HYPERBRANCHED POLYGLYCEROLS WITH BISPHENOL A CORE AS GLYCEROL-DERIVED COMPONENTS OF POLYURETHANE WOOD ADHESIVES

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Two hyperbranched polyglycerols (HBPGs) and one oligoglycerol containing bisphenol A in the core of the molecule were synthesized from glycerol carbonate and applied as polyols in 2-component polyurethane adhesive systems. It was shown that mechanical performance of the joints made in solid wood depended on the hydroxyl functionality of the polyglycerol as well as on the type of the isocyanate used as a cross-linker. The shear strengths of the best-performing joints exceeded that of the substrate. Eventually, it was proved that hyperbranched polyglycerols might be convenient glycerol-derived raw materials for polyurethane adhesives.

Keywords: Adhesives for wood; Glycerol; Hyperbranched polyglycerols; Polyurethane

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INTRODUCTION

Due to an increasing interest in environmentally-friendly technologies based on the renewable resources – including biodiesel i.e. fatty acid methyl esters (Behr *et al*. 2008), bioethanol from lignocellulosic resources (Cardona *et al.* 2010; Gírio *et al*. 2010), or synthetic rubber made from biomass (Anonymous 2010), as well as interest in finding new applications for them and making them an alternative to petroleum-based feedstocks, research on conversion of renewable resources to value-added products or intermediates applicable in adhesive technology has also been intensified recently. There are numerous reports in the literature regarding studies on adhesives derived from bioresources. Haag *et al.* (2004) described microbially produced polysaccharide as a wood adhesive. Tannins (Moubarik *et al.* 2010; Geng *et al.* 2004) and soy proteins (Liu *et al.* 2007; Nordqvist *et al.* 2010; Liu *et al.* 2010) have also been reported as components for formaldehyde-free adhesives. Obviously, other approaches are possible, too. Many groups have focused their attention on the liquefaction of lignocellulosic biomass, since liquefied wood is recognized as being a convenient component of polyurethanes (Kurimoto *et al.* 2000; Wei *et al.* 2004) and polyurethane adhesives (Tohamura *et al.* 2005). Kunaver *et al.* (2010) described application of liquefied wood as modifiers of urea-, melamine-urea-, or melamine-formaldehyde resins. Juhaida *et al.* (2010) showed that liquefied kenaf core could be a source of polyols for polyurethane adhesives.

On the other hand, not only lignocellulosic biomass can potentially provide non-petroleum raw materials suitable for the development of novel adhesives. It is known that upon biodiesel production substantial amounts of crude glycerol are yielded as a by-product. Therefore, the quantity of additional glycerol that will enter the market by 2012 is estimated to reach 1.2 million tons (Zhou *et al.* 2008). Obviously, apart from the commonly known glycerol applications in pharmaceuticals, cosmetics, or alkyd resins, there is still a need for new fields of its utilization. One of the possible approaches was reported by Rokicki *at al.* (2005), where a transformation of glycerol to cyclic glycerol carbonate and subsequent environmentally benign synthesis of hyperbranched polyglycerols were described. Further, the functionalized hyperbranched polyglycerols were successfully used as low-cost toughening agents for epoxies (Parzuchowski *et al.* 2007).

In the literature, it has been shown that hyperbranched molecules can be efficient modifiers for vinylester–urethane hybrid resin (Gryshchuk *et al.* 2002), urea-formaldehyde resins (Essawy *et al.* 2009), or might provide building polyurethane networks when crosslinked with isocyanates (Nasar *et al.* 2003; Okrasa *et al.* 2008). Having in mind that hyperbranched hydroxyl-terminated polyglycerols are highly reactive towards isocyanates, Mamiński *et al.* (2011) recently showed that it was possible to develop fast-curing polyurethane adhesives based on hyperbranched polyglycerols. The authors proved that the presence of aromatic moieties within the hyperbranched molecule was crucial for mechanical performance of the polyurethane network and for high shear strength of the bond line. It was found that benzyl substituents distribution, regular within the inner zone of the molecule (secondary benzyls only) or statistical (primary and secondary benzyls) throughout the molecule, had comparable effect.

Thus, in this work an aromatic structure was fixed within the core of the hyperbranched molecule. The effect of the presence of a bisphenol A moiety in the core of hyperbranched polyglycerol on the performance of wood-to-wood adhesive joints was investigated. The approach allows for a wider utilization of renewable glycerol in adhesive technology.

