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Recycling of rigid polyurethane foam: micro-milled powder used as active filler in polyurethane adhesives

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ABSTRACT

Rigid polyurethane (PUR) foams are widely used as heat insulation material in construction industry or for electronic appliances manufacturing. After finishing their lifetime it is necessary to eliminate foam wastes. The aim of this study was to prepare a pair of industrial polyurethane adhesives of medium viscosity containing recycled rigid polyurethane foam. Three methods of milling were tested: knife-milling, two-roll milling and ball-milling. Only two-roll milling gives the PUR micro-powder usable for following adhesives modification. The micro-powder was used as passive filler in polyurethane adhesives and potential reactivity for polyol pack replacement was studied. Hydroxyl and amine numbers were determined in mixture with virgin polyol. One-component polyurethane prepolymer adhesive was prepared using various dosages of the micro powder and the tensile strength of bound wood was measured. As additional parameters also free film adhesive mechanical parameters were tested and particle size distribution of the micro powder was analysed. Two adhesive formulations were prepared for independent evaluation of the micro

powder reactivity. The results showed growing of the mechanical strength of wood bonding with growing dosage of the micro powder.

1. INTRODUCTION

Rigid polyurethane foams (Fig. 1) are widely used as heat and acoustic insulation materials in construction, home appliances and vehicle industries [1-6]. These highly crosslinked polymers based on isocyanate, isocyanurate and multifunctional polyols are obviously also modified with flame retardants which makes this material difficult for recycling [7-9]. Highly crosslinked polymer is very resistant against any chemolysis. Flame retardants bring to the possible product of chemolysis hardly describable contaminants. Burning of foam wastes leads to carbonation and dangerous gases evolving, for example hydrogen cyanide or nitrogen oxides, biodegradation of rigid polyurethane foam is extremely slow, it means polyurethanes do not belong to compostable plastics [10]. One method of physical (mechanical) depolymerisation via micronisation seems to be efficient for practical use [11]. Fine free flowing powder made by foam waste milling exhibits certain reactivity in new PUR system, so the milled product was studied as active filler in PUR adhesive prepolymer systems [12].

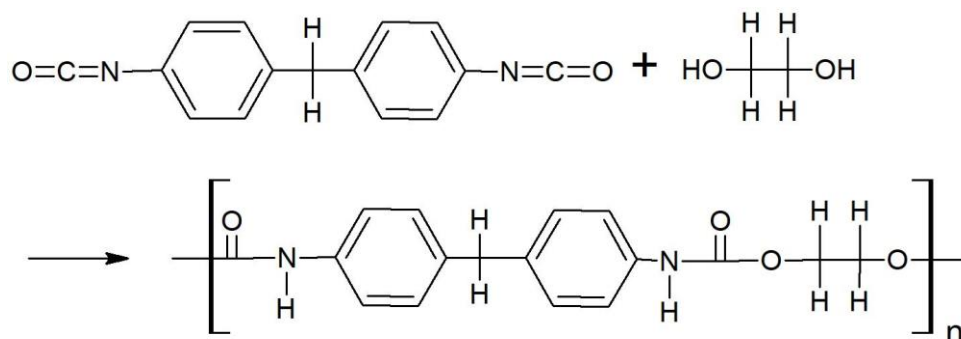


Fig. 1: Scheme of PUR polymerization.

Theoretically, four ways of PUR foam wastes removal could be used: dump deposit, composting, incineration or recycling. PUR foams are crosslinked polymers with good weather resistance, relatively good hydrolysis resistance and with practically no biodegradability [13]. The PUR macromolecule contains polyurethane and polyurea bonds. Polyurea bonds are concentrated in areas where difunctional isocyanate reacted with added water (as blowing agent) giving gaseous carbon dioxide and diamine; the diamine reacts in other steps with excess of diisocyanate resulting polyurea bonds). During burning the nitrogen containing parts of macromolecule are decomposed giving dangerous gases like hydrogen cyanide or nitrogen oxides. Because of its long-term weather resistance and slow and incomplete biodegradability the dampening or composting is not suitable way how to remove the rigid PUR foam waste. This is why some recycling method is preferred [14-15].

Rigid PUR foam wastes may be recycled mechanically or chemically [16]. Due to the highly crosslinked nature of the rigid PUR foams the chemical depolymerisation is very difficult and not so effective for industrial use. High energy request 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 diphenyl methane diisocyanate (MDI) [17-18]. 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 problematic hygienic properties [1, 19].

Unlike of the flexible PUR foams used in furniture industry, the rigid PUR foams are relatively stiff and it means more suitable for mechanical depolymerisation by micro-milling. Flexible PUR foams have glass transition temperature about -50°C and their milling without cryogenic conditions is practically impossible. In contrast to flexible foams the rigid foams

have glass transition temperature closer to the ambient temperature and their milling is realistic also without deep freeze conditions.

Mechanical recycling of the PUR foams is industrially usual process [11, 16]. 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. Rigid foam wastes can be milled to the form of fine powder and used as adhesive fillers or as spillage absorbent [12, 19].

The novelty of the following study is considered in new approach to the addition of powdered material to a binder system. Recycled PUR powder is not taken as filler but as an active ingredient of the whole system. Certain reactivity of recycled PUR powder was measured and two various one-component polyurethane prepolymer adhesives exhibit improved mechanical properties when a part of polyol package was replaced with recycled powder. This method could save some virgin polyol consumption thanks to the natural reactivity of the recycled PUR foam waste. For evaluation of the recycled PUR powder reactivity with isocyanates the hydroxyl and amine numbers determination in mixture with virgin polyol were used.

