

Research on Influence of Polyurethane Adhesive Modified by Polyurethane Filler Based on Recyclate

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An adhesive bonding technology represents a prospective method of diverse materials connecting. Polyurethane (PUR) adhesives namely are used in an area of the adhesive bonding of wood and cellulose - based products. They gradually substitute formaldehyde-based adhesives. A higher reactivity of isocyanates with any compound having moving hydrogen namely, i.e. e.g. water, etc. is a significant disadvantage. An elimination of this negative factor is possible by adding a filler, e.g. PUR recyclate – based. The aim of the research is to determine an adhesive bond strength of the PUR adhesive modified with microparticles of crushed PUR foam (waste from a building – an insulation material). Improving of a tensile lap-shear strength and a material recycling of the PUR foam are expected aims. Also a reduction of the adhesive price is a secondary output. Results of mechanical tests were supported by conclusions from a scanning electron microscopy (SEM) analysis with an aim to evaluate the interaction between the adhesive and the recycled filler. A diffusion of the adhesive into a wooden surface would occur at the wooden test samples and so mechanical properties of the modified adhesive would not be determined. This reason led to the research on the modification of the PUR adhesives LEAR D4, PP-6a17 and PP-7a within the adhesive bonded metal bond (a structural carbon steel S235J0). The research results proved a positive influence of the modification of the PUR adhesive with the microparticles of the PUR recyclate. The tensile lap-shear strength was increased. Results of SEM analysis proved a good wettability.

Keywords: Cyclic degradation, Elongation at break, SEM, Strength, Tensile test

1 Introduction

The adhesive bonding technology represents a rapidly developing method of diverse materials connecting at the present [1]. A huge offer of adhesives is a great advantage of this technology. A low peeling resistance and a technological difficulty of a uniform application of the adhesive to the adherent are probably the most significant disadvantages. The main aim of the adhesive bonding technology is a creation of such bond which provides maximum strength and quality of the adhesive bond at minimum costs. Following points are recommended to follow for the creation of such bond:

- To adequately modify and clean the adherent surface before the application of the adhesive
- To suitably choose the adhesive type corresponding to application conditions
- To ensure the uniformity and a constant layer of the adhesive
- To take into regard external factors which can influence the adhesive bond [2].

Many researches deal with possibilities how to increase the adhesive bond strength [3]. They are e.g. composite – based materials where fibres are used as a reinforcement or particles are used as the filler [4]. These ways determine contemporary trend of the adhesive modification not only in terms of mechanical properties improving, but also for a purpose of the adhesive price reduction [5, 6].

A transfer of a stress between a matrix and particles influences the adhesive bond strength. As far as the parti-

cles are well cohesive, the stress can be effectively transferred from the matrix to the particles which distinctly increases the adhesive bond strength [7, 8].

It is necessary to emphasize that the improvement of mechanical properties of particle composites depends on suitably chosen type of the filler, the particle size and their concentration [9]. Generally it is possible to say that the mechanical properties of these composites depend on the particle size, a wettability of the adhesive and a way of the particle applying [10]. The wettability of the adhesive is a fundamental factor influencing an adhesive bond strength [11].

PUR – based adhesives are used when adhesive bonding the wood and cellulose products above all [12] and they gradually substitute formaldehyde – based adhesives. High elasticity of the bond resisting to a dynamic loading, a resistance to increased moisture and weather effects are the advantages of these adhesives comparing with other industrially used adhesives. Higher reactivity of isocyanates with any compound having a mobile hydrogen (water, alcohol, acid or amine) is a potential disadvantage of PUR – based adhesives [13].

Some scientific teams dealt with a modification of PUR adhesives and their mechanical properties [12, 14, 15, 16, 17]. A modification of PUR adhesives with PUR recyclate can eliminate a creation of the bond with free hydrogen and so optimize a process of closure and hardening due to a possibility to regulate a portion of the recyclate.

