

Adhesives based on recycled polyurethane foam for wood based materials

K. Dimitrov¹, V. Yavorova², M. Herzog¹, S. Nenkova^{2*}

¹Technische Hochschule Wildau, DE-15745 Wildau, Germany

²University of Chemical Technology and Metallurgy, Sofia, 1756, Bulgaria

Submitted September 26, 2016 ; Revised March 1, 2017

Wood materials are increasingly being used in the construction of structural beams, sports equipment, etc. This study was carried out to investigate a new adhesive materials based on recycled polyurethane (PUR) foam. Mechanical tests, DSC, and FTIR were used to study the properties of the composites. After preparing the two-plate systems (beech, oak, walnut and pine tree) glued by the new adhesives and compared with adhesives based on polyvinyl acetate (PVA) the bonding strength and resistance of delamination were determined. Bond strength and water resistance (resistance of delamination) of two wooden plates bonded by the new adhesives were tested using standard methods. The highest shear strength of 16.1 MPa was received with oak wood bonded by the PUR adhesive. All samples prepared with the PUR adhesive were subjected to shear strength testing showing that the PUR adhesive is superior to PVA. In the water resisting test wood species bonded by PUR adhesive had a higher delamination rate than those bonded using PVA glue.

Keywords: Adhesive, recycling, polyurethane, wood

INTRODUCTION

Adhesives based on polyurethanes (PUR) are used in a wide range of application such as woodworking, furniture building or restoration, boat building and repair, cabinet making and millwork, stone, tile and masonry processing, light aircraft building and repair, crafts, composites production and many others. With respect to the different composition and applied methods as well as versatility in PUR chemistry, various types of PUR adhesives are available in the market, solvent based, solvent-less or water-borne. PUR adhesives usually contain a number of urethane groups in the molecular backbone or they are formed during processing without consideration of the chemical composition of the chain. Thus, typical polyurethane adhesives may contain in addition to urethane linkages aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea and/or allophanate linkages, which are responsible to establishing the final properties [1].

Wood bonding is based on a complex chemistry considering hydrogen bonding, Van der Waals forces, crystallinity or the like. To bond wood to wood, urea or phenol formaldehyde resin based adhesives are available, but these are generally sensitive towards hydrolysis and also cleavage due to stress i. e. often observed in plywood [2-6]. To increase the mechanical properties of plywood, PUR adhesives were recently introduced [7] giving good results. Some disadvantages, e. g. shorter pot life, durability and higher costs, are observed in acrylate based adhesives [8, 9].

PUR adhesives are made from synthetic, oil based

chemicals. To avoid environmental pollution problems, cost effectiveness, recycling poly(ethylene terephthalate) PET based PUR wood composites and adhesives for rubber are object of current industrial interest [10,11]. The recycling of PET to polyols is a sound way to reduce the cost [12] of raw materials used to produce PUR adhesives.

Another source to produce polyols suitable as basic raw materials of adhesives is the recycling of PUR foams. Generally, there are two ways to recycle PUR foams: physical and chemical.

The chemical recycling of polyurethanes is based on the cleavage of urethane bonds by means of a suitable reagent releasing the polyols of the polymer chain and the oligo-ureas as the reaction product of the isocyanates. Various chemical procedures for decomposing used PUR foams have been developed [13-18]. The processes are usually carried out with solvents, glycols, and/or polyols at elevated temperatures usually in the presence of a catalyst. The solvents used in the decomposition reaction include water, alcohols, diols, polyols, inorganic or organic acids, amines, and alkaline compounds. When alcohols such as low molecule weight glycols are used as decomposing solvents, they transesterify the urethane linkages, resulting in short chain hydroxyl functional urethane oligomers, and the polyols used in the reaction of the original PUR foams are thus released [13]. This process is designated as glycolysis. The polyols recovered from glycolysis were re-used in PUR foam manufacturing, but with limited success. Currently, recovered polyols can only partially replace commercial polyols in a PU

*) To whom all correspondence should be sent:

E-mail: nenkova@uctm.edu

foam-forming reaction. The main obstacle is the presence of the oligoureas (the isocyanate component constitutes 20 to 50 % of the foams) either in the recycle or as waste product; in some glycolysis processes the oligoureas are further reacting [19, 20].