Improvement of the bonding properties is essential by above mentioned modification. Replacement of polyol in amount of 20% leads to the pasty adhesive consistency (sealant consistency) and the shear tensile strength of bond wood to wood was increased approximately 10 times for Formulation I (flexible glue) and or 2 times for Formulation II (rigid glue) respectively. Filling the adhesives with waste material powder together with decreasing the virgin polyol dosing brings the new point of view to the recycling process.

2. EXPERIMENTAL PART

2.1 MATERIALS

Chemicals used to characterize materials: glacial acetic acid (purity min. 98%, Lach-Ner, Czech Republic), perchloric acid (purity min. 68%, Lach-Ner, Czech Republic), acetic acid anhydride (purity min. 98%, Lach-Ner, Czech Republic), crystal violet (purity min. 90%, Penta Chemicals, Czech Republic), N,N-dimethylformamide (purity min. 99%, Penta Chemicals, Czech Republic), 1-methylimidazole (purity min. 99%, Merck, Germany), acetic acid anhydride (purity min. 98%, Lach-Ner, Czech Republic), tetrahydrofuran (purity min. 99,5%, Lach-Ner, Czech Republic), thymolphthalein (purity min. 90%, Penta Chemicals, Czech Republic), ethanol (purity min. 96%, Penta Chemicals, Czech Republic), Hydranal Methanol Rapid (Fluka – Honeywell, Romania), Hydranal Composite 5 (Fluka – Honeywell, Romania) .

Chemicals used to polyurethane prepolymers preparation: Lupranol 1000/2 (BASF AG Germany, diol, M_w 2000 $\text{g}\cdot\text{mol}^{-1}$, OH number 55 $\text{mg KOH}\cdot\text{g}^{-1}$), Lupranat MI (BASF AG Germany, monomeric 2,4'- and 4,4'-diphenyl methane diisocyanate, NCO content 33.5%, functionality approx. 2), Lupranat M20S (BASF AG Germany, oligomeric diphenyl methane diisocyanate; NCO content 31.5%, functionality approx. 2.7), Dabco DMDEE (catalyst, Evonik GmbH Germany (2,2'-dimorpholinildiethylether)).

2.2 PREPARATION OF SAMPLES

Rigid heat insulation PUR/PIR foam made in Kingspan CZ Company (Hradec Kralove, Czech Republic) was used in following experiments. The foam was not modified before testing. Sheets approximately 20 cm long, 10 cm wide and 2 cm thick were used for milling process. All the experiments were carried out under ambient conditions, i.e. at 22°C room temperature.

Initially there is necessary to provide physical depolymerisation, i.e. micro-milling of the PUR foam. It is important to note that rigid foams with closed cells are produced using cyclopentane blowing agent so also fire protection measures must be provided during experiment.

The simplest mill is constructed on principle of rotation knives. Laboratory knife mill Mavet SM-LAB, (Mavet CZ s.r.o., Czech Republic) was used for the experiment. Three knife mill operates at constant revolutions 900 min^{-1} with diameter of the chamber 150 mm. Pieces of rigid PUR foam in diameters about 10x2x2 cm were put in the feeding chamber of the mill manually. 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. The process is fast and easy to provide. The milled piece can pass through the milling chamber once only, so the process takes short time only.

Two-roll mill of Buzuluk Company, Czechoslovakia (1985), type 14201 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 a moment when the compression exceeds the limit of material flexibility. Shear force helps to grow broken crumb apart. Thanks to combination of these two effects the produced PUR powder is more compact than product from knife mill. Disadvantage of the two-roll mill is its low productivity (product flow in time). The cylinders of 200 mm diameter and 40 cm of

length were set with gap 0.15 mm. The revolutions of the first cylinder was set to 20 RPM, the second cylinder was +10% faster than for the first cylinder to provide higher shear milling forces. The material must pass minimally 20 times between milling rolls to get final particle size, it took 2 hours of milling time. The milling time is depending on the moment of spontaneous crumbling the compact foam piece to the powder. The treated foam is compressed to some compact semi-flexible plastic pieces in the initial stage of milling; after 20 passing those pieces between mill rolls suddenly the spontaneous disintegration occurred and the PUR/PIR material is transformed for powder. Next continuing of milling brings no visible improvement. Two roll milling method was compared with knife mill in point of milling time too. Whereas complete milling in knife mill was finished in 5 minutes, the two roll mill in the same time period worked just in the initial phase of milling, i.e. flexible deformation of PUR foam pieces.

The milled PUR foam has strong tendency to create agglomerates. To avoid this undesirable effect, the PUR powder gotten from two-roll mill was re-milled in planetary ball mill Fritsch (built year 1998) with stainless steel balls of diameter 10 mm/100 pieces and stainless steel bowl of diameter 125 mm for 3 hours at 400 RPM. The milling time for this operation was not compared with two roll mill technique because here we speak about an additional re-milling, not primary milling. Samples of the product were inspected by optical microscopy during the milling after 5, 15 and 30 minutes. No significant changes were observed in those three intervals. So then the sample was re-milled for 3 hours of the total time to get visible agglomerate reduction effect. The milling process was carried out directly in ambient of virgin polyol Lupranol 1000/2 which will be used in the adhesive formulation. The re-milling reduced the particle size a bit and reduced the occurrence of agglomerates.