The aim of the research is to determine the tensile lap-shear strength of the PUR adhesive modified with microparticles of crushed PUR foam (waste from a building – an insulation material). Improving of the tensile lap-shear strength and a material recycling of the PUR foam are

expected aims. Also a reduction of the adhesive price is a secondary output.

2 Material and Methods

The PUR recyclate (powder) of the particle size smaller than 50 μm was used for the research on the modification of PUR adhesives. A heterogeneous shape and size of the PUR recyclate particle subjected to SEM analysis can be seen in Fig. 1. The recyclate was produced by

PUR foam crushing in a two – roll crusher. A reduction of particles and a disruption of polymeric bonds occur during a milling. So it comes to a physical depolymerization. This foam was used as a heat insulation into building sandwich panels and it is specified as rigid PUR foam with closed pores, a blowing agent cyclopentane, 4,4 – diphenylmethane diisocyanate and polyisocyanurate based polymer, adicly reacted with polyether polyols with a functionality 3 – 5 and default molecular mass around 500 – 1000 g/mol.

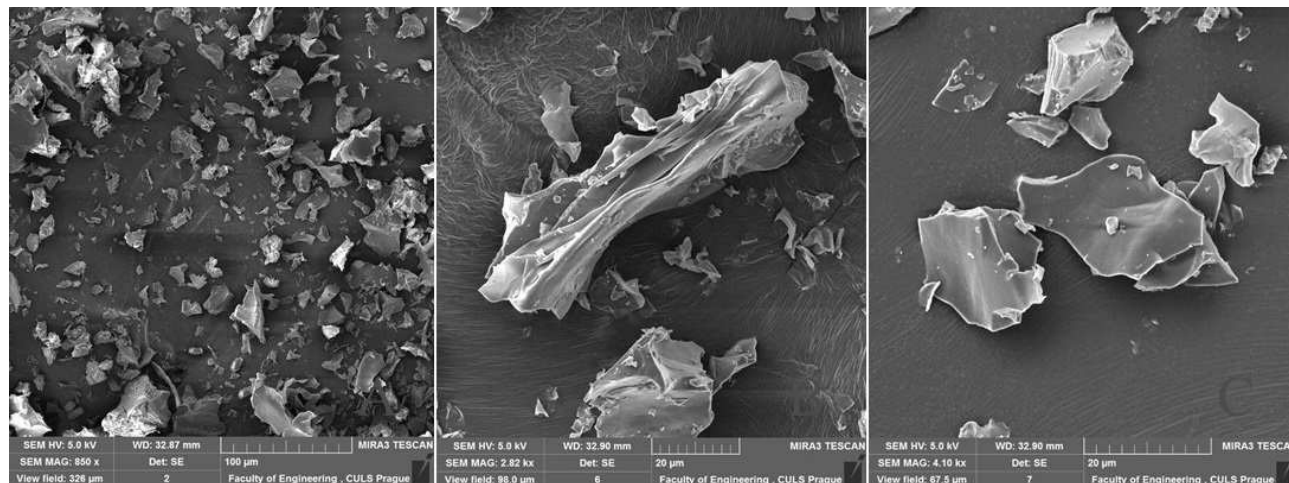


Fig. 1 Particles of PUR recyclate: A: MAG 850 x, B: 2.82 kx, C: 4.10 kx

Three types of one – component PUR adhesives were used. A commercially sold adhesive LEAR D4, marked as R, with a specification for the adhesive bonding of wood, namely difficult to adhesive bonded joinery. Further, the adhesive PP-6a17, with a mark A, specified as one – component prepolymer of an excess of aromatic polyisocyanate based on MDI (4,4 – diphenylmethane diisocyanate) and polyether polyol with a functionality 2 – 3 and a default molecular mass 1000 – 2000 g/mol. The adhesive PP-7a, with a mark B, specified as one – component prepolymer of an excess of aromatic polyisocyanate based on MDI (4,4 – diphenylmethane diisocyanate) and polyether polyol with a functionality 2 – 3 and a default molecular mass 2000 – 3000 g/mol.