In this paper we describe an attempt to synthesize polyether polyols out of PUR foams to form the basis of adhesives for gluing wood products. This is a continuation of previous work to develop wood composite materials using polyurethane recycling

polyols as the binder [21-24]. The process used was the glycolysis of PU foam using di-n-butylamine and dipropylene glycol as cleavage reagents and solvent. The oligomers obtained were utilized to synthesize the PUR adhesives. The synthesized adhesives were used the wood to wood bonding system. The bond strength and the delamination strength were measured by shear strength and water resistance delamination tests.

EXPERIMENTAL

Materials

For the synthesis of the PUR adhesive, the following materials were used:

The polyol, obtained from the glycolysis of flexible PUR foam (using 60 % of PUR foam, 4 % b. w. of di-n-butyl amine in dipropylene glycol) is characterized by a hydroxyl number of 460 mg KOH/g and an amine number of 46 mg KOH/g, and polymeric diphenylmethane diisocyanate (pMDI) with an isocyanate content of 31,5 %, supplied from BASF Schwarzheide GmbH.

For the preparing of the samples, four sorts of wood were used: beech, oak, walnut and pine.

Instruments used for characterization

Differential scanning calorimetry was performed by a DSC 204 Phoenix, Netzsch GmbH, and the FTIR analyses were carried out using a Fourier Transform IR spectrometer Varian 600 IR Series in the wave-number range 600 – 4000 cm⁻¹.

Microscopy was performed using a light digital microscope model VHX-5000 (Keyence). It was used to study and determinate the bond layer and the interfaces of the samples.

Mechanical properties (tensile shear strength test) of the samples were examined on a Zwick Z020. A small pressure tank was used for the water delamination tests.

Preparation of the PUR adhesives

Preparation of polyurethane adhesives was carried out by reacting the polyol obtained from the glycolysis of the flexible PUR foam with the aromatic polyisocyanate (pMDI) employing an isocyanate index of 120 based on the sum of hydroxyl and amine

number.

Preparation of the samples

Samples for the tensile shear strength tests were prepared according to DIN EN 204 standard from beech, oak, walnut and pine wood plates (longitudinal) by cutting stripes of 150 mm length, 20 mm width and 3 mm thickness out of blocks. Figure 1 shows the parameters of the samples.

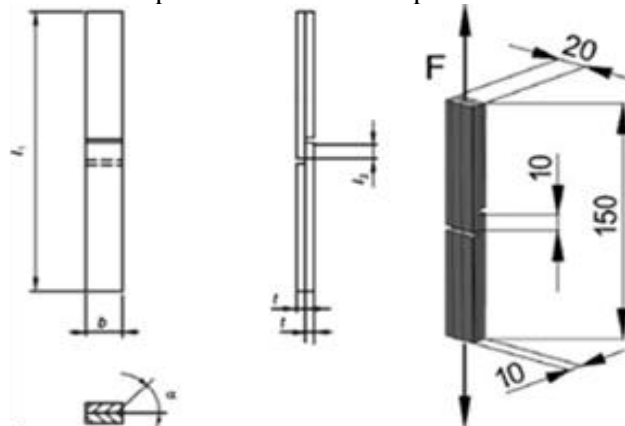


Figure 1. Sample parameters for tensile shear strength test according to DIN EN 204. Legend: $l_1 = 150$ mm, $l_2 = 7$ mm, $b = 20$ mm, $t = 5$ mm.

Samples for water delamination tests were prepared according to DIN EN 302-2 standard from beech, oak, walnut and pine wood.

RESULTS AND DISCUSSION

Differential scanning calorimetry

DSC analysis was used to investigate the thermal properties of the PUR adhesive. Figure 2 presents the curves of the DSC analysis.

