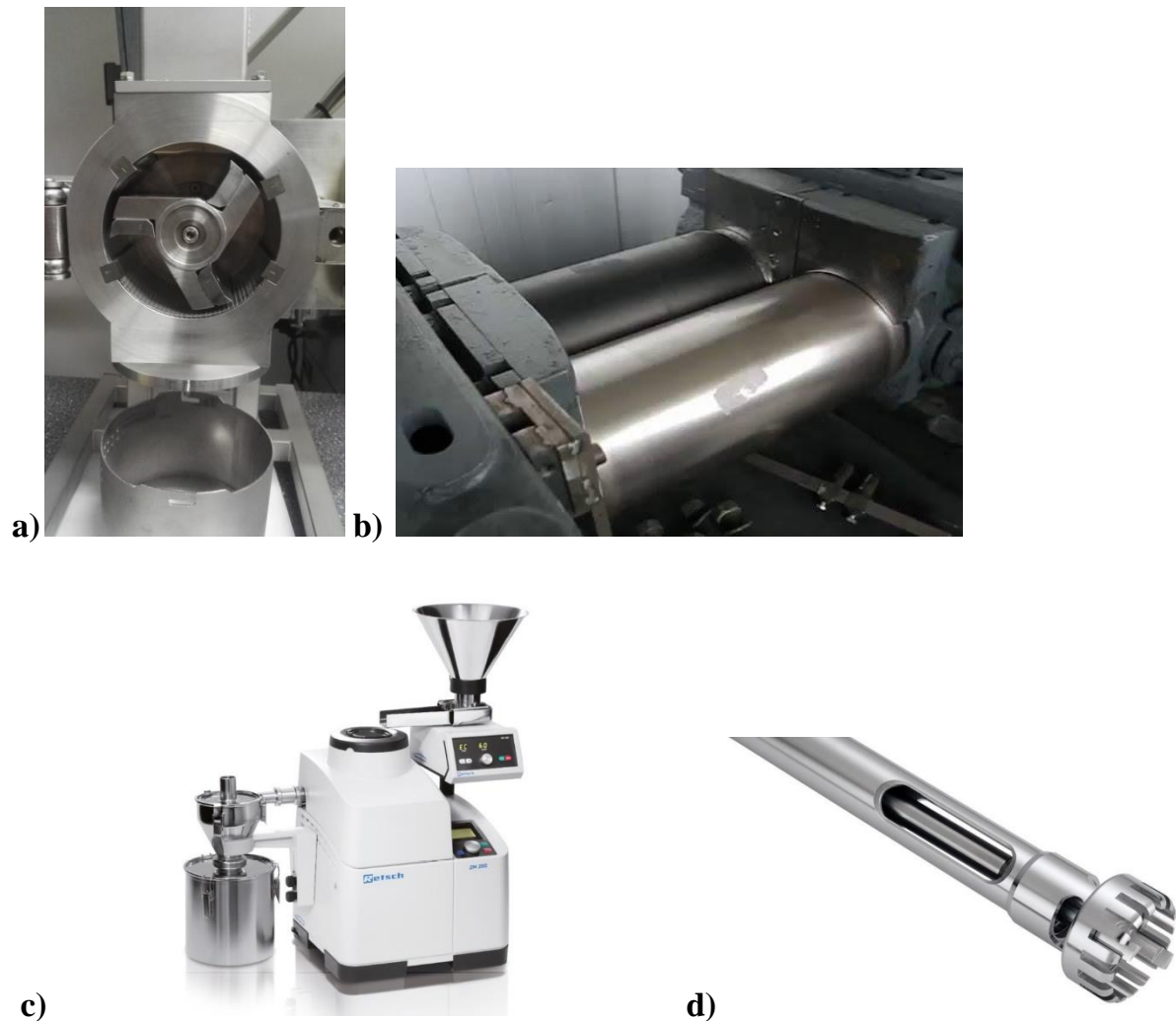
Laboratory **knife mill** Mavet SM-LAB, (Mavet CZ s.r.o., Czech Republic) was used for the experiment. The milling at fixed revolutions  $900 \text{ min}^{-1}$  is very fast process. 50 grams of the powder is ready in 5 minutes during single passing the material through the mill. Output stainless sieve with mesh 0.5 mm was used [22].

**Two-roll mill** works with two main disintegration forces: high shear tension and very high compression of the milled material. Chemical bonds in macromolecules are broken under strong external forces in the weakest point of the chains. Shear force helps to grow broken crumb apart. Thanks to combination of these two effects the formed PUR powder is more compact than product from knife mill. Disadvantage of the two-roll mill is its low productivity (product flow in time). Two-roll mill of Buzuluk Company, Czechoslovakia (1985), type 14201 was used. 20 times repeated passing the material between cylinders was carried out [22]

Decreasing the milling temperature increases the polymer rigidity which is useful for easier disintegration. **Cryogenic ultra-centrifugal mill** Retsch ZM 200 with sieve  $80 \mu\text{m}$  was used. Cooling was provided by liquid nitrogen [22]. The cryomilling was organised and provided in Tomas Bata University in Zlin.

The contact with air humidity is significant disadvantage of above mentioned milling methods. There is risk of water adsorption on the milled particles. It is why the **dispersion milling in ambient of polyol** was studied. Mill IKA S50N – G45G was used for this purpose. During dispersion process the suspension of the rigid foam crumb is transported in the dispersion head where due to share forces between rotor and stator the material is micronized. In fact, we may say that it is variation of the knife mill working in liquid ambient.

Photos of the mills are presented on figure 4.



**Fig.4:** Mills: a) Knife mill Mavet SM-Lab and sieve 0,5 mm; b) Two-roll mill Buzuluk 14201; c) Ultra-centrifugal mill Retsch ZM200 for cryogenic milling; d) Dispersion tool IKA S50N-G45G for milling of rigid PUR foam in ambient of polyol (source: leaflet IKA®-Werke GmbH & Co. KG, SRN)

## Adhesive formulation for testing of active micro-milled PUR powder

To evaluate the active filler properties the adhesive formulations based on BASF raw materials was suggested. The formulation is typical for flexible one-component polyurethane adhesive.