Adhesive bonds were prepared according to the Czech standard CSN EN 1465. A structural carbon steel S235J0 was used for the research. Dimensions of used adherents corresponded to above mentioned standard ($100 \pm 0.25 \times 25 \pm 0.25 \times 1.5 \pm 0.1$ mm) and an overlapping size of adherents too (12.5 ± 0.25 mm). A surface of adherents was mechanically and chemically treated. The mechanical treatment of the adherent consisted in a grit blasting of the area for the adhesive application. An abrasivum Garnet MESH 50 was used. The chemical treatment consisted in a cleaning (degreasing) of the area for the adhesive in a bath of acetone.

Adhesives, above mentioned, were modified with the PUR recyclate in a weight concentrations 0 %, 5 %, 10 %, 15 %, 20 %, 25 % and 30 %. The concentration 30 % was determined as a final because higher concentrations caused a surfeit of the adhesive and it was not possible to apply them on the adhesive bonded material.

The adhesive bonding technology itself consisted in

the application of the modified adhesive on one adherent, dipping the applying layer into the water and overlapping of the layer with second adherent. This process was determined on a base of a preparative research which aimed to determine a suitable treatment of the adhesive bonded surface. Adhesive bonds were loaded with a weight 750 g and left for 48 hours at a temperature 21 ± 2 °C and a moisture 62 ± 5 %.

The tensile strength test was performed based on the standard CSN EN 1465 in a universal testing machine LABTest 5.50ST with a sensing unit AST type KAF 50 kN and an evaluating software Test&Motion. A deformation speed was set as $1 \text{ mm} \cdot \text{min}^{-1}$. The deformation speed was chosen with a regard to a destruction time of the adhesive bond prescribed by the standard 65 ± 25 s. A failure type of the adhesive bond was determined according to ISO 10365.

A mutual interaction between the adhesive and the recyclate was investigated by means of SEM analysis. SEM MIRA 3 TESCAN with an accelerating voltage (HV) 5 kV was used for this analysis. Samples were dusted with gold by means of a device Quorum Q150R ES – Sputtering Deposition Rate. Measured data were statistically evaluated in a program STATISTICA, namely by means of the statistical method Anova F – test. A hypothesis H_0 indicates that there is no statistically significant difference ($p > 0.05$) among tested data. A hypothesis H_1 denies the hypothesis H_0 and it presents that there is a statistically significant difference among tested data ($p < 0.05$).

3 Results and discussion

A dimension of crushed PUR waste based microparticles is obvious from a histogram presented in Fig. 2 which

shows their distribution according to the size. The main sizes of the microparticles were in the interval from 5 to 15 μm (100 %). An average dimension of the microparticle fraction was determined as $13.84 \pm 10.34 \mu\text{m}$. The research proved that the results are in the interval with the size of particles declared by a producer, i.e. to 50 μm .

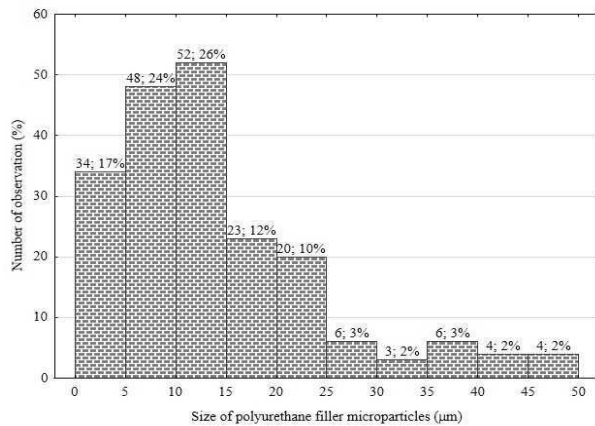


Fig. 2 Histogram of frequency of microparticle PUR waste based filler used in polymer composite adhesive

