

Influence of Using Recycled Polyurethane Particles as a Filler on Properties of Polyurethane Adhesives for Gluing of Wood

Štěpán Hýsek,^{a,*} Přemysl Šedivka,^a Martin Böhm,^a Ondřej Schönfelder,^b and Rudolf Beran^c

Fillers can greatly affect the properties of adhesives, and this research aimed at enhancing the performance of adhesives by using different concentrations of fillers. This paper describes the influence of using recycled polyurethane particles (powder of particle size from 10 µm to 50 µm) as a filler on some properties of polyurethane adhesives for the gluing of wood. Two kinds of one-component, moisture-curing polyurethane adhesives were used. The observed properties were the contact angle between the wood and adhesive droplet, and the strength of bonded joints (shear strength). From the results, it was concluded that the contact angle increased with an increase in filler (in the entire observed range from 0% to 15% filler). The content of filler also affected the strength of bonded joints and their thermal stability. The strength of bonded joints decreased with an increase in filler content when samples were conditioned in cold water. However, the strength of bonded joints increased with an increase in filler content when samples were boiled in water.

Keywords: Adhesive; Polyurethane; Recycled foam; Wood; Contact angle; Strength of joints

Contact information: a: Department of Wood Products and Constructions, Faculty of Forestry and Wood Sciences, The Czech University of Life Sciences Prague, Kamycka 129, Prague 165 21, Czech Republic; b: Department of Wood Processing, Faculty of Forestry and Wood Sciences, The Czech University of Life Sciences Prague, Kamycka 129, Prague 165 21, Czech Republic; c: Faculty of Chemical Technology, University of Pardubice, Studentská 57, 532 10 Pardubice, Czech Republic;

* Corresponding author: hyseks@fld.czu.cz

INTRODUCTION

The use of polyurethane adhesives in many industrial fields is becoming increasingly common. Their range of application includes not only the construction, automotive, and wood processing industries, but also the manufacturing of wind turbines and aircrafts (Desai *et al.* 2003b; Patel *et al.* 2009; Clerc *et al.* 2017; Najib *et al.* 2017). Because polyurethane adhesives cure without the need to add a curing agent, they are characterised by an easier reticulation method than epoxy adhesives, leading to reduced production costs. Another advantage of polyurethane adhesives is the high flexibility of the bond, which contributes to resistance to dynamic strain and good shock-absorbing properties (Clauß *et al.* 2011; Najib *et al.* 2017).

For many years, research has endeavoured to develop properties of polyurethane adhesives for various application areas by combining different modifications (Deka and Karak 2009; Patel *et al.* 2009). The physical and chemical properties of adhesives can be adjusted by changing the components comprising the adhesive mixture, which are added during prepolymer synthesis (Desai *et al.* 2003a; Deka and Karak 2009; Volkova *et al.* 2013). Besides plasticisers, organic solvents, wetting agents, rheological agents, and

catalysers, fillers are commonly used as well. Fillers are used for various purposes, and the replacement of a more expensive polymer is but one of the many reasons (Sedliačik *et al.* 2006; Šmidriaková and Kollár 2010). In addition, fillers can improve the mechanical properties, workability, thermal and dimensional stability, and flame retardation of polymers (Li *et al.* 2008; Clauß *et al.* 2012). Various types of filler materials are used for improvement of the aforesaid properties in adhesives.

Inorganic filler materials include silicon, calcium, kaolin, chalk, *etc.* These materials have been studied in combination with various types of adhesives, such as phenol-formaldehyde, urea-formaldehyde, and epoxy adhesives (Clauß *et al.* 2011, 2012). Modification of polyurethane adhesives using organic fillers can be achieved by adding plant- or animal-based polymers to factory-made adhesive mixtures (Šmidriaková and Kollár 2010). Another solution is the addition of polyurethane (PUR) powder and polyurethane dispersion (Clauß *et al.* 2012). Mansouri and Pizzi (2007) studied the addition of particles of a PUR fraction to urea-formaldehyde and phenol-formaldehyde adhesives. Their research indicates that addition of polyurethane particles to the adhesive mixture significantly improves the physical properties of the adhesive and its water resistance. Another possible type of modification used currently is the modification of adhesive polymers using nanotechnologies (Dodiuk *et al.* 2006; Deka and Karak 2009).

The goal of this research project was to modify a polyurethane adhesive for the gluing of wood using a powder made of recycled polyurethane foam. The use of the powder as a filler in a polyurethane adhesive can considerably modify the base polyurethane. Therefore, this approach may provide unique combinations of properties, and reduce the costs of input materials in polyurethane manufacturing through utilization of waste.