Adhesives formulations

Two formulations based on purchased BASF raw materials were suggested to evaluate the active filler properties. Formulation I is typical for flexible one-component polyurethane adhesives, while formulation II is suggested as stiff (rigid) one-component polyurethane adhesive.

This study is focus on one-component adhesives. One-component adhesives work different way. The polyisocyanate part is used in excess to give liquid polyurethane prepolymer – one-component adhesive. The prepolymer with free isocyanate groups provides crosslinking by air humidity during adhesive curing. Final properties of one-component adhesive are optimised empirically to achieve desired viscosity and rigidity (flexibility respectively) of the crosslinked adhesive. 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.

Below mentioned formulations (Table 1) were selected for the planned experiments with the active PUR powder filler. In case of Formulation I it was flexible adhesive and Formulation II it was rigid adhesive.

Table 1: Components of formulations.

Formulation	Weight [g]			
	Lupranol 1000/2	Dabco DMDEE	Lupranat MI	Lupranat M20S
I	63.0	0.2	37.0	-
II	58.0	0.1	-	42.0

In the following experiments a certain part of the polyol package was replaced with micro-milled PUR foam waste originated from two-roll mill.

2.3 MEASUREMENTS AND CHARACTERIZATION

Characterization of PUR materials

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. Samples were placed on carbon tape and gold coated with a 7 nm thick layer. Analyses were performed at the accelerating voltage between 5 and 20 kV.

Particle size measurements were performed on the instrument Laser granulometer CILAS 1090 (Orleans, France) with measuring range 0.04-500 μm in the wet state (in water with Tickopur TR7 as dispersing agent). The volume mean diameter (D) was automatically calculated. The results were evaluated using Evaluating software Size Expert.

The amine number of the polyol was determined by volumetric titration according to EN 1877-2 [20] using automatic titrator Mettler Toledo T50 and glass electrode Mettler Toledo DG 113 SC (range 0-12 pH). Lab software LabX ver. 3.1 was used. The theoretical amine number was calculated according to the equation (1):

$$\text{Amine number theor.} = [(Z \times 56.11) / M] \times 1000 \quad [\text{mg KOH.g}^{-1}] \quad (1)$$

where Z is the number of amino groups in the molecule and M is the molecular weight of the compound.

Method is based on ASTM D 4274-16, method E [21]. The hydroxyl number is determined by back potassium hydroxide titration of acetic acid released from excessing acetic acid anhydride after sample acetylation catalysed by 1-methylimidazole ambient of N,N-dimethylformamide. The hydroxyl number was calculated according to the equation (2):

$$\text{OH number theor.} = (A - B) \times 0.5 \times f \times 56.11 / w \quad [\text{mg KOH.g}^{-1}] \quad (2)$$

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.

For hydroxyl number determination the automated titrator Mettler Toledo T50 was used, equipped with glass electrode Mettler Toledo DG 113 SC (range 0-12 pH). The titrator features the software LabX ver. 3.1.

Free flowing powder density is measured as (3):

$$D = w/V \quad [\text{g.dm}^{-3}] \quad (3)$$

where D is the free flowing powder density, w is the sample weight and V is the sample volume. Volume is measured in volumetric cylinder without any compressing the powder sample.

Sedimentation tendency of PUR powder re-milled in ambient of polyol by ball-mill was observed visually. Beakers with 50 ml of volume were used to compare re-milled sample (ball-mill) with the same sample before re-milling. Both samples were let without any movement or agitation for 24 hours and then the difference in the sediment level was observed.

Water content in polyol modified with recycled PUR was determined by Karl Fischer volumetric method with automated titrator Mettler Toledo T5, electrode DM 143 SC and lab software LabX Titration 10.0. The procedure is detailed in standard ISO 760:1978 (rev. 2016) Determination of Water - Karl Fischer Method (General Method) [22].

Characterization of adhesives

Viscosity was measured with Brookfield DVE viscometer using spindle No. 6 at various revolution speeds. Samples were conditioned at 22°C.

For mechanical strength determination the tensile strength machine Hegewald & Peschke Inspect Table 5 kN was used. Movement speed 100 mm.min⁻¹ 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 [23]. The effective specimen length is 34.93 mm and its width is 6.4 mm. The free film thickness was measured as 0.15 mm. 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 [24] where bound area consist of overlap 2 cm long and 2 cm wide. Spruce wood pieces 2 cm wide, 5 cm long and 5 mm thick were used. Wood pieces were glued together with the tested adhesives using pressure 0.05 MPa for 1 hour and the tensile test was done 24 hours after specimen preparation.

3. RESULTS AND DISSCUSION

Scanning electron microscope

The observation of the particles was available at magnification 500 times and 2000 times, although the low sharpness depth causes lower quality of the three-dimensional objects captures such as PUR particles. Unlike the soft polyurethane foam, the structure of the rigid foam contains closed cell window of spherical and polyhedral shapes [25-26]. The sharp-edged particles originated from two roll mill are shown in Figure 2a and 2b. The morphology of the particles is very complicated and the particles are characterised with branches and remaining broken cells shape. On the other hand, in the Figure 2c and 2d it is possible to see a different particle morphology of powder prepared by knife mill. The branched structure is eliminated, particle shape is not so sharp and remains of cells are no more visible.