The sample of the PUR adhesive was placed into DSC pans and sealed. The sealed pan was placed into a DSC instruments and cooled at a rate of 10°C/min (with liquid nitrogen as coolant) from room temperature to – 100°C and then heated at two thermal cycles with 10 K/min. The first run of the sample was performed by heating the sample from – 100°C to 120°C in the DSC pan, holding for 10 min at this temperature (to erase the thermal history) by slow cooling at 10 K/min to –100°C and followed heating up to +250°C.

The second run was performed by heating from – 100°C to +250°C. The DSC curve in Fig. 2 shows that little gas loss occurs in the range between 50 and 80°C, while in the second run this peak has disappeared. The gas loss could not be attributed to the polymer structure but probably to gas dissolved in the adhesive or attached to the urea or urethane bonds. Such gas loss is well known to be typical in the case of DSC investigations of polyurethane foams but this is attributed to absorbed water or residual foaming agents. The DSC curve shows furthermore a

relaxation peak in the glass transition region hinting to structural re-arrangements in the polymer structure.

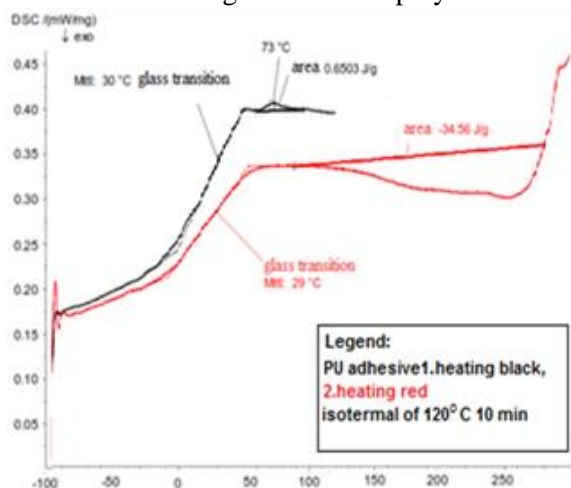


Figure 2. Differential scanning calorimetry of PU adhesive

At about 100°C in the first run a post-reaction occurs probably as a result of (probably structurally hindered) free isocyanate groups reaction with the water contained in the wood or with hydroxyl groups of cellulose or lignin catalyzed by the residual amines in the recyclate. It is further assumed, based on the FTIR spectra (see below) that transamination reactions of urethane groups available into urea groups occur with the cleavage of those urethane oligomers in the recyclate polyol which have not been cleaved in the synthesis. In the second run, the glass transition is well defined at +30°C as the transition of the mixed polyetherurethane phase of the glycol used in the recycling process and the liberated long-chain polyether polyol of the foam. Beginning again at 100°C, there is a broad exotherm maximum showing that the post-reaction occurs also in the second run but now with participation of a trimerization reaction of the isocyanate groups or further urea formation by a cleavage reaction of weaker urethane groups. A small endotherm maximum at about 230°C reflects the melting of the crystalline oligourea phase originating from the oligoureas present in the flexible PUR foams with oligomers of 2 to 22 units in case of p-MDI.

FTIR

Infrared spectroscopy was used for studying the PUR structure of the adhesive. FTIR analysis performed in the polyol and the PUR adhesive is depicted in Figure 3. Characteristic bands of the hydroxyl groups occur at about as a broad peak due to hydrogen bonded and non-bonded hydroxyls at 3400 cm⁻¹, at 3353 cm⁻¹ the maximum of the NH-peak is seen. In the polyol this peak is shifted to 3328 cm⁻¹ due to hydrogen bonded NH of the oligoureas. At 2280 cm⁻¹ a very small peak is seen originating from free isocyanate groups due to steric hinderance