EXPERIMENTAL

Materials

Two kinds of one-component (1C), moisture-curing, polyurethane adhesives were formulated: PUR01, which was made of polyether polyol with an initial molar mass of 2000 g/mol to 3000 g/mol (405 g) + catalyst (0.8 g) + polyisocyanate based on 4,4,-diphenylmethan-diisocyanate (620 g) + UV-stabilizers (10.3 g), and PUR02, which was made of polyether polyol with an initial molar mass of 1000 g/mol to 2000 g/mol (405 g) + catalyst (0.5 g) + polyisocyanate based on 4,4,-difenylnmethandiisocyanate (540 g). The recycled polyurethane foam was used as a filler to modify the polyurethane adhesives. The recycled foam was powder from PUR/PIR (combination of polyurethane and polyisocyanurate) foam and contained particles of dimensions from lower than 50 µm (see Fig. 2). Micro-milling of foam on a two-cylinder grinder was used to produce the powder from rigid PUR/PIR foam (utilized as heat insulation in civil engineering) with a closed cell structure. The initial molar mass of PUR/PIR foam was 500 g/mol to 1000 g/mol. The powder was mixed with the adhesives using weight powder ratios of 5%, 10%, and 15%, with 0% as a reference. All of the chemicals were supplied by STACHEMA CZ s.r.o. (Kolín, Czech Republic). Beech wood (*Fagus sylvatica*) obtained from the Central Bohemian Region, Czech Republic, was used to produce samples for the determination of strength of bonded joints. Beech wood with straight graining and a nominal density (700 kg/m³ ± 50 kg/m³) was selected. The angle between the tree rings and the bonded surface was between 30° and 90°.

Methods

The structure of the raw and modified adhesives was characterized using a MIRA 3 electron microscope (Tescan Orsay Holding, Brno, Czech Republic), with a secondary electron detector operated at 15 kV acceleration voltage.

Contact angle analysis is widely used to characterize the interaction between liquid and solid materials (Walinder and Ström 2001; Aydin 2004). To determine the wetting properties of the modified adhesives, the contact angle of the adhesives and a wood surface (planned radial beech wood) was measured using a Krüss DSA 30E goniometer (Krüss GmbH, Hamburg, Germany). The static contact angle was measured and 30 measurements were taken for each adhesive modification type. To minimize the influence of variation in the wood surface, five wood samples for each adhesive modification type were used, and on each sample, six droplets were deposited. The volume of the resin droplet was 10 μL and a measurement was made 5 s after the deposition.

Preparation of test specimens, measurements of the strength of bonded joints, and an evaluation of the results were conducted in accordance with the standards EN 204 (2001) and EN 205 (2003). Test specimens were manufactured according to Fig. 1 from beech wood, which was air-conditioned at 20 $^{\circ}\text{C}$ with a relative humidity (RH) of 65%. The adhesive weight was 160 g/m^2 to 180 g/m^2 . Then, 60 test specimens (2 types of adhesives \times 4 degrees of powder content \times 10 test samples) were produced with test procedure number 1, 60 test specimens were produced with test procedure number 2, and 60 test specimens were produced with test procedure number 3.

The first test was conducted 7 days after bonding (test sequence number 1, further marked as a1), and the specimens were air-conditioned at 20 $^{\circ}\text{C}$ with a relative humidity (RH) of 65%.

After 7 days in standard conditions, specimens from the second test group were immersed for 4 days in water at 20 $^{\circ}\text{C} \pm 5^{\circ}\text{C}$, and then immediately tested (test sequence number 2, further marked as a2).

The third test was conducted in such a way that after 7 days the samples were immersed for 6 h in boiling water and then placed in water at 20 $^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 2 h, and then immediately tested (test sequence number 3, further marked as a3). These three tests were performed for each adhesive combination.

The shear test was performed using a TIRAtest 285 E222 universal testing machine (TIRA GmbH, Schalkau, Germany). The specimen was strained with a tensile force until breach, and the greatest exerted force, F_{max} , was recorded. The speed of the loading was constant at 6 m/min as required by EN 205 (2003).