One-component adhesive is prepared with over-stoichiometric amount of diisocyanate causing NCO group termination of the prepolymer molecules. The prepolymer with free isocyanate groups provides crosslinking by air humidity during adhesive curing. Polyisocyanate part gives rigidity of the cured adhesive and reduces viscosity of the prepolymer, while polyol part is responsible for cured adhesive flexibility and high viscosity of the prepolymer. Of course, also choice of the reagents has the essential importance to the result, because molecular weight and functionality basically control the crosslinking network and the prepolymer viscosity [22].

Below mentioned formulation was selected for experiments with the active PUR powder filler.

1C PUR adhesive (for active PUR powder testing) [22]:

Lupranol 1000/2\* 63.0 g as polyol (diol)

Dabco DMDEE 0.2 g as catalyst

Lupranat MI \*\* 37.0 g as isocyanate

\* *OH number 55 mg KOH/g, Mw 2000 g.mol<sup>-1</sup>*

\*\* *Monomeric 2,4'- and 4,4'-diphenyl methane diisocyanate, NCO content 33.5%, functionality approx. 2*

In the following experiments a part of the polyol package (5,10 or 20%) was replaced with micro-milled PUR foam.

## Determination of particle size of micro-milled rigid foam

Particle size measurements were performed on the instrument Laser granulometer CILAS LD 1090 with measuring range 0.04-500  $\mu\text{m}$  in the wet state. The results were evaluated using Evaluating software Size Expert.

## Determination of amine number

The amine number of the polyol (mg KOH/g) was determined by volumetric titration according to EN 1887-2 and the theoretical amine number was calculated according to the equation:

$$\text{Amine number}_{\text{theor.}} = [(Z \times 56.11) / M] \times 1000$$

where Z is the number of amino groups in the molecule and M is the molecular weight of the compound. Titration was provided by automatic titrator Metler Toledo.

## Determination of hydroxyl number

Method is based on ASTM D 4274-99, method E. The hydroxyl number (mg KOH/kg) is determined by back potassium hydroxide titration of acetic acid released from remaining acetic acid anhydride after sample acetylation catalysed by 1-methylimidazole in ambient of N,N-dimethylformamide. The hydroxyl number was calculated according to the equation:

$$\text{OH number}_{\text{theor}} = (A - B) \times 0.5 \times f \times 56.11 / w$$

where A is the blank sample KOH consumption volume, B is the KOH solution consumption, f is the KOH solution factor, w is the sample weight in grams.

## Viscosity

Viscosity was measured with Brookfield DVE viscometer using spindle #6 at various revolution speeds. Samples are conditioned to 22°C.

## Mechanical testing

For mechanical strength determination the tensile strength of the free adhesive film the machine Hegewald & Peschke Inspect Table 5 kN was used [22]. Movement speed 100 mm.min<sup>-1</sup> was set. Maximal force is taken as the result and recalculated for shear strength or tensile strength from the overlap bond area or the free film sample thickness and width respectively.

Free film mechanical testing was carried out on the specimen according to Standard ASTM D3574, Test E. Free film was prepared by crosslinking of the liquid adhesive film on siliconised paper. Dry film was used for testing 24 hours after its preparation.

Test of tensile shear strength of bond wood to wood was carried out by Standard EN 302-1 using equipment TIRAtest 2850 (TIRA GmbH, Germany) with load cell 50 kN [22]. Clamps movement speed was set to 50 mm.min<sup>-1</sup>. Bond area consists of overlap 2 cm long and 2 cm wide. Spruce wood pieces of 2 cm width and 5 cm length were used. Quotient of measured maximal force and known bond area gives tensile strength in unit MPa.

## Scanning electron microscope (SEM)

Samples of milled polyurethane foam were compared by means of a high-resolution scanning electron microscope Quanta 450 FEG (FEI) using a secondary electron detector. Analyses were performed at the accelerating voltage between 5 and 20 kV. Samples were placed on carbon tape and gold coated with a 7 nm thick layer [22].

## **Preparation of flexible PUR foam samples for depolymerisation**

A commercial flexible PUR foam is usually combined with various pigments, fillers (typically calcium carbonate), and flame retardants (typically tris(2-chloroisopropyl) phosphate) [12, 13]. It may be confusing to interpret the decomposition products of commercial foam. For this reason, the pure flexible PUR foam formulation was used in all experiments, and the foam was prepared first. It is a typical flexible PUR foam formulation based on polyether-polyol without any additives.

The foam was prepared from the two packages. In the first step, the polyol pre-mix was prepared (66.0 g Lupranol 2072, 3.0 g water, 0.15 g Dabco T900, 0.05 g Dabco 33LV, 0.15 g Dabco BL 11, and 3.2 g Dabco DC 5906). In the second step, the isocyanate (36.0 g Lupranate T80) was quickly added and vigorously stirred for 10 seconds. The foam maturation took one day, and its density was approx.  $30 \text{ kg.m}^{-3}$  [23].

## **Process of partial depolymerisation**

The process of liquefaction (partial depolymerisation) is described in the following procedure. An amount of 43 g of flexible PUR foam (synthesised by the process described above) was put in the reagent sulphonation flask equipped with a low-speed high torque mixer, inlet of inert gas (nitrogen) and thermometer. In the next step, 45 g of propylene carbonate (PC) as the non-reactive medium and 1 g of potassium acetate (KAc) as the catalyst were added to the flask. The flask was heated in a heating mantle or on oil bath. The temperature of the depolymerisation was set at  $130^\circ\text{C}$  [23]. This temperature corresponds to the initial spontaneous depolymerisation temperature typical for studied flexible PUR foams referred to in the literature [14]. KAc is normally used as a catalyst for gel reactions in polyurethane chemistry [15, 16]. This catalyst is not a volatile compound compared to common tertiary amines (most widely used catalysts), which is its advantage in the process carried out at elevated temperature [15].