EXPERIMENTAL

Instrumentation

Viscosity of the branched polymers was measured at 23ºC on a Brookfield DV II+ Pro viscometer equipped with a spindle no. 64. Measurements of the molecular weights were made by Size Exclusion Chromatography (SEC) on a GPC Shimadzu apparatus with a PSS Gram 100 column (300 mm × 8 mm) using DMF as an eluent at 35°C with flow rate 1 mL/min and polymethylmethacrylate standards for the calibration. FTIR spectra were recorded in KBr pellet on Bio-Rad FTS165 instrument. Each spectrum was taken as an average of 32 scans at a resolution of 4 cm^{-1}.

Materials

Polymeric methylenediphenyldiisocyanate (PMDI, 36 wt % NCO) was obtained from Huntsman Co. Hexamethylene diisocyanate (HDI, 49.9 wt % NCO) and poly(hexamethylene diisocyanate) (PHDI, 21.8 wt % NCO) were used as obtained from

Aldrich. A modified dimethylpolysiloxane polyether (Structol®, Germany) was used as a compatibilizer. Tin dibutyl dilaurate was used as catalyst. Glycerol carbonate (4-hydroxymethyl-1,3-dioxolane-2-on) was synthesized from glycerol and dimethyl carbonate according the procedure described by Rokicki *et al.* (2005).

Oligomeric 2,2'–bis[4-(2,3-dihydroxy propoxy) phenyl] propane (Bis4OH) and hyperbranched polyglycerols Bis51 and Bis101 bearing polyether backbones of different molecular weights and number of OH groups (Fig. 1) resulting from branching monomer-to-core molecule molar ratios of 2:1, 5:1 and 10:1, respectively, were synthesized according the procedure described below. The number of hydroxyl groups was confirmed by NMR (Fig. 2).

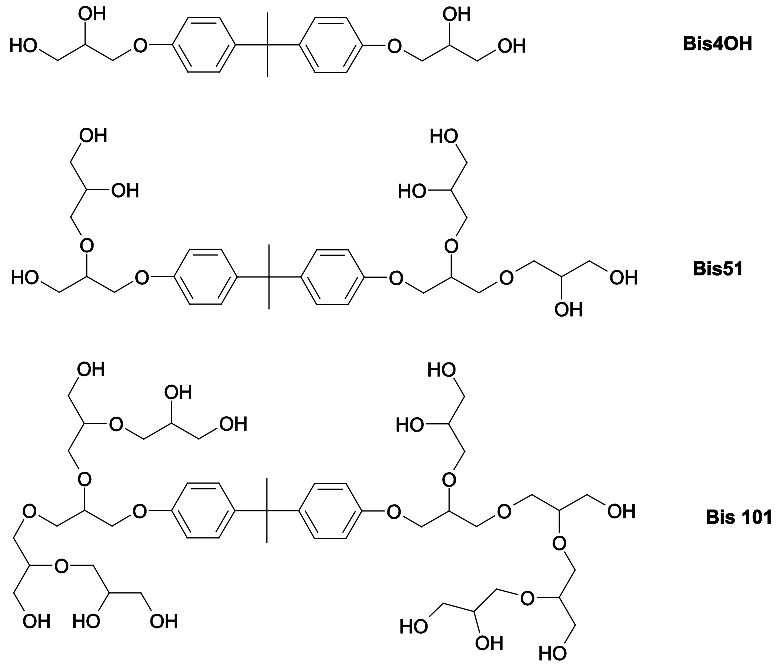

Fig. 1. Theoretical structures of the hyperbranched polyglycerols with bisphenol A in the core of the molecule

Methods

Synthesis of polyglycerols

Representative procedure for Bis51: In a 3-neck reactor equipped with magnetic stirrer, condenser, and dripping funnel, 5.70 g (25 mmol) bisphenol A and 0.042 g (0.75 mmol) potassium hydroxide were molten at 170ºC and then 14.76 g (125 mmol) glycerol carbonate was added drop wise for 20 hrs. The reaction was performed until depletion of glycerol carbonate (disappearance of 1791 cm^{-1} band) was confirmed by FTIR spectroscopy.

Similar procedures with different reagents ratios were made for the syntheses of Bis4OH and Bis101.