in the polymeric MDI. The bands of the carbonyl groups occur at 1726 cm⁻¹, and 1706 cm⁻¹, resp. The band at the higher wavenumber corresponds to non-hydrogen-bonded urethane CO which is smaller in the adhesive, that at 1706 cm⁻¹ to the hydrogen bonded carbonyl group of the carbonyl-C=O which is correspondingly stronger in the adhesive. The three bands observed between 2966 cm⁻¹ and 2869 cm⁻¹ were attributed to symmetric and non-symmetric stretching of the C-H bonds in the various hydrocarbon groups of the aliphatic chains and the aromatic rings. In Figure 3, the wavenumber of the NCO peak of pMDI should be in the range of 2270-2250 cm⁻¹ but there is only a very small peak. Further, at 1680 cm⁻¹ as a shoulder and at 1598 cm⁻¹ as a band are seen the amid bands of the urea groups present both in the recyclate polyol and the adhesive originating from the decomposition of the PUR foam. At 1412 cm⁻¹ is the amid IV of the urethane group located.

However, the existence of peaks of amide groups –N-H at 3298 cm⁻¹, 1510 cm⁻¹ and 1530 cm⁻¹, the twin carbonyl urethane group at 1706 cm⁻¹, 1726 cm⁻¹, the carbamate group –CN at 1530 cm⁻¹ and the –C-O-C group at 1221 cm⁻¹ proved the urethane formation in the PUR adhesive, the band at 1588 cm⁻¹ the existence of urea groups derived from the oligoureas in the original foams.

According to Clemitson [25], the existence of the peak at 1730 cm⁻¹ is designated to a non-hydrogen bonded carbonyl urethane group –C=O while the peak at about 1706 cm⁻¹ is considered a hydrogen bonded carbonyl urethane group.

The polyol ether group is shown by the peaks at 1083 cm⁻¹ and 1066 cm⁻¹.

Microscopy

Figure 4 shows the PUR adhesive layer between the wood samples. The microscope investigation was used to calculate the thickness and the structure of the adhesive layer.

The PUR bonding layer in the examples of beech and oak do not show a homogeneous structure, many gas filled cavities were determined. This result can be explained with the availability of water in the raw reagents or, more probable, in the wood. The composites made with PUR adhesive and pine or walnut have a layer of approximately 130 μm for pine and about 30 μm for walnut, respectively.

The composites made with PVA adhesive using beech, oak and walnut (see Figure 5) showed the adhesive layer being between 13 μm and 20 μm. PVA and pine wood has a thickness of ≈ 60 μm.

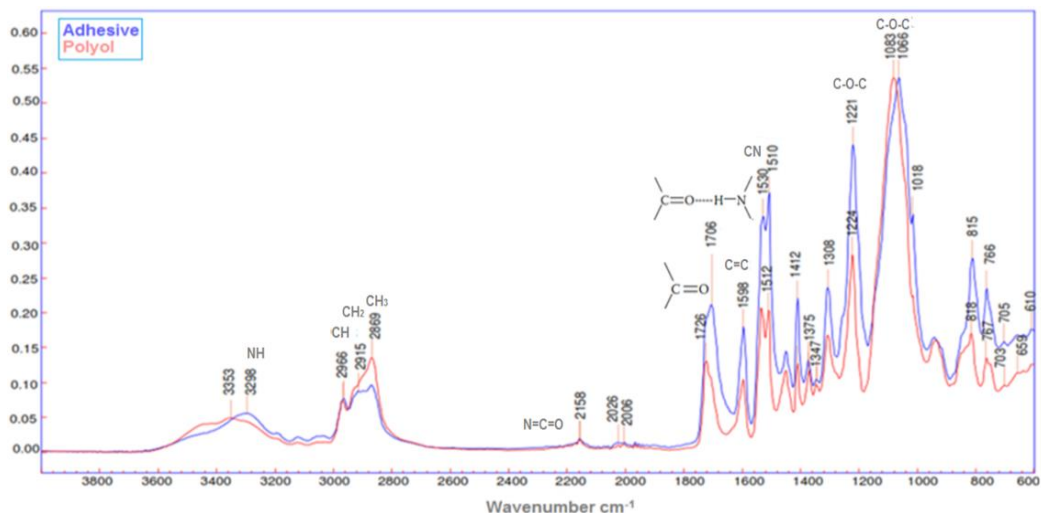


Figure 3. FTIR of the recycling polyol in red and the adhesive in blue.