PC was used for heat transfer and as a catalyst carrier medium, which is not consumed during the process. It is aprotic polar solvent with high dipole moment (4.9 D). Based on the chemical analysis, the complete process took 30 minutes from the start of heating until the end of the reaction, excluding 10 minutes of preheating to reach  $130^\circ\text{C}$ . The PUR foam changed from the solid-state to liquid immediately after reaching  $130^\circ\text{C}$ , forming an amber homogenous liquid and remaining the same for the next 30 minutes of heating [23]. Apparatus for partial PUR foam depolymerisation is presented on the figure 5.



*Fig. 5: Apparatus for partial flexible PUR foam depolymerisation: oil bath, reflux condenser, nitrogen gas inlet, and high-torque mixer*

### **Preparation of adhesives from depolymerised PUR foam**

First, an unseparated depolymerisation product (even containing a non-reactive medium PC) was used for the formulation of two 2C adhesives (Adhesive 1 and Adhesive 2). In the next step, the recycled polyol was separated from the depolymerisation product. For this purpose, the depolymerisation product was subjected to vacuum distillation (145°C, 13 mbar) of the remaining propylene carbonate. Distillation residue, i.e., the separated recycled polyol, was used to prepare 1C adhesive (Adhesive 3) [23].

The two-component (2C) PUR adhesive formulation with unseparated depolymerisation product (Adhesive 1) was prepared from the following components:

#### *Polyol pack A*

liquid unseparated depolymerisation product	97,6 wt.%
maleic acid (inhibitor)	2,4 wt.%

#### *Isocyanate pack B*

Lupranate MI (pure 4,4-MDI)	100,0 wt%
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Mixing ratio A:B = 40:60.

The inhibitor was used because nitrogen-containing depolymerisation by-products cause a strong autocatalytic effect. The pot life of 30 minutes was reached.

The 2C PUR adhesive formulation with unseparated recycled product mixed with pure polyol (Adhesive 2) was prepared from the following components:

*Polyol pack A*

Liquid unseparated depolymerisation product	50,0 wt.%
Lupranol 1005/1 (pure polyol)	50,0 wt.%

*Isocyanate pack B*

Lupranate MI (pure 4,4-MDI)	100,0 wt.%
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Mixing ratio A:B = 40:60

The formulation of Adhesive 2 is the same as Adhesive 1, however without the addition of an inhibitor (maleic acid). The polyol pack consists of a mixture of the liquid recycled product and pure polyol in a ratio of 1:1. The exclusion of the inhibitor from the formulation was carried out by diluting the recycled product with pure polyol. The pot life of this mixture was 20 minutes.

The 1C PUR adhesive formulation (Adhesive 3) was prepared from the following components:

Recycled polyol phase	44,0 wt.%
Dabco DMDEE (blowing catalyst)	0,5 wt.%
Lupranate M20S (polymeric 4,4-MDI)	55,5 wt.%

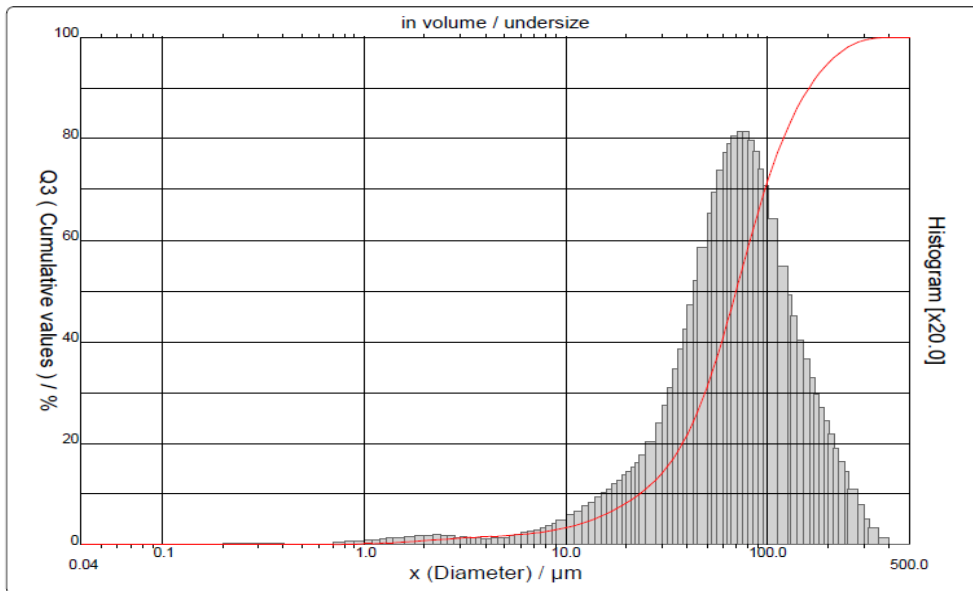
## Results

Dissertation proceeded two ways. **The first way** was focused to micro-milling of the rigid foam and measurement of the chemical reactivity the prepared PUR powder. Because measurable chemical reactivity of the powder was observed, the powder was used as partial replacement of the polyol by preparation of 1C PUR adhesive [22].