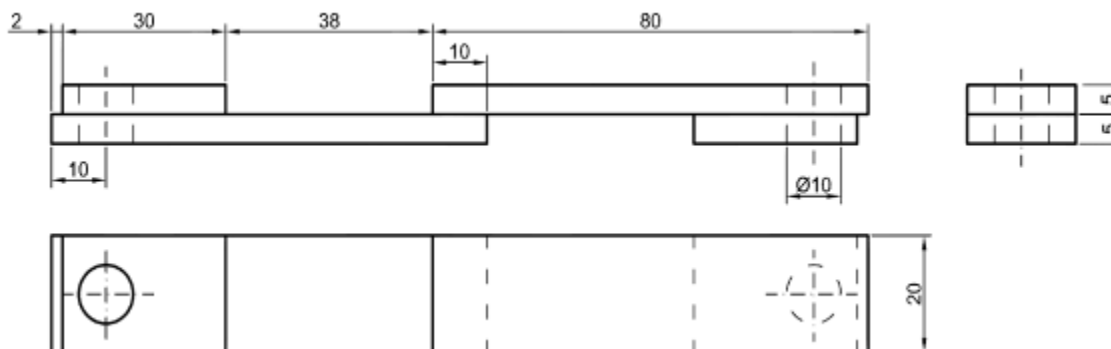


Fig. 1. Diagram of the lapped test sample

Expression of results

The strength of the bonded joint (τ ; N/mm²) was calculated using the following formula,

$$\tau = \frac{F_{\max}}{l_2 \times b} \quad (1)$$

where F_{\max} is the greatest exerted force (N), l_2 is the length of the bonded test surface (mm), and b is the width of the bonded test surface (mm).

A one-way analysis of variance (ANOVA) was used for statistical data evaluation. The post-hoc Tukey (HSD) test was employed to determine the significant differences between group means. Computations were conducted using Statistical12 software (StatSoft CR s.r.o., Prague, Czech Republic). A significance level of $\alpha = 0.05$ was selected.

RESULTS AND DISCUSSION

Figure 2 depicts a scanning electron microscope (SEM) picture of a PUR/PIR powder, and Fig. 3 depicts the surfaces of hardened PUR02 and the surface of hardened PUR02 modified by the PUR/PIR powder. In Fig. 2, one can see that particle dimensions of used filler were higher, than in previous studies (Dodiuk *et al.* 2006; Clauß *et al.* 2012). Therefore it was expected that used powder would behave as inert filler. Figure 3 shows typical changes in structure of modified adhesives (Clauß *et al.* 2012); these changes are visible not only on the cross section, but also on the surface. It can be seen that there was a difference between the reference adhesive and modified adhesive. The adhesives modified with powder had a rougher surface that was caused by the powder particles.