The tensile shear strength test (see Figure 5) shows that the PUR adhesive is characterized by higher values in case of walnut, oak, or pine wood bonding but in case of beech PVA is superior. Comparing the average values of bonding strength, the highest value (16.11 MPa) was obtained for the oak wood sample bonded by PUR adhesive. The bonding strength of beech wood glued with the PUR adhesive was lower (8.77 MPa) than in case of the other wood types.

The samples of walnut and pine wood bonded by the PUR adhesive were (14.42 MPa) and (11.98 MPa), respectively. However, small differences were observed for different compositions of the adhesives.

Mechanical properties of materials

The strength of the bonded samples of walnut, oak and pine wood with the PU adhesive gave higher values than the bonded samples using the PVA adhesive.

The information about the bond strength of the adhesives corresponds to the investigation of the surface of the samples after the tensile test, see Figure 7.

In 90 % of the samples the adhesive film was not delaminated from the wood but a cohesive failure of the wood was observed. The orange colouring was used to show the site of destruction of the wood structure. From Figure 7 it is to be seen why the

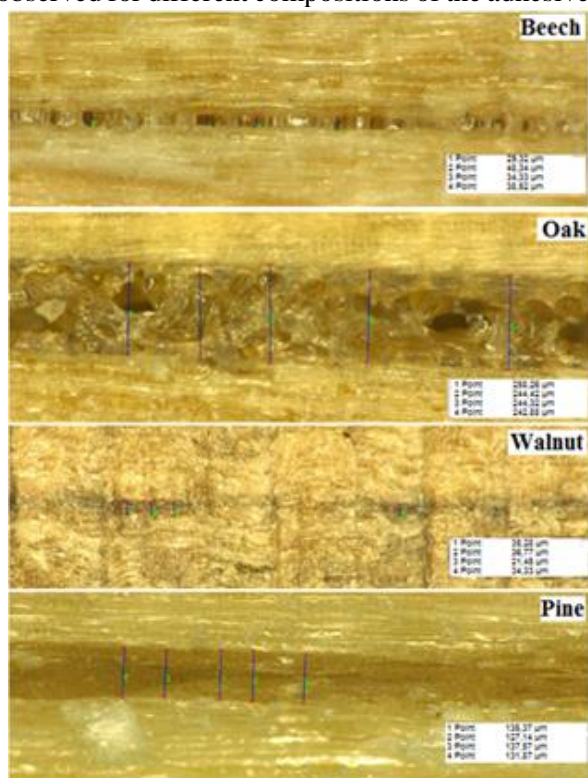


Figure 4. Light microscopy of PU adhesive layer.