The rigid foam, in this case, was milled into smaller parts than by two roll milling. Figure 2e and 2f show ball milled particles, which were prepared originally in liquid. Particles were rinsed with ethanol and dried before SEM analysis. The particles also have an irregular shape with blunt edges like those of a knife mill, but they are visibly even finer and their size is very diverse.

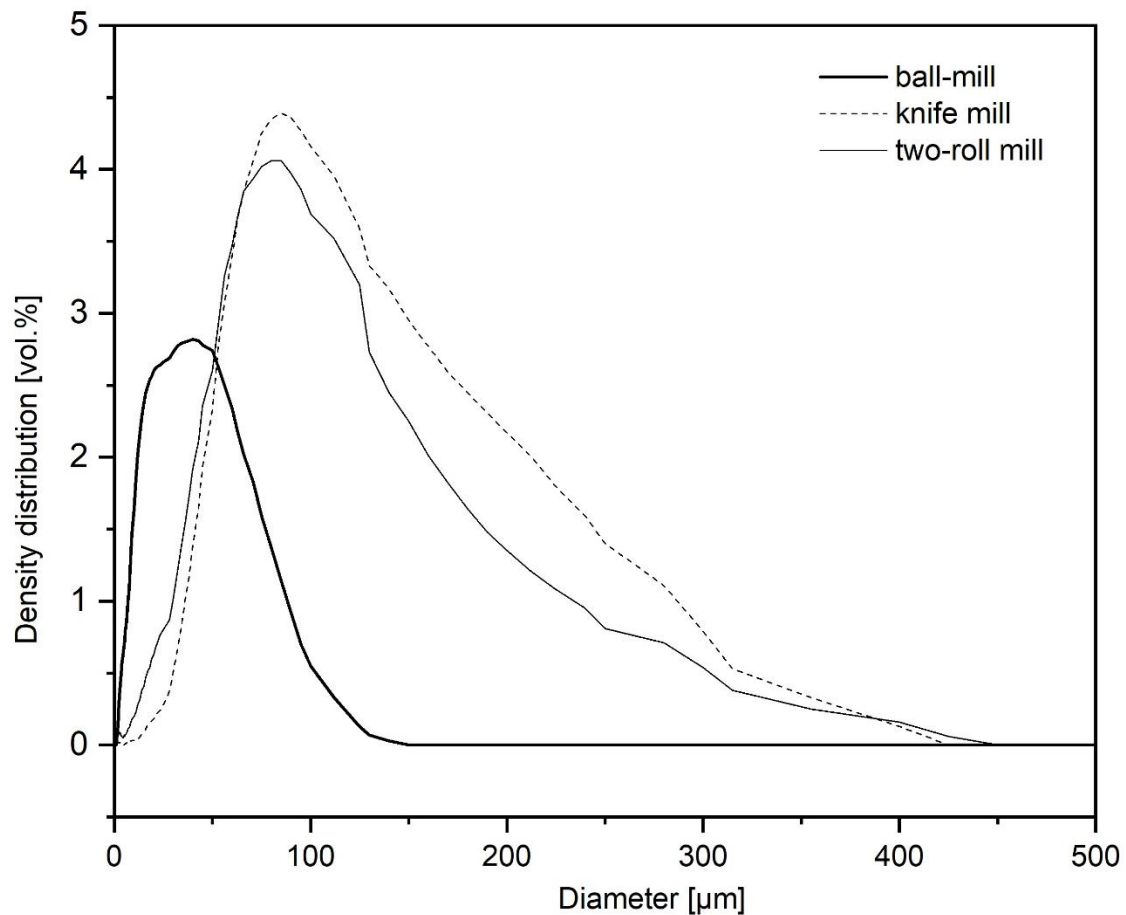
Fig. 2: SEM photographs of the PUR powder prepared on two roll mill, mag. 500x (a), from two roll mill mag. 2000x (b) from knife mill with mag. 500x (c), from knife mill mag. 2000x (d) and by ball mill with mag. 500x (e), by ball mill with mag. 2000x (f).

Particle size distribution

The particle size distributions of the rigid PUR foam after the milling are demonstrated in the Figure 3. The density distribution shows the particles in a given size range by percentage of the total sample volume. Each sample has only one main size fraction. Particle size from ball-mill milling ranged from 0.2 to 140 μm ($D = 29.40 \mu\text{m}$), from knife mill range from 0.1 to 425 μm ($D = 106.65 \mu\text{m}$) and from two-roll milling from 0.3 to 400 μm ($D = 82.87 \mu\text{m}$). For knife mill and two-roll mill shows the graph a maximum of diameter between 70-90 μm . This means that according to the data from the laser granulometer are particles from two-roll mill finer than particles made by knife mill. In order to simplify the measurement process, it is convenient to define the particle size using the software that employs a default scattering model for spherical particles. Particles from the two roll mill are not finer, they have just needle shape, which was caused by the rupture of closed cells. We know from the literature, that exists a very poor correlation between image analysis and laser diffraction is in case of needle shaped particles [27-28]. The needle-shaped particles diffract the laser beam depending on the average orientation of the particles in the beam [29]. The

probability of diffracting the beam based on needle length rather than width is small and, therefore, the effect on the data generated by differing needle lengths could be expected to be the smaller particle size distribution. We must place more trust in direct observation rather than in the results of calculation from measuring software. According to these reasons we expect, that particles from two roll mill are bigger on average than the values that were measured.