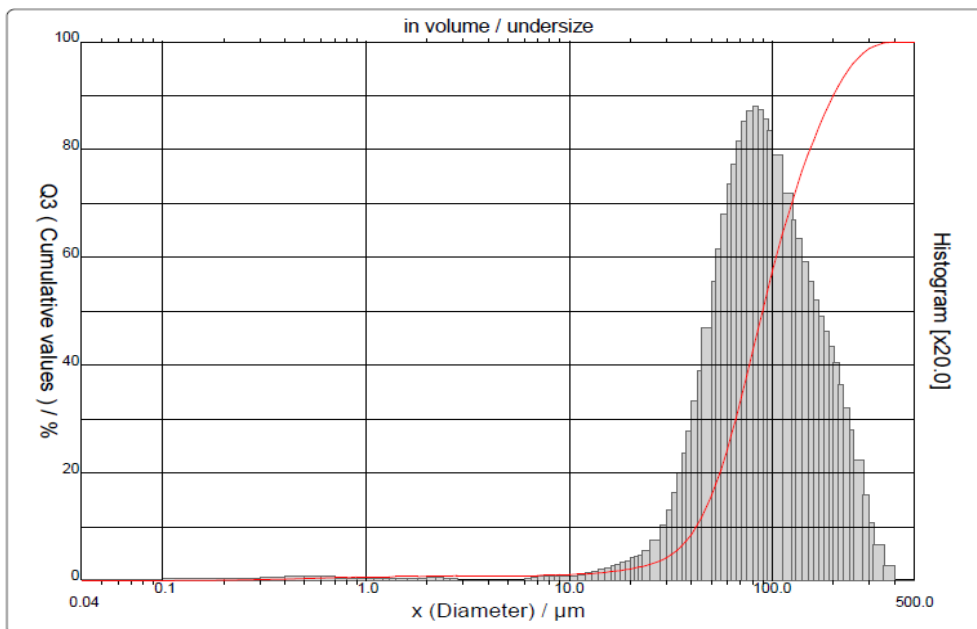
**The second way** of the dissertation was dedicated to chemical recycling of the flexible foam. First, the common methods of chemolysis were studied. Here was confirmed that the chemolysis is high energy input process (200°C, 4 hours) with reagent consumption (glycol, glycerol, etc.) and unusual secondary waste formation (substituted polyurea) [17]. Then a unique method of partial depolymerisation of the PUR foam was developed. This novel method is based on reversal reaction of polyurethane polymer in ambient of polar aprotic medium (propylene carbonate) and in presence of non-volatile gelling catalyst with mild reaction conditions (130°C, 30 minutes). Product of the partial depolymerisation it is brown liquid consisting of solution the recycled polyol and low-molecular fusible resin in propylene carbonate. Products of the depolymerisation were used for 2C and 1C PUR adhesives formulation.

## Result of micro-milling the rigid PUR foam

As described above, four milling methods were tested. Dispersion in polyol showed too high warming during milling due to high viscosity of the particle suspension in polyol. It is not suitable method. Milling at cryogenic condition is efficient however very expensive process. Milling with knife mill is very fast process giving particle size suitable for using as filler in adhesives. Similarly two-roll mill gives suitable particle size. Particle size analysis is described on figure 6.



a) Two-roll mill; particles diameter at 10%: 23 μm, at 50%: 70 μm, at 90%: 160 μm

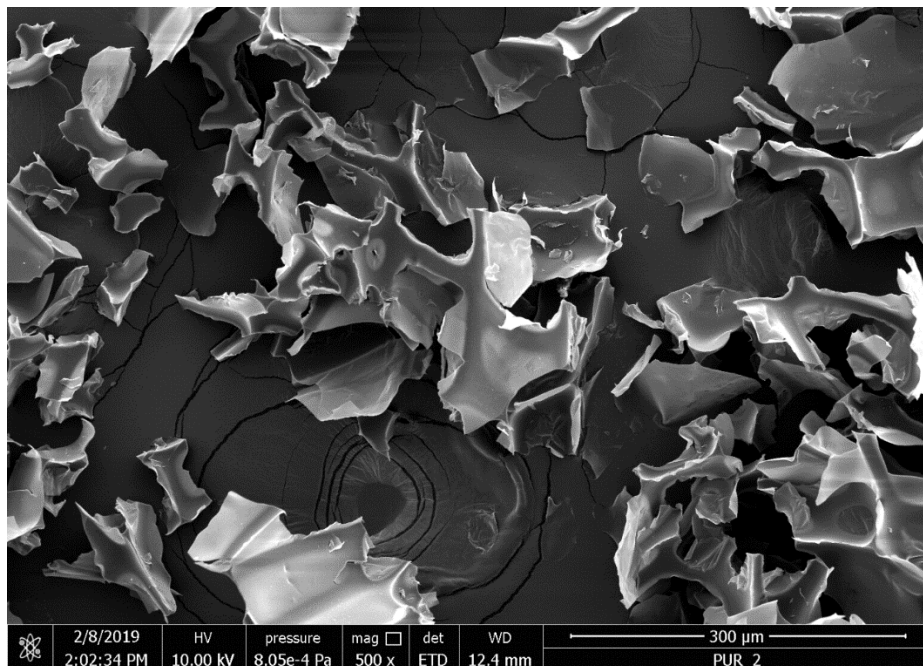


b) Knife mill; particles diameter at 10%: 42 μm, at 50%: 89 μm, at 90%: 199 μm.

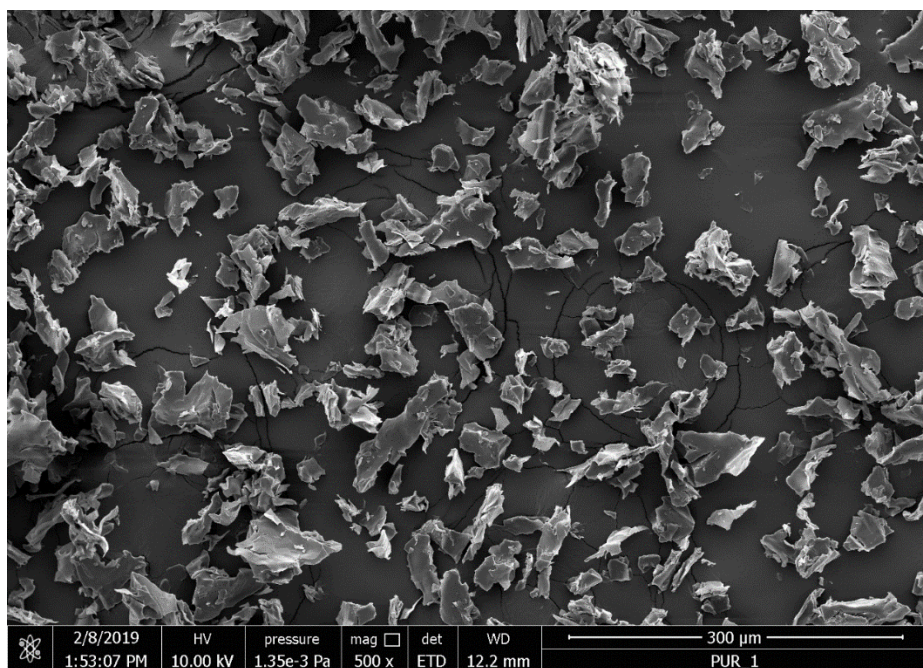
Fig. 6: Particle size analysis of milled particles: a) two-roll mill; b) knife mill [22].