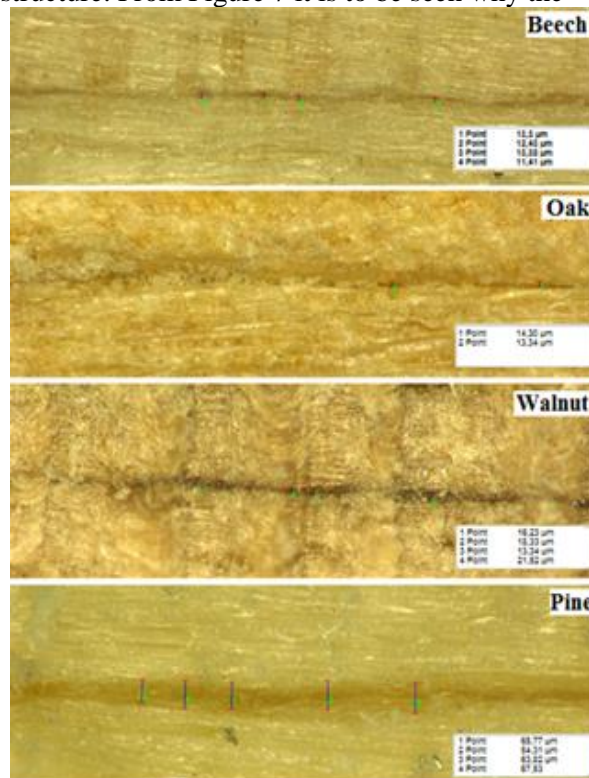


Figure 5. Light microscopy of PVA adhesive layer

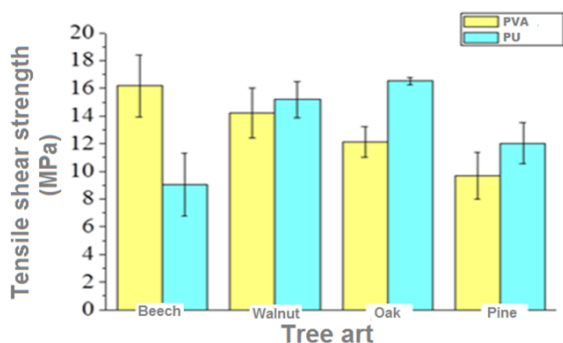


Figure 6. Tensile shear strength test of adhesives.

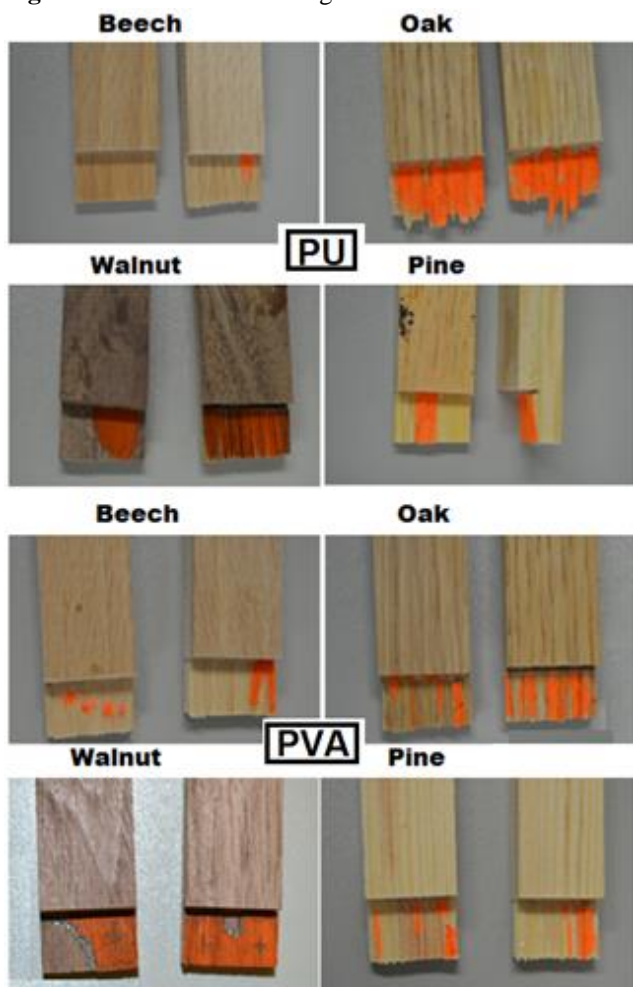


Figure 7. Surface inspection after shear tensile strength test.

samples of beech bonded with the PUR adhesive have lower shear tensile strength than the other samples. The bonding strength between the adhesive and the wood structure was too low to form a stable composite. One reason maybe the surface structure of the wood sample. The beech wood plates had very smooth surfaces.

Resistance of delamination

Water resistance of the adhesives (for exterior application) was tested by using the method described in standard DIN EN 302-2. Three cycles according to the conditions shown in Table 1 were

performed.

Table 1. Measurement conditions of delamination test.

Processing	Parameter	Unit	Value
Treatment	Water		
	Temperature	°C	10 – 25
	Duration	min	15
	Pressure	kPa	600±25
	Duration	h	1
Drying	Number of water cycle	-	2
	Air temperatur	°C	65±5
Drying	Duration	h	20
	Number of cycle	-	3
Number of cycle	Number of complete cycle		3
	One cycle consist of two water cycles and drying		

Water-soaking and drying tests of the composites made of the four wood types and the adhesives showed that the adhesive based on PVA had a better water resistance than the PUR adhesive. The results are depicted in Figure 8.