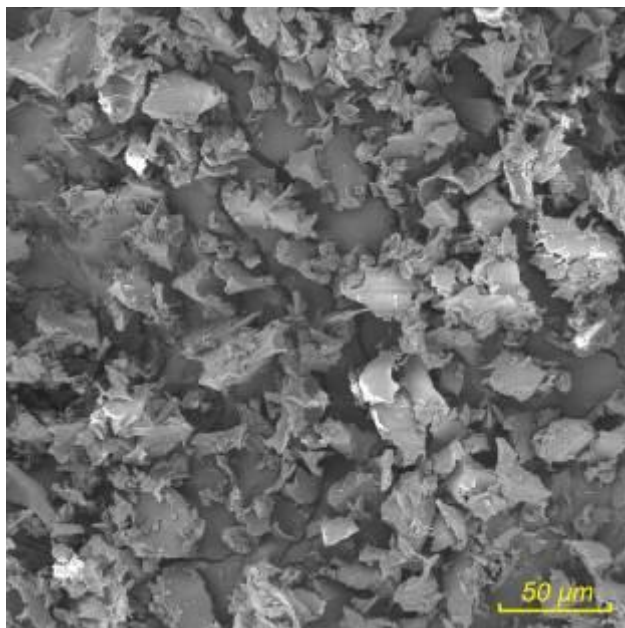


Fig. 2. SEM image of polyurethane powder

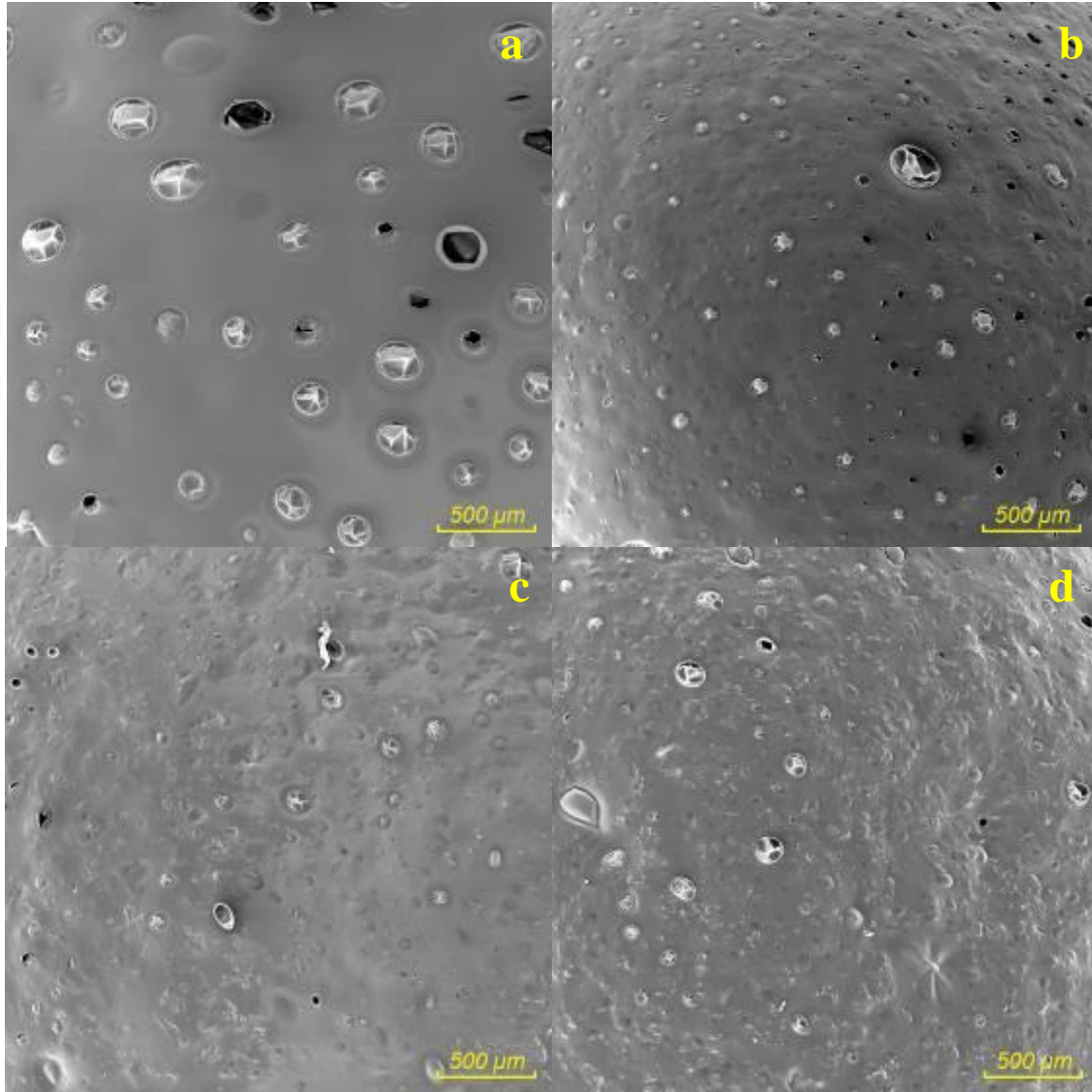


Fig. 3. Surface of hardened PUR02 without powder (a), hardened PUR02 with 5% powder (b), hardened PUR02 with 10% powder (c), and hardened PUR02 with 15% powder (d)

Figure 4 shows the results from an analysis of variance of the measured contact angles. The appropriate statistical significances of the differences are stated in Table 1. As shown, for both kinds of polyurethane adhesives the contact angle increased with an increase in powder content, within the entire interval of powder content of 0% to 15%. However, the particular increments of the contact angle decreased with an increase in powder content. Fillers have a significant effect on viscosity of modified adhesives (Benhadjala *et al.* 2015; Ruanpan and Manuspiya 2018), which affect contact angle as well. Since the increasing viscosity and adhesive contact angle is an undesirable effect, further decreasing of filler's particle dimensions could lead to modified adhesive with lower contact angle between wood and adhesive (Benhadjala *et al.* 2015).