The specific result of milling is obtained by additional re-milling of the PUR powder originated from two-roll mill by additional ball-mill treatment. The milling process was carried out in suspension of the powder in polyol Lupranol 1000/2, the mixture contained 10% of the PUR powder and 90% of the polyol. Ball-milled specimens have maximum in range from 35 to 45 μm . The effect of milling to particle size is very often studied by the influence of milling time. Gonella et al. used drain mixer and after 6 minute were prepared the finest particles in maximum range from 180-255 μm [30-31]. The particle size distribution usually became broader and shift to finer sizes with prolonging milling time [32]. The particle size distribution in our case became narrower and shifted to finer sizes with ball milling. We can assume that the milled material from ball mill has the smallest particles and probably it will also contain finer particles that have not been detected because of instrument limitations.



*
 Fig. 3: Demonstration of particle size distribution of the rigid PUR foam milled by different methods.

The effect of re-milling improved anti-settling behaviour, it is demonstrated on the Figure 4. The sedimentation tendency is compared by samples after 24 hours from the moment of their preparation. The sedimentation is significantly faster for sample of PUR powder originated from two-roll mill. The high tendency of sedimentation is demonstrated by a clear level above the deposited layer (Figure 4a). The particles from ball mill has different tendency to setting (Figure 4b). The differences in particle morphology may be used as explanation of the different viscosity modification by these two powder types. Branched particles work as anchors among them, they are creating solid phase network with reduced particles mobility. Generally smaller particles in suspension have stronger thickening effect

than bigger particles at the same concentration. Similarly, narrow particle size distribution would give higher viscosity than suspension with broad particle size distribution. However in our case the particles' geometry plays the dominant role.

Fig. 4: Settling tendency of ball-mill re-milled PUR powder in polyol (b) is lower than sample without re-milling (a). The picture is obtained after 24 hours of homogenisation.

Measurement of free flowing density

The free flowing density is dependent on the particle shape, particle size, and particle size distribution of the powder. PUR powders prepared by dry milling in two roll mill and/or knife mill have also different free flowing densities. PUR powder originated from two roll mill exhibits density 218 g.dm^{-3} . PUR powder prepared by knife mill is characterized by density 53 g.dm^{-3} . Although the particle size measurement by laser granulometer showed very similar main particle size about 100 micrometers for methods of two roll mill and or knife mill their free flowing densities are very different. The main reason consist of different particle morphology as it is shown on Fig. 2. Compact, scale-shaped particles originated from two roll mill may be oriented more ordered than widely branched particles originated from knife mill. Free space among branched knife mill particles is much bigger than for smooth particles from two roll mill, then the free flowing density of knife mill powder is significantly lower.

Free flowing density of the sample from ball mill could not be measured. This sample was milled directly in the ambient of non-volatile polyol and the milled sample remained in the liquid state only.

Viscosity of polyurethane one-component adhesive (PUR prepolymer)

The main processing parameter is viscosity of the blend polyurethane adhesive and PUR powder in practise. Addition of micronized polymer with relatively large active surface to the adhesive will increase the mixture viscosity. Besides the particle size also the morphology of particles will play important role as it was outlined in SEM microscopy chapter and laser granulometer above. The target is to obtain the polyol with maximal possible PUR powder dosage, as it is point of any recycling. Exceptionally high mixture viscosity is unwelcomed. Viscosity curves of adhesives in relation to the PUR powder dosing are available in the Figure 5.

As it is visible, the viscosity of mixture with PUR powder from knife mill is extremely high for any practical use.

In comparison with this fact, the viscosity of mixtures with two-roll milled powder is much more acceptable. Main particle sizes of PUR powder originated from knife mill and or two roll mill are about 100 micrometers for both. Particle size distributions are also similar (see Fig. 3 above). In spite of this fact the viscosities of modified adhesives are very different (mainly at PUR powder dosage above 10%). The difference can be explained with different particle morphology (see Fig. 2 above). Importance of the branched particles geometry was discussed also in chapter *Measurement of free flowing density*. Influence of particle size and particle size distribution in PUR prepolymer on viscosity is based on the same principle as the sedimentation tendency of these powders in polyol (see Fig 4). Generally, the finer particles have stronger thickening effect however in our experiments the particle sizes of PUR powders from knife mill and two roll mill were similar about 100 micrometers, so this parameter does not play the principal role. PUR micro-milled powder by method of knife mill was excluded for next experiments due to extremely high blend viscosity. Obvious industrial adhesives for woodworking exhibit viscosity range between 8-20 Pa.s, exceptionally up to 30 Pa.s. For example, adhesive Jowapur 686.20 [32] has typical viscosity 10.5 Pa.s. Adhesive Loctite

Purbond HB S 309 Polyurethane Glue [34] has viscosity 20 Pa.s. Higher viscosity level complicates possible methods of the adhesive application. Of course, for viscosity over 200 Pa.s there is possible to use methods for pasty sealant application, suitable for small-area bonding. Sample of powder re-milled in ball mill was not used for mixing in adhesives, because the method of recycled product preparation is very long time consuming and impractical.