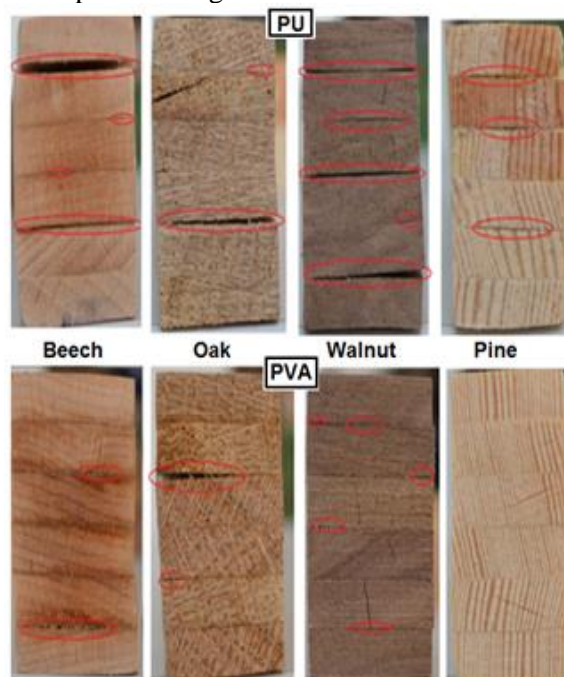


Figure 8. Visual inspection of selected test specimens after the delamination test.

The specimens with PVA adhesive (lower series) showed only a few cracks, while the specimen with the PUR adhesive lead to extensive cracking of the wood material. The highest resistance against delamination was observed in case of the pine wood with both types of adhesives (without delamination for PVA). Only 2 of the 8 samples fulfilled the standard requirements: they suffered less than 5 % delamination.

CONCLUSIONS

- The recycling method of the flexible PUR foam was successful. The obtained polyol was stable and it has been used in synthesis of adhesive glue for wood based materials.
- Based on the results of this study, PUP foam wastes could be de-composited into recycled polyols and formulated into adhesives for wood with comparable or even improved performances than commercial products. This could help providing a potential new way of utilizing PU wastes as well as developing new adhesive systems for wood or plywood manufacturing.
- The adhesives prepared from recycled polyol presented shorter gel time and greater dry bonding strength than those prepared from PVA.
- The highest resistance against delamination was observed in case of the pine wood with both types of adhesives (without delamination for PVA).