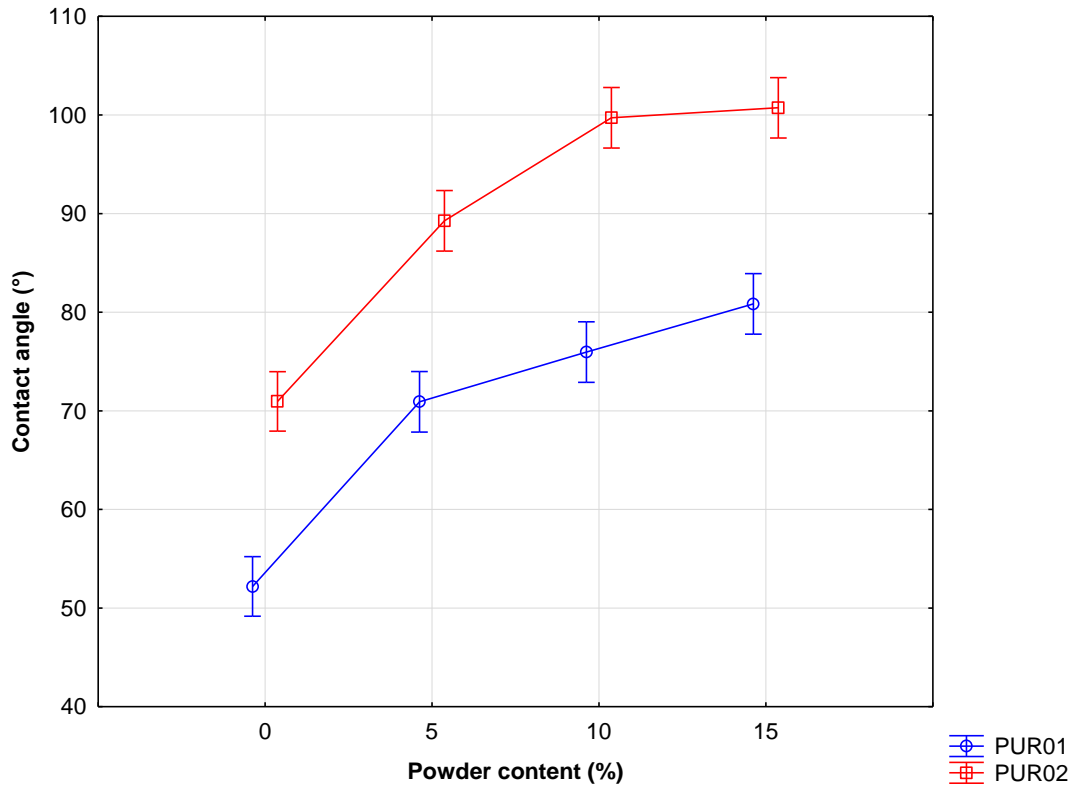


Fig. 4. Effect of powder content and adhesive type on contact angle

Table 1. Statistical Significance of Differences in Fig. 2 (According to Tukey Test)

Powder Content (%)		0	0	5	5	10	10	15	15
Powder Content	Adhesive Type	PUR01	PUR02	PUR01	PUR02	PUR01	PUR02	PUR01	PUR02
0	PUR01		s.	s.	s.	s.	s.	s.	s.
0	PUR02	s.		n.s.	s.	n.s.	s.	s.	s.
5	PUR01	s.	n.s.		s.	n.s.	s.	s.	s.
5	PUR02	s.	s.	s.		s.	s.	s.	s.
10	PUR01	s.	n.s.	n.s.	s.		s.	n.s.	s.
10	PUR02	s.	s.	s.	s.	s.		s.	n.s.
15	PUR01	s.	s.	s.	s.	n.s.	s.		s.
15	PUR02	s.	s.	s.	s.	s.	n.s.	s.	

s.- significant; n.s.- not significant

Figure 5, where a three-factor analysis of variance is depicted, shows the influence of the strength of joints (shear strength) on powder content, adhesive type, and conditions. As shown, the powder content affected the strength of joints. By conditioning under laboratory conditions (a1), the greatest shear strength was shown by the glue joints with 10% powder, and the effect of powder content on the strength of joints was unclear. By conditioning in water (a2), the strength of joints decreased with an increase in powder content. Finally, by conditioning in boiling water (a3), the addition of PUR/PIR powder increased the average values of the strength of joints, and it seemed that the optimum level was a 5% powder content. By hot water conditioning (a3) the addition of powder (5% ratio)

increased the shear strength from 0.7 MPa to 1.7 MPa for PUR01, resp. from 0.7 MPa to 2.4 MPa for PUR02. The increase of thermal stability of 1C PUR adhesives was also reached by addition of chalk as filler (Clauß *et al.* 2011); however in this study higher shear strength of bonded joints was reached.