It is obvious from the results presented in Fig. 3 that a positive influence of the modification of the PUR adhesive by microparticles of the waste PUR gained by the crushing showed itself. The strength of the adhesive bond was increased up of 132.1 % at the composite PUR adhesive R comparing with the PUR adhesive without the filler. Analogous trend of the adhesive bond strength results was found at the adhesive A. The strength was increased up of 347.6 % by the modification of the filler. The adhesive bond strength was increased with increasing weight concentration of the microparticle filler at both adhesives, namely to a marginal concentration 30 wt. %. The adhesive bond strength was also increased at the adhesive B owing to the modification of the PUR adhesive, up of 139.4 %. This increase was to 20 wt. %. Subsequently, the fall occurred. This fall was caused by a different viscosity of the adhesive and connected surfact of

the PUR adhesive with the filler which led to an adhesive failure inside the layer of the adhesive.

It is possible to say in terms of the statistical testing of a dependence of the adhesive bond strength on the weight concentration of the filler that the concentrations are non-homogeneous groups, i.e. that there is a statistically significant difference among tested parameters. The hypothesis H_0 was not certified, i.e. there is the difference among single tested parameters in the significance level 0.05 ($p = 0.0000$).

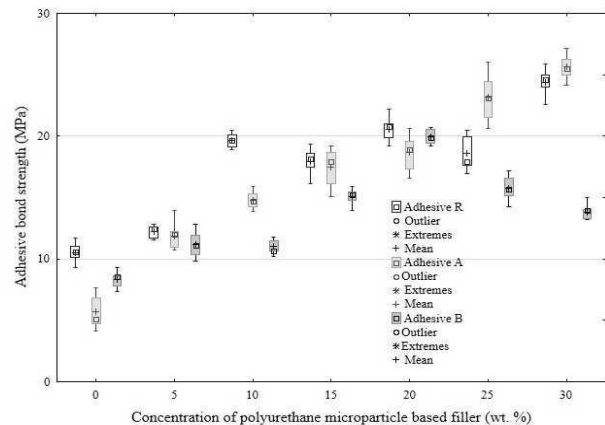


Fig. 3 Dependence of adhesive bond strength on filler concentration

SEM observation of the fracture surface of the adhesive bond and the composite layer of the adhesive was performed within the research. An overview fracture surface is evident in Fig. 4 to 7 A, more detailed view is in part B.

PUR adhesives showed an adhesive - cohesive type of the adhesive bonded material failure (fig. 4). The fracture surface did not change by the modifications with the microparticles of the waste PUR (fig. 5). However, the cohesive representation of the fracture surface was significantly increased by adding the filler. Highlighted adhesive and cohesive parts of the fracture surface are visible in Fig. 4 and 5.