Morphology of the particles is evident in the figure 7.



a)



b)

*Fig. 7: Morphology of the milled rigid PUR particles, SEM microscopy: a) knife mill (mag. 500x), b) two-roll mill (mag. 500x) [22].*

## Reactivity of the micro-milled rigid PUR foam and its addition to PUR adhesive

It is not feasible to measure OH and amine number directly by powder material. For this reason the indirect method was used. Powder was blended in the polyol with known OH and NH values and these parameters were measured by titration methods. Results are stated in the following table:

Sample	OH number (mg KOH/g)	Amine number (mg KOH/g)	Total OH+NH reactivity (mg KOH/g)
Virgin polyol (Lupranol 1000/2)	57.40±0.43	0.00±0,00	57.40
Virgin polyol + 10% of rigid PUR foam powder	53.30±0.71	4.60±0,21	57.90

Because micro-milled powder exhibits chemical reactivity useful in PUR chemistry, it was used as active filler in the adhesive formulation where 5, 10 and 20% of polyol was replaced with the powder [22].

During blending the powder in polyol the rheology was considered. It was found out that powder originated from knife mill is not suitable for this use because the sharp-edged particles increase the mix viscosity intensively. Rheology of the adhesives where part of polyol is replaced with rigid PUR powder is stated in the figure 8.

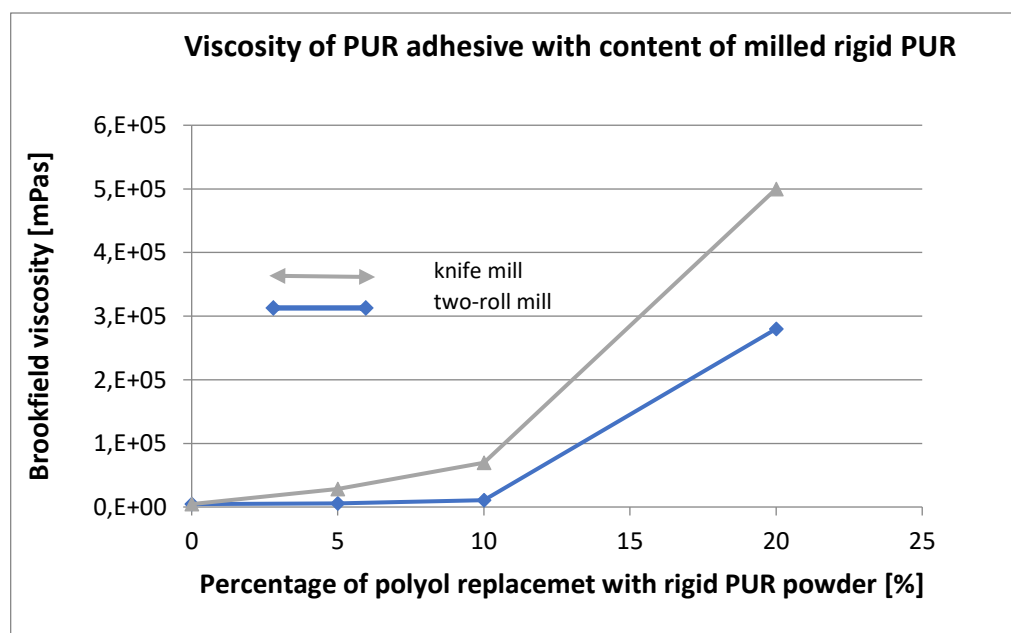


Fig. 8: Viscosity of the 1C PUR adhesive with partial replacement of polyol with micro-milled rigid PUR foam.

For practical use only powder manufactured in two-roll mill is considered. Adhesive parameters of modified 1C PUR adhesive are stated in the following table [22]:

Substitution of polyol by recycled PUR powder	Viscosity	Free film tensile strength	Free film elongation at break	Wood/wood bond tensile strength (at shear)	Remarks
	mPas	kPa	%	MPa	
0%	4600	1056	103,7	0,51	Very soft and flexible film
5%	5550	1198	80,8	2,30	
10%	11000	1307	24,5	3,84	
20%	280000	3400	30,0	5,45	95% cohesion wood failure

Graphically, the bond strength is showed in the figure 9.