From these results, it can be concluded that boiling water rapidly decreased the strength of bonded joints; however, the modification of PUR adhesives with PUR/PIR powder increased the thermal stability of bonded joints. In contrast, the resistance to cold water decreased with increase of powder content (Fig. 4). Due to the effect of higher temperature, which caused better crosslinking of reactive groups, the adhesive was hardened more (Clauß *et al.* 2011). Recycled foam has a high specific surface area of particles, and due to physical depolymerisation is the particle surface polar and contains functional groups (hydroxy- and amino-). The higher temperature caused degradation of steric barriers and thus additional reactions of functional groups with isocyanate groups of adhesive. This effect indicated that the PUR/PIR powder performed partly as an inert filler and partly as a catalyst. In general, the strength of joints was low; the level of 10 MPa (performance requirement for one component polyurethane for load-bearing timber structures according EN 15425 (2017) for conditioning a1) was reached in only two cases – PUR02 via conditioning type a1 and with powder content 0% and 10%. The performance requirement for conditioning a2 and a3, which is according EN 15425 (2017) 6 MPa, was not reached by any variant. When the results from the contact angle analysis were compared with the results of shear strength, the contact angle between the adhesive and wood surface for all levels of powder content was higher for PUR02. However, the shear strength of bonded joints with PUR02 was higher in all cases except one. The adhesive with lower wetting of the wood surface reached higher values of shear strength in these experiments; however, the wetting ability of an adhesive is not the only adhesive characteristic that affects the strength of bonded joints (Okkonen and River 1988; Banea and Silva 2009; Custódio *et al.* 2009; Moghadamzadeh *et al.* 2011; Budhe *et al.* 2015). In this case, a different adhesive formulation probably affected the results (Banea and Silva 2009; da Silva *et al.* 2009). Moreover, there was a big difference between the adhesives in conditioning type a1, the differences decreased when the bonds were soaked in water and boiling water.

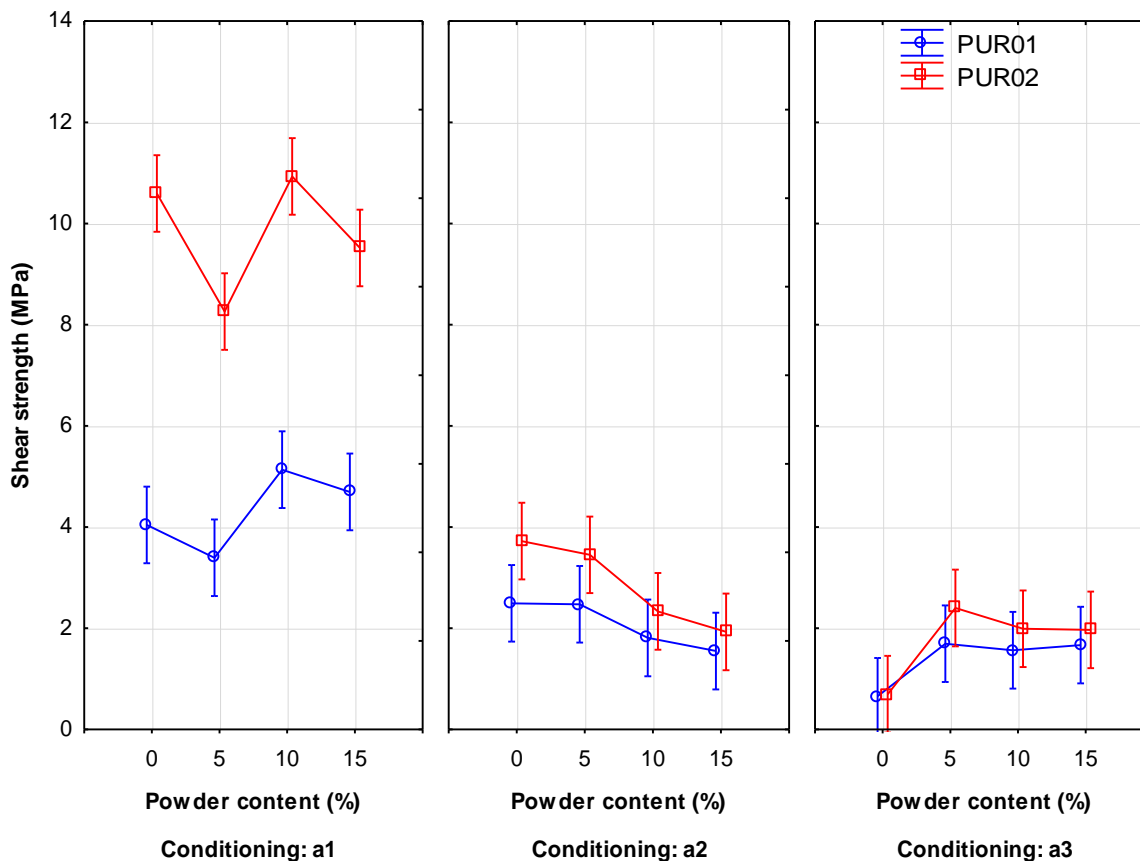


Fig. 5. Effect of powder content, adhesive type, and conditioning on the strength of bonded joints