REFERENCES

1. C. Strobeck, *International Journal of Adhesive & Adhesion*, **10**, 225 (1990).
2. M. Kreneski, F. Johnson, C. Temin, *Polymer Reviews*, **26**, 143 (1986).
3. A. Takemura, H. Mizumaehi, *Technomic Publishing Co.*, 25 (1991).
4. K. Badri, A. Ujar, Z. Othman, F. Sahaldin, *J. Appl. Polymer Sci.*, **100**, 1759 (2006).
5. G. Myres, *Adhesives Age*, **31**, 31 (1988).
6. R. Ebewele, B. River and G. Myres, *Eur. J. Wood & Wood Products*, **52**, 179 (1994).
7. F. Dias and F. Lahr, *Materials Res.*, **7** (3), (2004).
8. M. Vallat and B. Bessaha, *J. Appl. Polymer Sci.*, 76 665 (2000).
9. D. Jia and X. Liang, *J. Appl. Polymer Sci., Part B: Polymer Physics*, **32**, 817 (1994).
10. M. Fornasieri, J. Weiller Alves, E. Muniz, A. Filho, H. Otaguro, A. Rubira, G. Carvalho, *Composites* **42**, 189 (2011).
11. S. Desai, J. Patel², M. Patel, V. Sinha, *Indian J. Chem. Technol.*, **12**, 82 (2005).
12. R. Schaffrath, L. Skokova, G. Behrendt, R. Langenstrassen, *Poliuretanovye Tekhnologii*, **1**, 22 (2006).
13. G. Behrendt, B. Naber, *J. Univ. Chem. Technol. Metall.*, **44**, 3 (2009).
14. R. White, D. Durocher, *J. Cellular Plastics*, **33**, 477 (1997).
15. C. Wu, C. Chang, J. Li, *Polymer Degrad. Stability*, **75**, 413 (2002).
16. C. Wu, C. Chang, C. Cheng, H. Huang, *Polymer Degrad. Stability*, **80**, 103 (2003).
17. J. Lee, D. Kim, *J. Appl. Polymer Sci.*, **77**, 2646 (2000).
18. C. Molero, A. Lucas, J. Rodríguez, *Polymer Degrad. Stability*, **91**, 221 (2006).
19. D. Georgieva, S. Nenkova, G. Behrendt, *J. Univ. Chem. Technol. Metallurgy*, **42**, 345 (2007).
20. D. Georgieva, M. Markwardt, H.-D. Hunger, M. Herzog, G. Behrendt, *Polyurethan-Holz-Komposite und Verfahren zu ihrer Herstellung*, DE-OS 10 (2006) 021 266 (02. 05. 2006/ 23. 11. 2006).
21. D. Georgieva, R. Evtimova, R. Madzharova, G. Behrendt, *Composites Based on Recycling Products, Wood raw materials, and Polyurethanes*, Conference "Organic Precursors", Odessa, (2005).
22. D. Georgieva, S. Nenkova, M. Herzog, G. Behrendt, *BioResources*, **3** (3) 859 (2008).
23. V. Stoychev, B. W. Naber (*Lambda One Isoliertechnik GmbH*), *Verfahren zur Herstellung von Polyolkomponenten für Polyurethane aus Polyurethan-Hartschaumstoffen*, DE-OS 10 2009 026 898 (16. 12. 2010); EP 2 270 083.
24. M. Lezius, B. Naber, Bernhard (*BASF Schwarzheide GmbH*), *Verfahren zur Herstellung von Recyclatpolyolen*, DE 44 45 890 A1 (27. 6. 1996).
25. I.R. Clemitson, *Castable Polyurethane Elastomers*, Second Edition, *CRC Press, Taylor & Francis Group*, (2012).

ЛЕПИЛА ЗА ДЪРВЕСИНА БАЗИРАНИ НА РЕЦИКЛИРАНИ ПОЛИУРЕТАНОВИ ПЕНИ

К. Димитров¹, В. Яворова², М. Херцог¹, С. Ненкова²

¹*Техническо висше училище Вилдау, DE-15745 Вилдау, Германия*

²*Химико-технологичен и металургичен университет, София 1756, България*

Постъпила на 26 септември, 2016 г. ; коригирана на 1 март, 2017 г.

(Резюме)

Дървени материали все повече се използват като конструкционни материали, греди, спортни съоръжения, и т.н. Това изследване се провежда, за да се проучи нов залепващ материал базиран на рециклирана полиуретанова пяна. Получените материали са охарактеризирани чрез механични тестове, диференциално сканираща калориметрия и трансмисионна инфрачервена спектроскопия. За изследването са използвани четири вида дървесина (бук, дъб, орех и бор). Изготвени са проби с лепилото получено от рециклирани полиуретанови пени и са сравнение със стандартно лепило за дървесина на базата на поливинил ацетат (PVA). Силата на залепване и устойчивост на разслояване бяха определени. Якост и устойчивост на вода (устойчивост на разслояване) на две дървени плочи, свързани с новите лепила са изследвани при използване на стандартни методи. Най-високата якост на опън при срязване (16.1 МПа) е получена с дъбова дървесина, свързан с лепило от рециклирани полиуретанови пени. Всички проби, приготвени с лепилото на PUR бяха подложени на якост на опън при срязване. Изследването показваща, че лепилото получено от рециклирани ПУ пени превъзхожда стандартното лепило базирано на поливинил-ацетат.