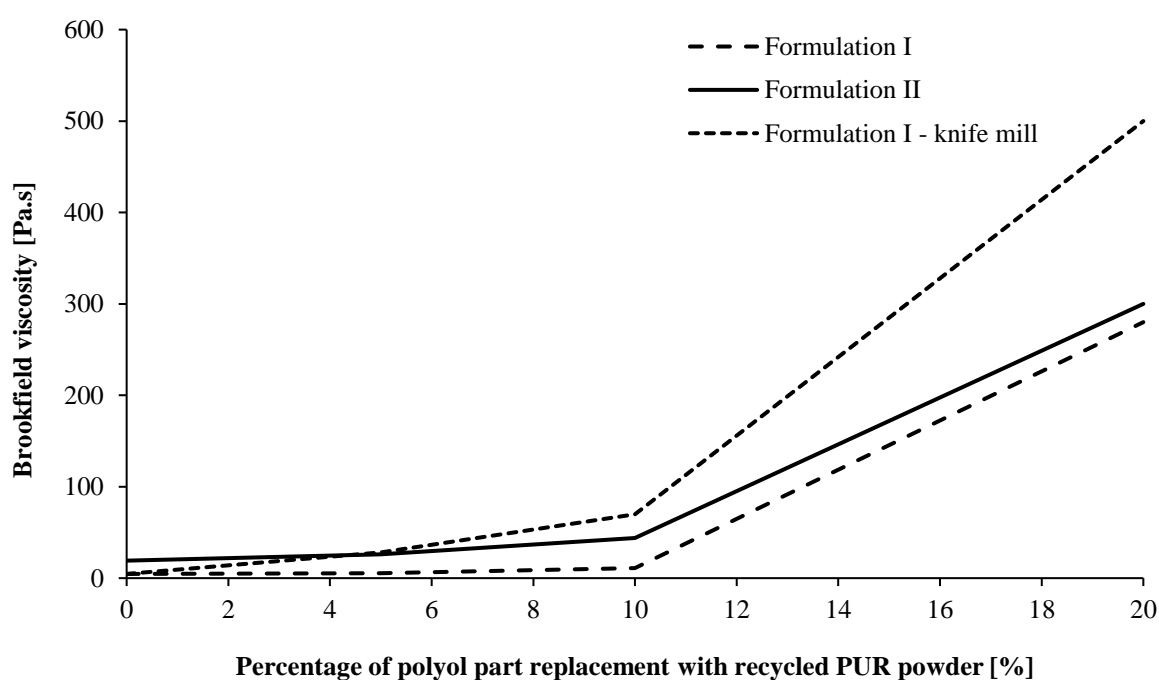


Fig. 5: Viscosity curve of polyurethane adhesives (prepolymers) containing PUR powder (two-roll mill and knife mill).

Reactivity of the modified polyol

Typical polyether polyol, such as Lupranol 1000/2, has pure hydroxyl reactivity. There is an assumption that micro-milled PUR powder will show also certain amine reactivity. For this reason the hydroxyl and amine numbers were evaluated for pure polyol

and for the model mixture with 0; 5; 10 or 20% of powder addition. The result is stated in the Table 2. All measurements were carried out twice.

Table 2: Influence of added PUR recycled powder on the polyol reactivity.

Sample	OH number [mg KOH.g ⁻¹]	NH number [mg KOH.g ⁻¹]	Water content [%]	Total OH+NH reactivity [mg KOH.g ⁻¹]
Virgin polyol (Lupranol 1000/2)	41.00±0.70	0.10±0.05	0.20±0.06	41.10
Virgin polyol + 5% by weight of rigid PUR foam powder	37.00±0.60	1.10±0.10	0.40±0.08	38.10
Virgin polyol + 10% by weight of rigid PUR foam powder	40.00±0.70	1.70±0.11	0.60±0.08	41.70
Virgin polyol + 20% by weight of rigid PUR	42.00±0.90	3.10±0.22	0.70±0.09	45.10

It is interesting to see that OH number was reduced with addition of PUR powder. It looks like “dilution” of polyol reactivity by PUR powder. On the other hand, the amine number was elevated from negligible value in pure polyol to value about 3 mg KOH.g⁻¹ in the mixture with 20% of recycled PUR content. Amine number value compensates partially the OH number decreasing. It means that PUR powder brings weak amine reactivity to the system. Because of adsorbed humidity on PUR powder surface the water content was elevated when PUR powder was added to the polyol. Water content partially distort the OH number values. The result also shows that during mechanical decomposition of the rigid PUR foam the bond C-N is weaker than bond C-O and the resulting amino- reactivity confirms this fact. It is in relation with the data cited in literature. Energy of bond C-O is 350 kJ.mol⁻¹, since for bond C-N it is 290 kJ.mol⁻¹ [35].

It is suggested in this study to calculate the total reactivity of the modified polyol by summation of the hydroxyl and amine number for this specific case if the modified polyol is suggested just for new polyurethane binders’ preparation. Both hydroxyl and amine groups have the same reactivity via active hydrogen with the isocyanate groups of polyisocyanate and they behave like the same reaction units with similar molecular weight. Although the reaction rates of OH and NH are different, the reaction may be realized on the both reactive groups by the same addition mechanism.

As known, amines catalyses the polyurethane reaction systems, so some acceleration of the crosslinking reaction may be observed.

Adhesive parameters

Adhesives prepared according to the formulations above mentioned were modified with PUR micro-milled powder by method of two-roll mill. Powder was used as secondary “polyol” replacing corresponding amount of the pure polyol. It means that the PUR powder was not used as filler but as chemically active component in the PUR adhesive system. Complete results are stated in the table 3. All measurements were done twice.