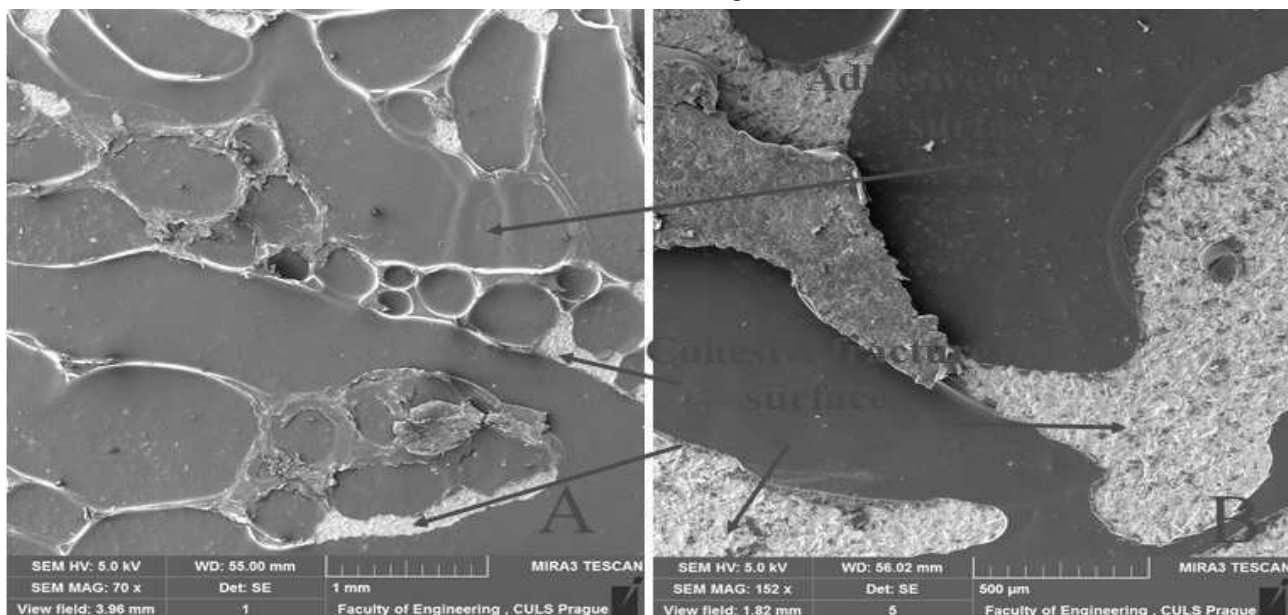


Fig. 4 Fracture surface of adhesive – cohesive type of adhesive bond with PUR adhesive: A: MAG 70 x, B: MAG 152 x

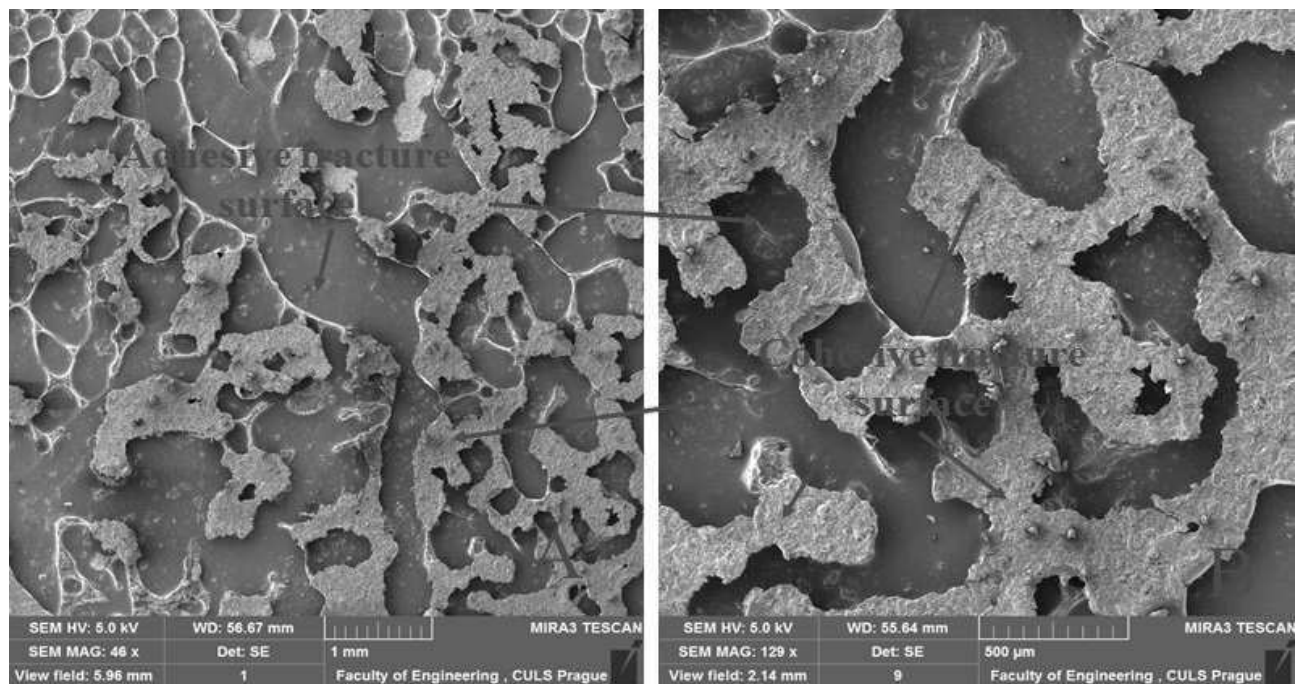


Fig. 5 Fracture surface of adhesive – cohesive type of adhesive bond with PUR adhesive with 10 wt. % of filler on base of PUR microparticles: A: MAG 46 x, B: MAG 129 x