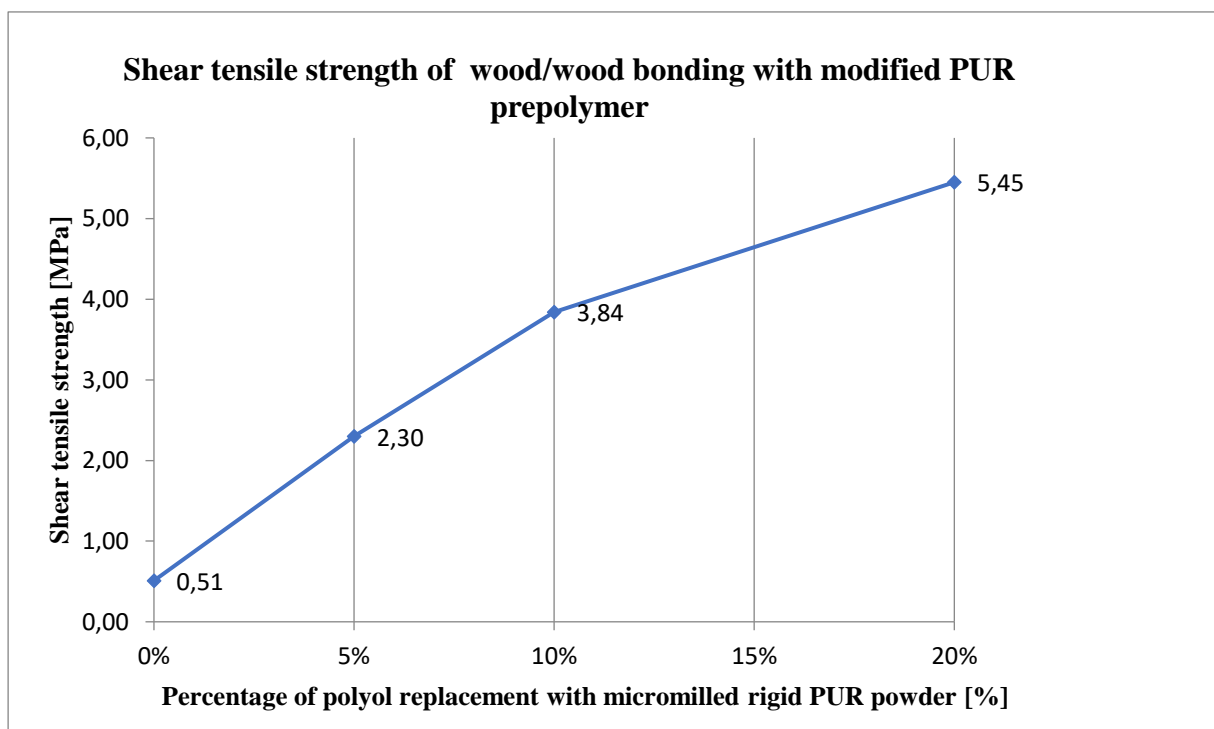


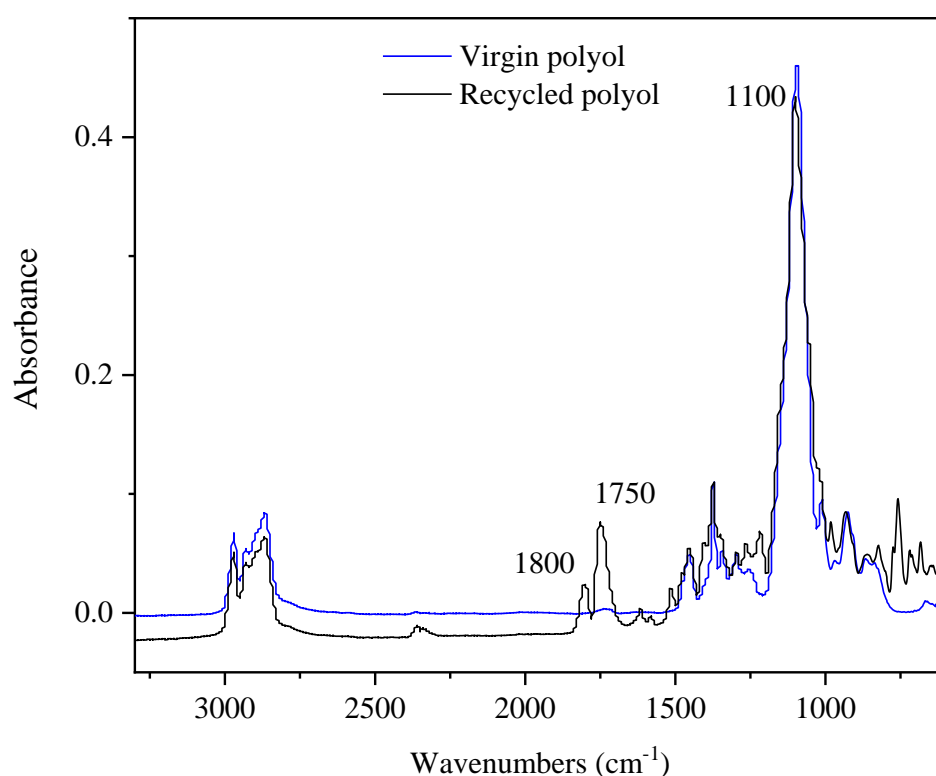
Fig. 9: Tensile strength (at shear) for wood to wood bonding with partial replacement of polyol in 1C PUR adhesive [22].

The practical bonding tests showed that presence of micro-milled particles increases the bond strength. If parameters strength and viscosity are combined, we could say that adhesives with 10% of polyol replacement have optimal properties for wood to wood bonding [18].

## Result of partial depolymerisation of the flexible PUR foam

Flexible foam depolymerised via process described above looks like low-viscosity brownish liquid. After PC removal by vacuum distillation (145°C, 23 mbar) the product is split in to two phases: upper colourless polyol and lower dark brown solid resin with melting point about 70°C. Yield of the recycled polyol is 70,8% (calculated on polyol weight used for foam preparation). Other polyol remains bound in the resinous by-product [23].

Infrared spectral analysis confirmed that the recycled polyol is identical with the virgin polyol used for foam synthesis. FT-IR spectra are shown on figure 10 and 11.



*Fig. 10: FT-IR spectra of recycled polyol and virgin polyol: the peaks at 1800 and 1750 cm<sup>-1</sup> indicate contamination with propylene carbonate.*