Molecular weight distributions from SEC were as follows: Bis4OH: M_n = 1343, M_w = 994, D = 1.35; Bis51: M_n = 714, M_w = 450, D = 1.56; Bis101: M_n = 852, M_w = 514, D = 1.65

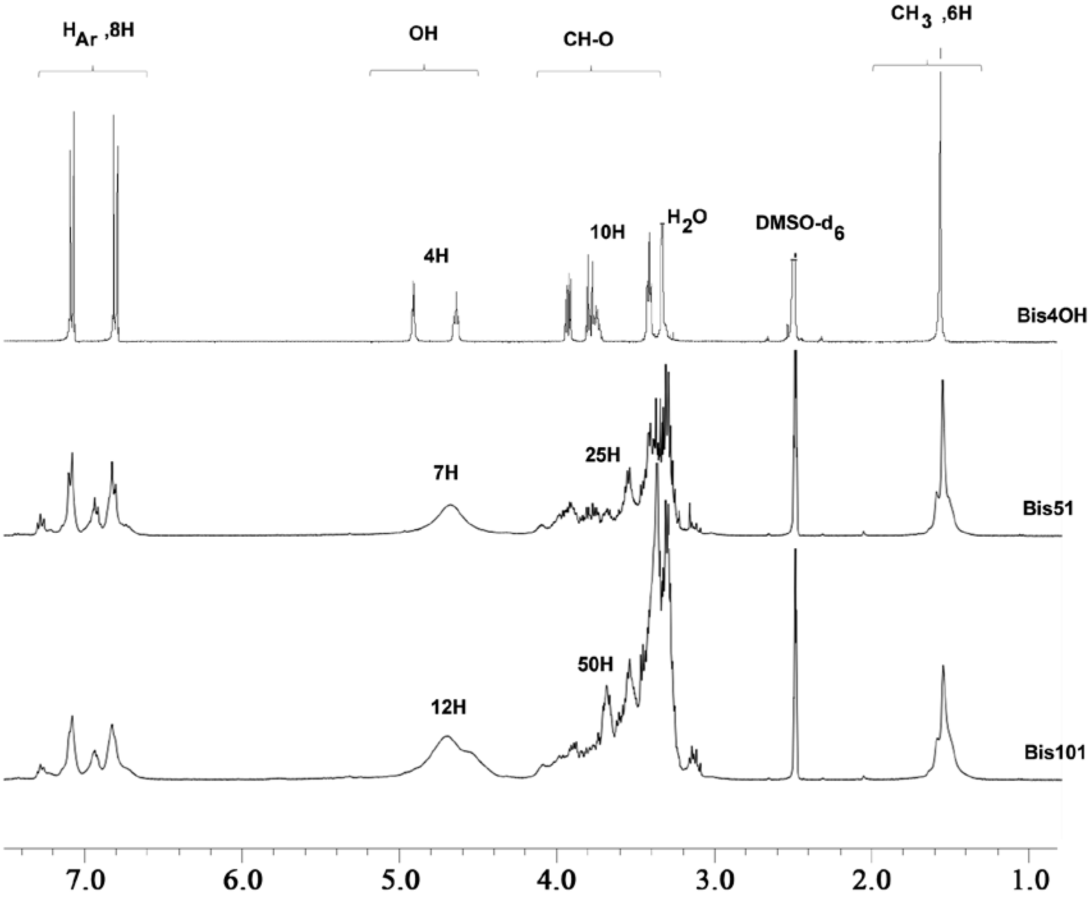

Fig. 2. NMR spectra of the studied polyglycerols

Hydroxyl value (L_{OH}) determination

L_{OH} values of polyols were determined using a phthalation method (PN-C-89052-03:1993 standard): a portion of polyol (0.20 g) was dissolved in 25 mL phthalic anhydride : pyridin : imidazole (165 g : 1000 ml : 25.7 g) mixture and refluxed for 15 minutes. Then distilled water (25 mL) was added, the mixture was cooled to room temperature and titrated with 0.5 M KOH. L_{OH} values were calculated from the equation:

$$L_{OH} = (V_0 - V) \times n \times 56.1/m \tag{1}$$

where V_0 is the volume of KOH solution used for titration of blank sample (mL), V is the volume of KOH solution used for titration of a sample (mL), n is KOH solution concentration (mol/L), and m is the weight of a sample (g). L_{OH} values are shown in Table 2.

NCO/OH ratio calculation

The calculations were based on L_{OH} values of the respective polyols and NCO values of the isocyanates used in the experiments. Stoichiometric amount of an isocyanate was calculated using the following formula,

$$m_{iso} = \left(\frac{\sum m_{polyol} \times L_{OH}}{56100} \right) \times \frac{4202}{c_{iso}} \tag{2}$$

where m_{iso} is the stoichiometric amount of isocyanate (g), m_{polyol} is the amount of a polyol component (g), L_{OH} is hydroxyl value of a polyol component (mg KOH/g), and c_{iso} is NCO content in an isocyanate (wt %). NCO/OH ratios were derived from true weight components' ratios.

Test specimens

Shear strength tests were performed on beech (*Fagus sylvatica*) specimens of moisture content 5.2 % and density 697±15 kg/m^3. Test specimens were prepared and tested according to the EN 205 standard.