Fig. 6 represents the fracture surface of the PUR adhesive from which its typical porous structure is evident. The PUR adhesive modified with microparticles of the PUR filler is obvious from Fig. 7. A strong interaction between the filler and the adhesive is evident from Fig. 7.

It can be presumed about a good wettability. It was ascertained by SEM analysis that the porosity was reduced by adding the filler which had a good interaction with the adhesive (Fig. 7). The porosity belongs among important factors of composite systems negatively influencing their mechanical properties [18].

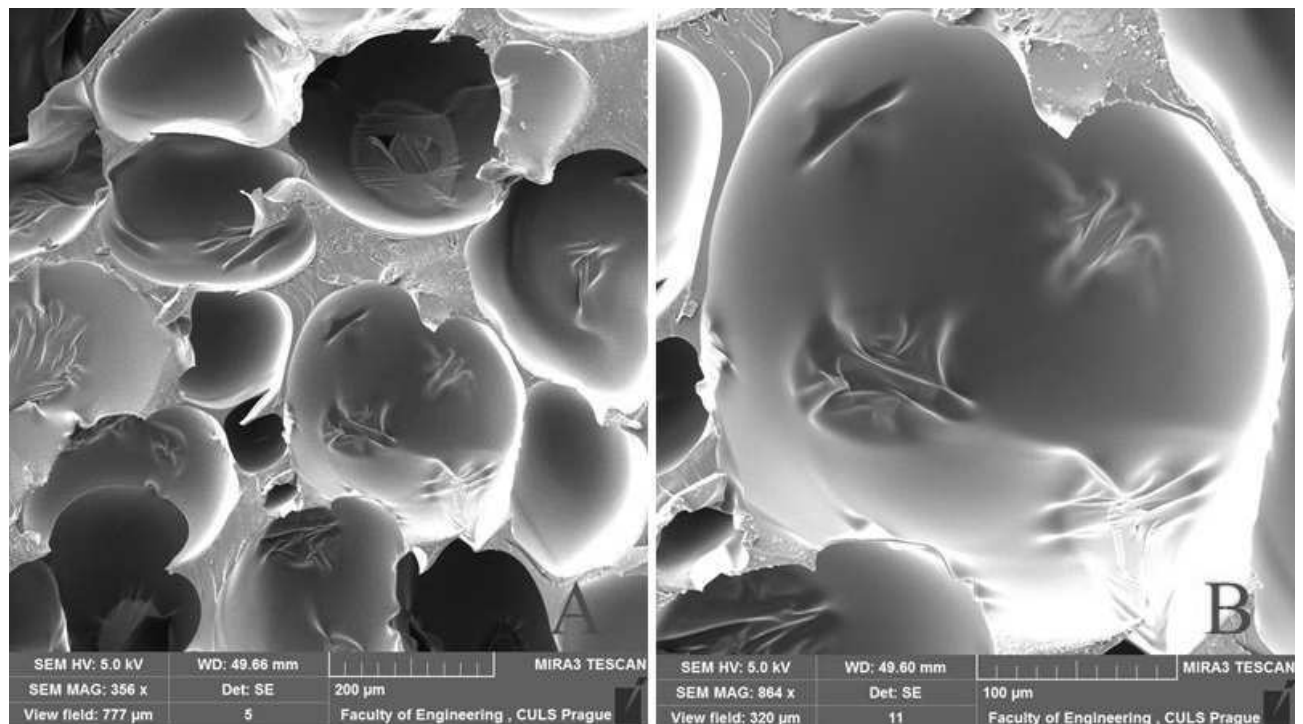


Fig. 6 SEM micrographs of fracture surfaces of PUR adhesive: A: MAG 356 x, B: 864 x.