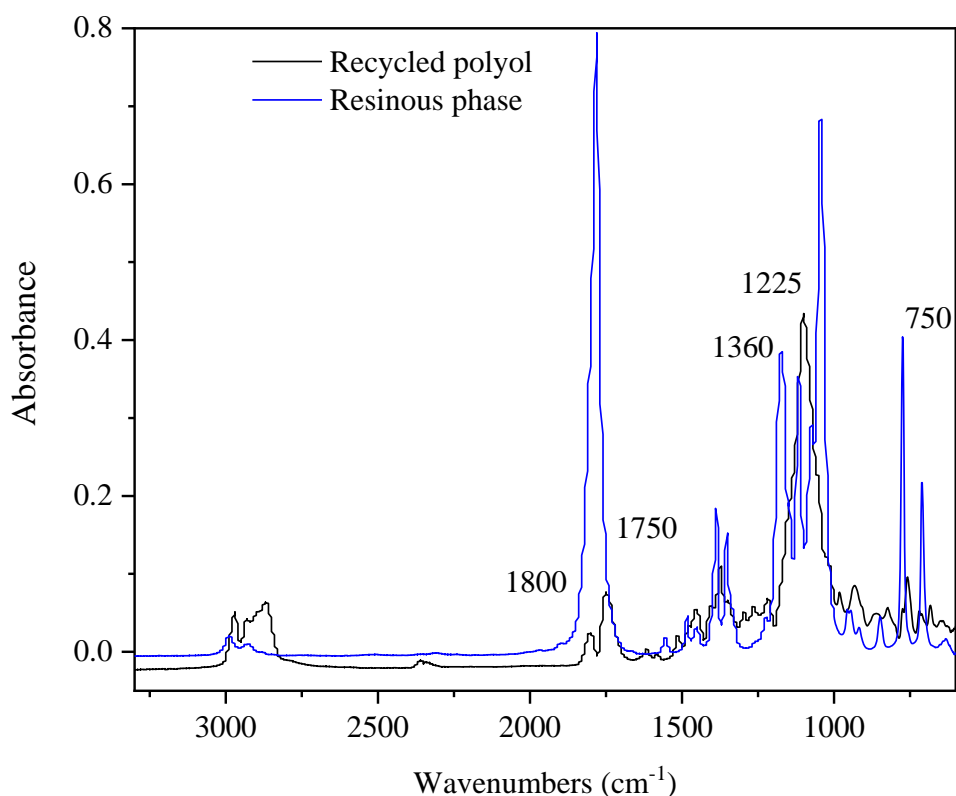


Fig 11: FT-IR of recycled polyol vs. resinous phase: the resinous phase gives spectrum with character of polyurethane. Its contamination with propylene carbonate is visible.

The identity of the recycled polyol was confirmed also by gel permeation chromatography with refractive index detector (GPC-RI) vs. polystyrene calibration.

Chromatograms of the virgin polyol and recycled polyol are illustrated on figure 12a, 12b and numerically presented in the following table [23]:

Sample	$M_n$ (g.mol <sup>-1</sup> )	$M_w$ (g.mol <sup>-1</sup> )	Polydispersity Index
Virgin polyol	5175	5666	1,09
Recycled polyol	4587	5199	1,13
Resinous phase	321	453	1,41

$M_w$  of the recycled polyol and virgin polyol are almost identical. The difference between measured and declared value (3500 g.mol<sup>-1</sup>) may be explained by polystyrene calibration of GPC column which is not identical macromolecule like polyol.

Resinous phase exhibits low molecular weight which is in relation with its low melting point (value 453 g.mol<sup>-1</sup> stated in the table above).

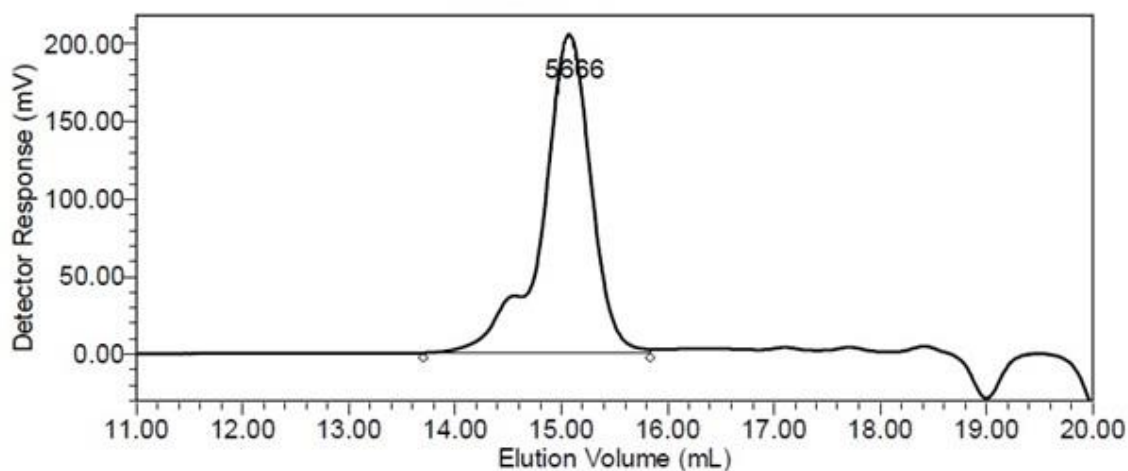


Fig. 12 a: GPC of the virgin polyol,  $M_w = 5666 \text{ g.mol}^{-1}$ .

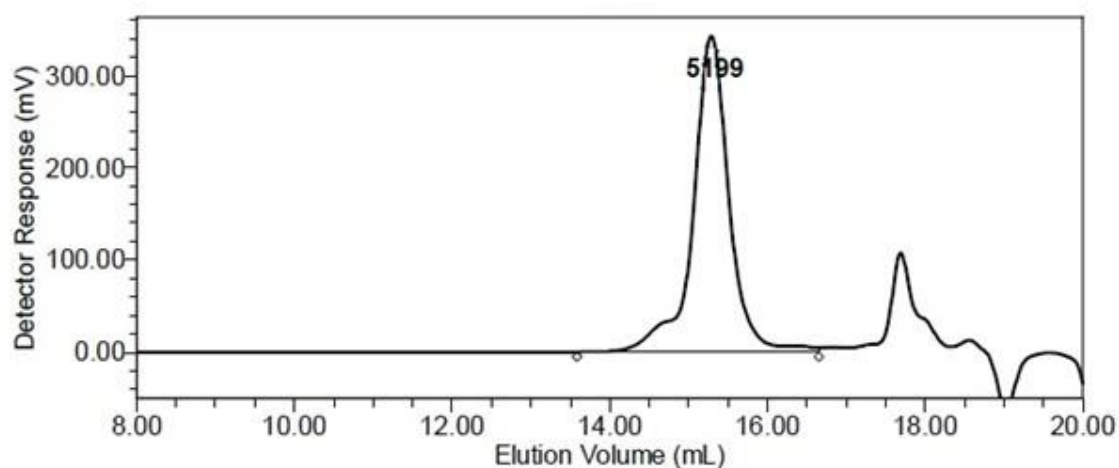


Fig. 12 b: GPC of recycled polyol,  $M_w = 5199 \text{ g.mol}^{-1}$  (PC contamination at 17,5 ml)

### Elemental analysis of the PUR foam and resinous phase

The meaning of elemental analysis is to reveal if the nitrogen (originated from diisocyanate monomer) is concentrated in the resinous phase, or not. Result of the analysis is presented in the following table [23]:

Sample	C (%)	H (%)	N (%)	O (%)
Flexible PUR foam	61,92±0,02	8,73±0,05	5,67±0,11	23,68
Resinous by-product	62,09±0,09	6,99±0,06	8,69±0,06	22,23

It is interesting to see that resinous product contains 50% more nitrogen than original PUR foam. It is evident that resinous phase keeps the nitrogen in polyurea and polyurethane bonds those are not degradable by partial depolymerisation process.