CONCLUSIONS

1. The addition of polyurethane powder as a filler to 1C moisture-curing polyurethane adhesives increased the strength of bonded joints boiled in water; however, samples immersed in cold water showed a decrease in the strength of bonded joints.
2. The contact angle between the wood and adhesive droplet increased with an increase in polyurethane powder content. However, the contact angle was not observed to have any influence on the strength of bonded joints.
3. The addition of polyurethane powder as a filler to 1C moisture-curing polyurethane adhesives affected the structure of hardened adhesives, which was observed by SEM on the surface of the hardened adhesive.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Whole University Grant Agency of the Czech University of Life Sciences Prague, Project No. 20174305 “Modification of polyurethane adhesive for bonding of lignocellulose materials with polyurethane recycle as a filler”.

REFERENCES CITED

- Aydin, I. (2004). "Activation of wood surface for glue bonds by mechanical pretreatment and its effects on some properties of veneer surfaces and plywood panels," *Appl. Surf. Sci.* 233(1-4), 268-274. DOI: 10.1016/j.apsusc.2004.03.230
- Banea, M. D. and da Silva, L. F. M. (2009). "Adhesively bonded joints in composite materials: An overview," *Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials Design and Applications* 223(1), 1-18. DOI: 10.1243/14644207JMDA219
- Benhadjala, W., Gravouelle, M., Bord-Majek, I., Béchou, L., Suhir, E., Buet, M., Louarn, M., Weiss, M., Rougé, F., Gaud, V., and Ousten, Y. (2015). "Inorganic/organic nanocomposites: Reaching a high filler content without increasing viscosity using core-shell structured nanoparticles," *Applied Physics Letters* 107(21), 211903. DOI: 10.1063/1.4936339
- Budhe, S., Ghumatkar, A., Birajdar, N., and Banea, M. D. (2015). "Effect of surface roughness using different adhered materials on the adhesive bond strength," *Applied Adhesion Science* 3(1), 1-10. DOI: 10.1186/s40563-015-0050-4
- Clauß, S., Dijkstra, D. J., Gabriel, J., Karbach, A., Matner, M., Meckel, W., and Niemz, P. (2012). "Influence of the filler material on the thermal stability of one-component moisture-curing polyurethane adhesives," *J. Appl. Polym. Sci.* 124(5), 3641-3649. DOI: 10.1002/app.35223
- Clauß, S., Allenspach, K., Gabriel, J., and Niemz, P. (2011). "Improving the thermal stability of one-component polyurethane adhesives by adding filler material," *Wood Sci. Technol.* 45(2), 383-388. DOI: 10.1007/s00226-010-0321-y
- Clerc, G., Brülisauer, M., Affolter, S., Volkmer, T., Pichelin, F., and Niemz, P. (2017). "Characterization of the ageing process of one-component polyurethane moisture curing wood adhesive," *Int. J. Adhes. Adhes.* 72, 130-138. DOI: 10.1016/j.ijadhadh.2016.09.008
- Custódio, J., Broughton, J., and Cruz, H. (2009). "A review of factors influencing the durability of structural bonded timber joints," *Int. J. Adhes. Adhes.* 29(2), 173-185. DOI: 10.1016/j.ijadhadh.2008.03.002
- da Silva, L. F. M., Carbas, R. J. C., Critchlow, G. W., Figueiredo, M. A. V., and Brown, K. (2009). "Effect of material, geometry, surface treatment and environment on the shear strength of single lap joints," *Int. J. Adhes. Adhes.* 29(6), 621-632. DOI: 10.1016/j.ijadhadh.2009.02.012
- Deka, H., and Karak, N. (2009). "Vegetable oil-based hyperbranched thermosetting polyurethane/clay nanocomposites," *Nanoscale Res. Lett.* 4(7), 758-765. DOI: 10.1007/s11671-009-9313-y
- Desai, S. D., Emanuel, A. L., and Sinha, V. K. (2003a). "Biomaterial based polyurethane adhesive for bonding rubber and wood joints," *J. Polym. Res.* 10(4), 275-281. DOI: 10.1023/B:JPOL.0000004630.77120.bb
- Desai, S. D., Patel, J. V., and Sinha, V. K. (2003b). "Polyurethane adhesive system from biomaterial-based polyol for bonding wood," *Int. J. Adhes. Adhes.* 23(5), 393-399. DOI: 10.1016/S0143-7496(03)00070-8
- Dodiuk, H., Belinski, I., Dotan, A., and Kenig, S. (2006). "Polyurethane adhesives containing functionalized nanoclays," *J. Adhes. Sci. Technol.* 20(12), 1345-1355. DOI: 10.1163/156856106778456573