Bonding procedure

At the first step, an aliquot of a polyglycerol was thoroughly mixed with glycerol (1:0.5, w/w). It was necessary for the systems to decrease their viscosities to an applicable level as shown in Table 1.

Then one or two weight equivalent(s) of the respective isocyanate were added (HBPG + glycerol / isocyanate ratio was 1.0 or 2.0). In the case of HDI, addition of 1.5 wt % of silicon compatibilizer improved miscibility of the components. Afterwards, tin dibutyl dilaurate (0.2 %wt) was added as catalyst.

The adhesive was immediately applied (120 g/m^2) onto the specimens of dimensions 300 × 50 × 5 mm^3. Assemblies of two were subjected to 30 min bonding in the press at 60ºC and a pressure of 1.5 N/mm^2. The bonded samples were kept at 20 ±2ºC and 65 ±5% relative humidity for 7 days.

Shear strength tests

Test samples (150 × 20 × 5 mm^3) of the lap area *ca*. 200 mm^2 were subjected to shear strength tests. Twenty samples were tested in each series. The reference samples were bonded with a commercial emulsion polymer isocyanate (EPI) adhesive system under the same conditions.

Statistical analysis

Significance of differences between average shear strengths was calculated using Student t-test at 95% confidence interval.

RESULTS AND DISCUSSION

Hyperbranched polyglycerols (HBPGs) were used as polyol components of 2-component polyurethane adhesives. High initial viscosities of the polyglycerols (Table 1) made it necessary to dilute them with glycerol at a 1:0.5 (w/w) ratio, so that lowered viscosities allowed for better substrate wetting and processing of the systems. The viscosities of the neat and diluted polyglycerols systems are shown in Table 1.

Table 1. Viscosities of the Hyperbranched Polyglycerols and Glycerol-diluted Systems

HBPG	Viscosity [Pa·s]	
	HBPG	HBPG / glycerol*
Bis4OH	430 (50ºC)	210 (23ºC)
Bis51	55 (23ºC)	27 (23ºC)
Bis101	18 (23ºC)	11 (23ºC)

*1:0.5, w/w

Based on hydroxyl values of the polyglycerols and glycerol (Table 2), the isocyanates were added at two levels – 1.0 and 2.0 weight equivalent(s). The resultant NCO/OH ratios are shown in Table 3. The discrepancies between M_n, M_w, and theoretical molecular weights of polyglycerols resulted from different hydrodynamic radii of linear and branched polymers. Such a phenomenon was already observed before (Parzuchowski *et al.* 2008).

Table 2. Hydroxyl Values of the Studied Polyols Calculated from the Theoretical Molecular Weights and Determined from Titrations

polyol	m.w.	calculated L_{OH}	L_{OH} [mg KOH/g]	M_n	M_w	D
Bis51	598.7	655	631	714	450	1.56
Bis101	969.1	693	674	852	514	1.65
Bis4OH	376.4	595	618	1342	994	1.35
glycerol	92.1	-	1800	-	-	-

Due to the high hydroxyl functionality of the polyglycerols, i.e. 4, 7, and 12 for Bis4OH, Bis51, and Bis101, respectively, short gel times at ambient temperature were possible to achieve (Table 3). The adhesives were found to be sufficiently reactive for fast curing. However, additional hydroxyls introduced to the system within glycerol obviously contributed to the observed eventual reactivity. As shown in Fig. 3, the performance of the joints was satisfactory and the obtained strengths were higher than those of the control EPI series.

Table 3. Gel Times at 20ºC and NCO/OH Ratios of the Studied 2-component Polyurethane Adhesive Systems

HBPG + glycerol	isocyanate	Gel time [min]		NCO/OH ratio	
		components weight ratio		components weight ratio	
		1.0	2.0	1.0	2.0
Bis51	HDI	2	immiscible	0.65	-
Bis51	PHDI	10	4	0.28	0.57
Bis51	PMDI	15	2.5	0.46	0.92
Bis101	HDI	4	3	0.63	1.27
Bis101	PHDI	13	6	0.27	0.55
Bis101	PMDI	15	3.5	0.47	0.95
Bis4OH	HDI	immiscible	immiscible	-	-
Bis4OH	PHDI	5	4	0.29	0.57
Bis4OH	PMDI	30	5	0.48	0.96

Performance of the Adhesive Systems

The obtained results of shear strengths of the joints made in solid beech for the formulations bearing 1 or 2 weight equivalent(s) of an isocyanate are presented in Fig. 3a-c. The data indicate the differences between the strengths of the joints in the respective series that seem to be affected by the molecular weights of the polyglycerols used. One sees that all the formulations based on Bis51, regardless of the isocyanate used, exhibited better performance than the reference EPI. Moreover, strengths of the formulations with Bis51 and HDI or PHDI exceeded those for the PMDI-crosslinked samples, which is surprising, since one can expect that stiff aromatic segments within the polymeric network should increase its mechanical properties.