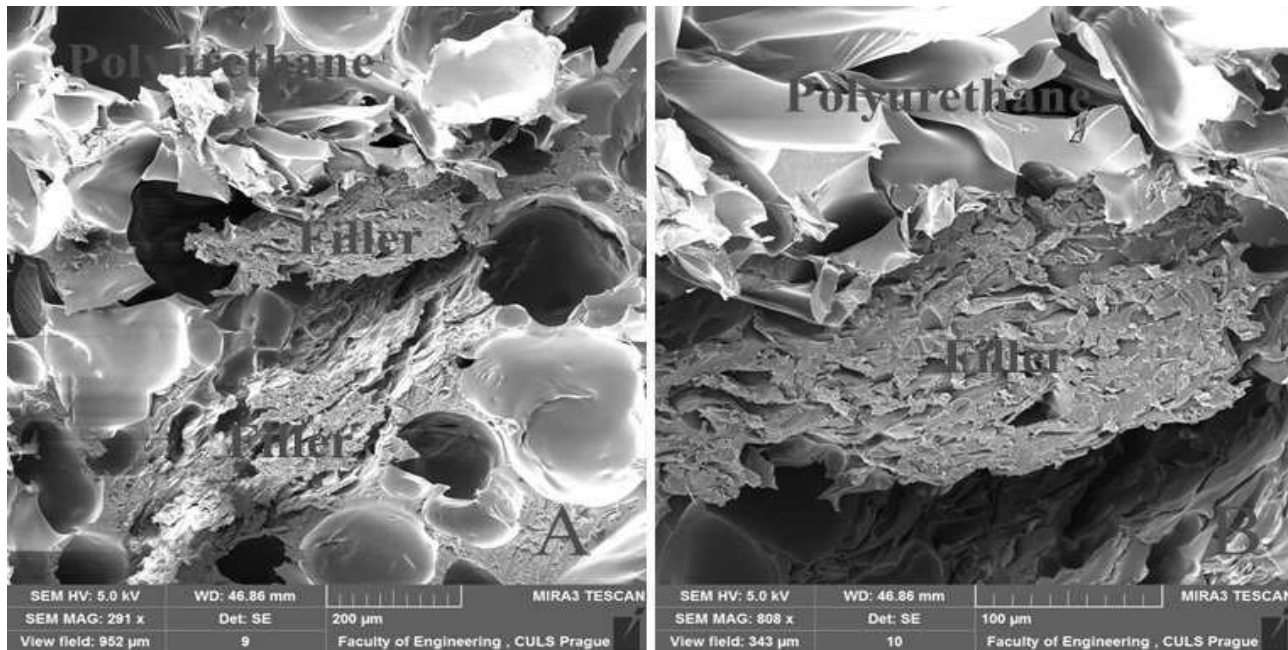


Fig. 7 SEM micrographs of fracture surfaces of PUR adhesive with 10 wt. % of filler on base of PUR microparticles: A: MAG 291 x, B: 808 x.

The research results certified conclusions stated in a similar research focused on a modification of PUR adhesives. The tensile strength was increasing by adding the filler up to the concentration 10 wt. % [14].

4 Conclusions

The research describes a possible utilization of microparticles of crushed PUR, i.e. the secondary raw material from the recylation process, as the filler in the PUR adhesive. A material utilization of the waste is essential for the environment. The filler in the form of PUR microparticles to the dimension 50 μm can be effectively used in the area of fillers into tested PUR adhesives. The modification of the PUR adhesive with waste crushed PUR microparticles showed itself in a positive way on the adhesive bond strength. The considerable increase of the adhesive bond strength at all three PUR adhesive occurred, however, to different filler concentrations. The PUR adhesive and the filler were of good mutual wettability. Also, the porosity of the adhesive was decreased which leads to the adhesive bond strength increase.

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