- EN 204 (2001). "Classification of non-structural adhesives for joining of wood and derived timber products," European Committee for Standardization, London, United Kingdom.
- EN 205 (2003). "Adhesives – Wood adhesives for non-structural applications- Determination of tensile shear strength of lap joints," European Committee for Standardization, London, United Kingdom.
- Li, Z., Huang, Y., Ren, D., and Zheng, Z. (2008). "Structural characteristics and properties of polyurethane modified TDE-85/MeTHPA epoxy resin with interpenetrating polymer networks," *J. Cent. South Univ. T.* 15(3), 305-308. DOI: 10.1007/s11771-008-0057-0
- Mansouri, H. R., and Pizzi, A. (2007). "Recycled micronized polyurethane powders as active extenders of UF and PF wood panel adhesives," *Holz. Roh. Werkst.* 65(4), 293-299. DOI: 10.1007/s00107-006-0168-y
- Moghadamzadeh, H., Rahimi, H., Asadollahzadeh, M., and Hemmati, A. R. (2011). "Surface treatment of wood polymer composites for adhesive bonding," *Int. J. Adhes. Adhes.* 31(8), 816-821. DOI: 10.1016/j.ijadhadh.2011.08.001
- Najib, M. F., Nobari, A. S., and Nikbin, K. (2017). "Modification and evaluation of a FRF-based model updating method for identification of viscoelastic constitutive models for a nonlinear polyurethane adhesive in a bonded joint," *Int. J. Adhes. Adhes.* 74, 181-193. DOI: 10.1016/j.ijadhadh.2017.01.013
- Okkonen, E. A., and River, B. H. (1988). "Factors affecting the strength of block-shear specimens," *Forest Products Journal* 39(1) 43-50.
- Patel, M. R., Shukla, J. M., Patel, N. K., and Patel, K. H. (2009). "Biomaterial based novel polyurethane adhesives for wood to wood and metal to metal bonding," *Mat. Res.* 12(4), 385-393. DOI: 10.1590/S1516-14392009000400003
- Ruanpan, S., and Manuspiya, H. (2018). "Synthesized amino-functionalized porous clay heterostructure as an effective thickener in waterborne polyurethane hybrid adhesives for lamination processes," *International Journal of Adhesion and Adhesives* 80, 66-75. DOI: 10.1016/j.ijadhadh.2017.10.005
- Sedliačik, M., Sedliačik, J., and Potapova, O. (2006). *K Problematike Lepených Spojov*, [Problematic of glued joints], TU vo Zvolene, Zvolen, Slovakia, pp. 75.
- Šmidriaková, M., and Kollár, M. (2010). "Modifikácia polyuretánových lepidiel biopolymérmi na lepenie dreva s vyšším obsahom vlhkosti [Modification of polyurethane adhesives with biopolymers for gluing of wood with higher moisture content]," *Acta facultatis xylogologiae Zvolen* 52(1) 75-83.
- Volkova, E. R., Tereshatov, V. V., Karmanov, V. I., Makarova, M. A., and Slobodinyuk, A. I. (2013). "Polyurethane adhesive composition cured at room temperature," *Polym. Sci. Ser. D.* 6(2), 120-124. DOI: 10.1134/S1995421213020159
- Walinder, M. E. P., and Ström, G. (2001). "Measurement of wood wettability by the Wilhelmy method. Part 2. Determination of apparent contact angles," *Holzforschung* 55(1), 33-41. DOI: 10.1515/HF.2001.006

Article submitted: November 12, 2017; Peer review completed: February 2, 2018;
Revisions accepted: February 14, 2018; Published: February 16, 2018.
DOI: 10.15376/biores.13.2.2592-2601