### Usage of the depolymerised products in 1C and 2C PUR adhesives

Unseparated mixture after PUR foam depolymerisation contains also nitrogenous compounds with expected autocatalytic effect in PUR chemistry [23]. For this reason this replacement of polyol was inhibited with addition of maleic acid in the formulation “Adhesive 1”. In the formulation “Adhesive 2” the reactivity was decreased by dilution with pure polyol Lupranol 1005/1 in ratio 1:1. Adhesive 1 and Adhesive 2 were conceived as two component PUR adhesives for wood where part B consists of pure MDI.

Separated recycled polyol was used for preparation of 1C PUR adhesive (“Adhesive 3”). Preparation of the adhesives is described in part *Preparation of adhesives from depolymerised PUR foam*.

Properties of adhesives are summarised in the following table [23]:

Sample	AVG Tensile strength on wood/wood / N.mm <sup>-2</sup>	Note
Adhesive 1 (2C) ( <i>non-separated recycled product + maleic acid</i> )	2.12±1.04	Cohesive wood failure at the break in one case of 4 measurements
Adhesive 2 (2C) ( <i>non-separated recycled product + pure polyol</i> )	4.19±0.4	Cohesive wood failure at the break in all 4 cases of 4 measurements
Adhesive 3 (1C) ( <i>separated recycled polyol</i> )	3.91±0.52	Cohesive wood failure at the break in 3 cases of 4 measurements

Adhesive properties of “Adhesive 1” were unsettled. “Adhesive 2” showed much better properties, typical for commercial adhesives [18]. Also one-component “Adhesive 3” gives good properties, usual at practical use.

### Possible use of resinous phase of PUR depolymerisation

Because resinous phase is rich with urea- or urethane- nitrogen and it is easily fusible oligomer, it should have exhibit reactivity with isocyanates. Simple reactivity test was carried out [23]:

Resinous phase (melted at 70°C)	20 g
Lupranat MI (pure 4,4,-MDI)	20 g

Both components were blended. The reaction is extremely fast, exothermic. Product of the reaction is rigid PUR foam with density about  $100 \text{ g.dm}^{-3}$ . This is typical density for rigid insulation foams [19].

Resinous phase of the depolymerisation could be used as specific polyol part in synthesis of rigid foams. There is also an assumption that suitable blend of polyester polyol and resinous phase could be useful raw material for polyurethane prepolymer hot melt adhesives. Such adhesives are applied by melting at  $100\text{-}140^\circ\text{C}$  [20].

## **Benefits and novel approach; conclusions**

The main goals of the author's work were:

- Recycling of the rigid PUR foam by micro-milling, testing the powder reactivity in PUR systems and usage of the recycled powder as replacement of polyol in PUR adhesive formulation
- Recycling of the flexible PUR foam by partial depolymerisation, analysis of the depolymerisation products and usage of the recycled products for PUR adhesive formulation

All of these goals were reached. Unfortunately it was not possible to recycle also isocyanate by depolymerisation method, as it is extremely reactive compound [23].

Micro-milled rigid PUR foam with particle size under  $100 \mu\text{m}$  is characterised with mild chemical reactivity (amino-groups) it may be used as partial replacement of polyol in PUR adhesives formulation. The adhesive properties are useful when replacement of polyol is about 10%. Replacement of polyol in range of 20% gives viscous products with pasty consistency, suitable maybe for sealants. The novel approach of this work consists of finding the possibility to use micro-milled foam as active component with chemical reactivity [22]. Then it works not only as filler but as real replacement of polyol.

Depolymerisation of flexible polyurethane is difficult due to crosslinked character of this polymer. It was discovered that aprotic polar medium with high dipole moment (propylene carbonate) in combination with suitable catalyst (potassium acetate) enables to reverse the chemical balance back to monomers at relatively low decomposition temperatures ( $130^\circ\text{C}$ ). While conventional polyurethane chemolysis requires high temperature ( $200^\circ\text{C}$  and more) and long reaction time (4 hours and more), studied method of liquefaction works at  $130^\circ\text{C}$  in tens of minutes. Additional benefit is zero consumption of the reaction media.

Product of the depolymerisation could be used directly as polyol component in 2C PUR adhesives but better result is reached with separated recycled polyol in 1C PUR adhesive. Secondary product of the depolymerisation, i.e. resinous phase, is interesting material suitable for rigid foam preparation or (probably) for hot melt PUR adhesive synthesis.



This work implies many other possibilities of research. For example:

- Use of resinous phase for the preparation of hot melt reactive PUR adhesives; ideally in combination with polyester-polyols. Study of properties of such prepolymers.
- Research into the recycling of the isocyanate component: here it is proposed to improve the method of binding the just cleaved diisocyanate into a complex with a suitable reagent such as  $\epsilon$ -caprolactam, MEKO (methyl ethyl ketone oxime) or phenol. Another possibility seems to be to optimize the arrangement of the depolymerization apparatus so that it is realistic to remove the isocyanate formed under high vacuum by distillation without the use of a masking / blocking agent (e.g. depolymerization in a thin film, in a special extruder, etc.).
- Research into the method of homogenization (i.e. emulsification or dispersion) of both partial depolymerization products so as to combine the polyol and resin phases into a single, liquid product, which can be further processed in the usual way in PUR chemistry (foams, adhesives, binders)
- Study of depolymerization catalysis to replace KAc (which promotes isocyanate cyclization) with another suitable catalyst that will better recover recycled isocyanate.
- Research of partial depolymerization also developed for rigid PUR foams based on MDI and lower-molecular multifunctional polyols.

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