For evaluation of PUR powder effect in the adhesives following parameters were analysed: free film adhesive tensile strength of crosslinked adhesives, elongation of the free film at break and wood to wood shear tensile strength of bonded test pieces. Data are collected in the table 3 and Fig. 6 describe the influence of PUR powder additive on the properties of the prepolymers (Formulation I and Formulation II) in the liquid state and the properties of crosslinked adhesives.

Table 3: Mechanical properties of PUR adhesives modified with PUR powder.

Sample	Viscosity [Pa.s]	Free film tensile strength [MPa]	Free film elongation at break [%]	Wood/wood shear tensile strength [MPa]	Bond failure type
F I/0%	4.60	1.06±0.12	103.70±6.65	0.51±0.04	Cohesive
F I/5%	5.55	1.20±0.25	80.80±3.96	2.30±0.27	Cohesive
F I/10%	11.00	1.31±0.29	24.50±3.25	3.84±0.20	Cohesive
F I/20%	280.00	3.40±0.14	30.00±14.28	5.45±0.07	95% wood failure
F II/0%	19.15	0.84±0.37	16.90±1.70	2.74±0.13	Cohesive
F II/5%	26.20	0.52±0.07	13.30±0.42	4.61±0.08	10% wood

					failure
F II/10%	44.00	0.82±0.23	7.70±1.41	5.28±0.40	Cohesive
F II/20%	300.00	2.57±0.24	9.30±3.68	5.63±0.57	60% wood failure

Symbol F I represents “Formulation I”, F II represents “Formulation II”. Both with described polyol replacement with PUR powder in % (steps 0%, 5%, 10% and 20%)

The bond failure is defined as “cohesive” when the bond rupture is made in adhesive film volume without any destruction of bound material. Percentage of the wood failure is calculated as a quotient of the area of wood rupture over total bond area which is 4 cm² for all above mentioned bond testing. Because wood is natural inhomogeneous material, the wood failure may occur is the bond strength is higher than cohesive strength of the wood.

If the adhesive is used for wood bonding, it is very important to evaluate the shear bond strength. The growth of the bond strength with growing PUR powder dosage is visible in the Fig. 6.

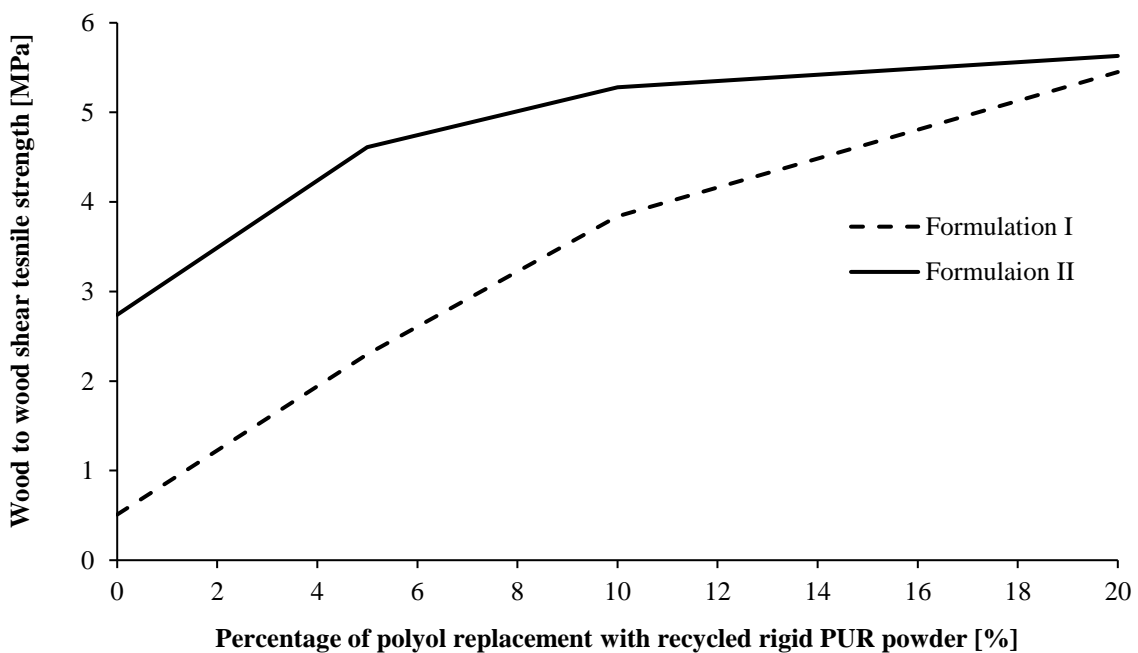


Fig. 6: Growth of the shear tensile strength with growing PUR powder content in the PUR adhesives (formulation I and II).

The adhesive formulation type I is dedicated to bonding of soft or flexible materials like polyurethane flexible foams, rubber crumb a flexible sandwich panels. Above mentioned method of adhesive modification by polyol part replacement with recycled PUR powder brings benefit of higher viscosity (suitable for low absorbing applications on porous substrates) and increased bond strength. Of course, the bond flexibility would be reduced as the free film elongation of the modified adhesive dropped down. High concentration of the active PUR powder filler (20% of polyol replacement) contributes to pasty consistency of the adhesive. For certain applications it may be a useful fact, namely for semi-flexible sealant manufacturing. Lower polyol replacement levels (5%, 10%) increase the viscosity only partially and almost linearly, as it is visible in the Fig. 12. The free film tensile strength of the Formulation I modified with 5 or 10% polyol replacement shows only minority changes compared with unmodified formulation. It may be explained like effect of chemically equivalent replacement of the polyol with the milled PUR powder. However for higher powder concentration (20% of polyol replacement) the intensive inter-particles interactions play the role and result probably to mechanical strengthening of the crosslinked adhesive film via rigid PUR particles. The same trend is visible also for the shear tensile bond strength for wood to wood joining. The effect of the bond strength improvement comes even with 5% of the polyol replacement and grows gradually also for 10 and 20% of replacements. Logically, the reverse trend is observed for the free film elongation. Addition of rigid PUR powder particles reduces of the free film flexibility significantly.

The formulation type II is suggested for rigid bond applications, for example wood construction elements bonding, production of the insulation sandwich panels made of wood

and rigid foams, particle wood panels, chipboards, plywood or veneering. This adhesive has relatively high viscosity also in its unmodified version. The polyol replacement with recycled PUR powder brings mainly improved bond strength, important for the complex durability and strength. Partial viscosity increasing at lower dosages (5% and 10% of the polyol replacement) is useful for reduction of the adhesive consumption and for better surface gaps and imperfectness levelling. Similarly like for Formulation I also here the viscosity growth is almost linear as function of the polyol replacement quantity. Dramatically increased viscosity at 20% level of the polyol replacement gives again pasty consistency (similar situation for Formulation I). Filling properties of the modified adhesive are also improved which is interesting for bonding of uneven or non-parallel surfaces. However the quantification of those effects is not matter of this study. The trends of the mechanical properties of the modified Formulation II are similar to behaviour of the Formulation I. It means that free film tensile strength demonstrates no growth for 5 and 10% polyol replacement and significant growing for 20% polyol replacement. Shear tensile strength of the bond wood to wood is influenced with polyol replacement via PUR powder significantly, mainly for 10 and 20% level of the replacement. Because the Formulation II creates relatively rigid crosslinked film also unmodified, the shear strength growth is not so remarkable compared to changes by Formulation I. Free film elongation for Formulation II is low due to the rigid character of the crosslinked adhesive film. This is why this parameter changes by polyol replacement are not important.

As it was shown on Fig. 4, the filled polyols before reaction with isocyanates have noticeable sedimentation tendency. It has several reasons. First, the polyurethane polymer density is generally higher than polyol density. The second, the particle size is quite high - maybe for nano-size the settling would be less significant. The third the particles have no surface stabilisation via anti-settling agents or dispersing agents creating repulsive electric

surface charge. For next adhesive development it could be an interesting challenge for optimisation.

Although the re-milling by ball-mill reduces the sedimentation tendency, it is not enough for in-can stability. The modified adhesive may be used just after the preparation, not after longer stay without time-to-time agitation.

4. CONCLUSIONS

Various milling methods of rigid PUR foam waste were studied. Selected method for following experiments is two-roll milling because the particle size is sufficiently small for maximal possible dosage and reactivity as well. Knife milling is very fast method, however it gives sharp edged powder with very strong thickening effect in liquid adhesive. It means that only minor amount of recycled PUR foam may be added to the adhesive and such recycling method loses its sense. The ball milling following the two roll milling is an impractical method for any practical use because of long-time consuming process and not so essential contribution to the better final result compared with simple two-roll milling.

Reactivity of the mixture polyol and PUR powder was evaluated by hydroxyl and amine number measurements. Because amine number in modified polyol has occurred, we assume that NH-CO bond in polyurethane chain is broken preferably by milling and brings amine reactivity to the adhesive system. No increasing of hydroxyl reactivity was observed by the polyol modification, however some hydroxyl reactivity fluctuation was caused by elevated water content in the polyol blend due to PUR powder hygroscopic character. Of course, the total reactivity is not modified significantly and may vary according to the PUR particle size and a composition of the original PUR polymer. Important is the fact that due to the certain surface reactivity the PUR powder can be bound in the adhesive system

chemically, not only by mechanical way. Then we can speak about polyol replacement with PUR powder.

Part of polyol was replaced with PUR micro-milled powder Viscosity of the modified adhesives and the mechanical properties of the bond were evaluated. Increasing of the PUR powder content in adhesives leads to the viscosity growth. Mainly at 20% dosage the viscosity becomes extremely high as result of intensive interaction between particles during adhesive mixing. For 20% polyol replacement we can speak more about physical filling the adhesive than about influence of chemical bonds. Similarly adhesive bond strength for wood to wood binding is increased by PUR powder addition; however the growth of strength with powder addition is not as steep as the viscosity growth. For lower dosage the PUR powder, i.e. 5% or 10% replacement of polyol, we can observe only slight properties modification and the PUR powder works really like a polyol replacement.

Adhesives modified by polyol replacement with PUR recycled powder show noticeable settling tendency; this tendency is lower for finely re-milled powder. This effect limits the use of modified adhesive for immediate use after blending or after stirring shortly before use.

Experiments carried out in this study proved that micro-milled rigid PUR foam waste can works as the active filler for one-component polyurethane adhesive. The limit dosing is defined by viscosity of the adhesive. We can recommend the polyol replacement of maximally 20% for any practical uses. The 10% polyol replacement can be taken as trouble-free dosing method.

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