On the other hand, the strengths of the joints made of the formulations based on Bis101 (1 to 1 ratio) were somehow lower than those observed for EPI – by 40% for HDI-, 23% for PMDI- and 24% for PHDI-crosslinked system. The formulations bearing oligomeric molecule Bis4OH made it possible to achieve strengths lower by 20% and 66%, for PHDI and PMDI respectively, than those of the reference adhesive.

In general, one can see that performance of the PHDI bondline series was excellent. Wood failure percentage for 2-equivalent series was 100%, and the strengths achieved 12.0 MPa, 11.0 MPa, and 11.0 MPa, respectively, for Bis4OH, Bis51, and Bis101, though the respective NCO/OH ratios were as low as 0.57, 0.57, and 0.55. This can represent a significant advantage, since the typical NCO/OH ratio in adhesives is near 1. The phenomenon can be explained by a very good intrinsic adhesive performance of PHDI, which, for all the formulations with 2 equivalents of the isocyanate, overwhelmed the effect of HBPG.

The effect of polyglycerol structure is clearer for the series with 1 equivalent of PHDI. The results presented in Fig. 3a show that the strengths of the Bis51-PHDI bondlines achieved 9.1 MPa and exceeded that of the reference EPI, while those of Bis4OH and Bis101 remained lower than reference EPI value. Statistical analysis between series bearing 1- and of 2-equivalents PHDI showed that a doubled amount of PHDI caused significant increase in strength for Bis4OH and Bis101, while differences for Bis51 were insignificant.

In the case of PMDI, the effect of the polyglycerol could be manifested, since even in below equimolar amount (1 weight equivalent, NCO/OH 0.46), the strengths of Bis51 series were satisfactory (Fig. 3b). But a doubled amount of PMDI did not affect bondline strength so much. The observed shear strength of the 1-equivalent series was 7.5 MPa while that of the 2-equivalent series was 8.5 MPa, and no statistically significant difference was found. However, average values exceeded the strength of the reference EPI.

In contrast to Bis51, both Bis4OH and Bis101 series cured with PMDI exhibited much poorer performance — when compounded with PMDI in 1 to 1 ratio, shear strengths were 3.2 MPa, and 5.6 MPa, respectively, and 2.7 MPa and 3.8 MPa when compounded in 1 to 2 ratio. A statistically significant increase was found for Bis51-PMDI series, but the wood failure rate was 0% in all series.

In the course of compounding of the studied HBPGs with HDI, polyglycerol Bis4OH was observed to be immiscible with hexamethylenediisocyanate, while Bis51 was miscible only in a 1 to 1 ratio. As data in Fig. 3c indicate, the strengths of Bis101-HDI bondlines remained below that of the reference value (7.2 MPa) and achieved 4.4 MPa and 4.9 MPa, respectively for 1 and 2 equivalents.

In all cases, the best performance was exhibited by the systems based on the polyglycerol Bis51. These observations may be explained by the hydroxyl functionality of polyglycerol Bis51 equal to 7 that was a compromise between the highly functionalized Bis101 (12 hydroxyls) and low functionalized Bis4OH (4 hydroxyls).

Low strengths of Bis4OH formulations obtained consecutively with PMDI and HDI may be ascribed to the low hydroxyl functionality of the polyglycerol - i.e. 4. On the other hand, low strengths of Bis101- PMDI and Bis101-HDI systems may result from high hydroxyl functionality, providing high cross-linking density, which subsequently resulted in high brittleness of the polymer network. Such a system lacks sufficient stress dissipation capability, so that a bondline fracture occurs at lower loads (Suo 1990; Stamper 1986).

Regardless of the presence of glycerol, which undoubtedly decreased mechanical strength of the polyurethane and had influence on the performance of the joints, it was shown that molecular weight of the polyglycerol molecule – being network nodes – as well as its hydroxyl functionality plays an important role in the resultant performance of 2-component adhesive system based on the hyperbranched polyglycerols. Also, one can see that these two parameters were manifested in the obtained strengths values. The degree of branching of the polyglycerols has been neglected in this discussion, since it is assumed to be close to ~ 0.5 for high conversion degrees (Rokicki *et al.* 2005).

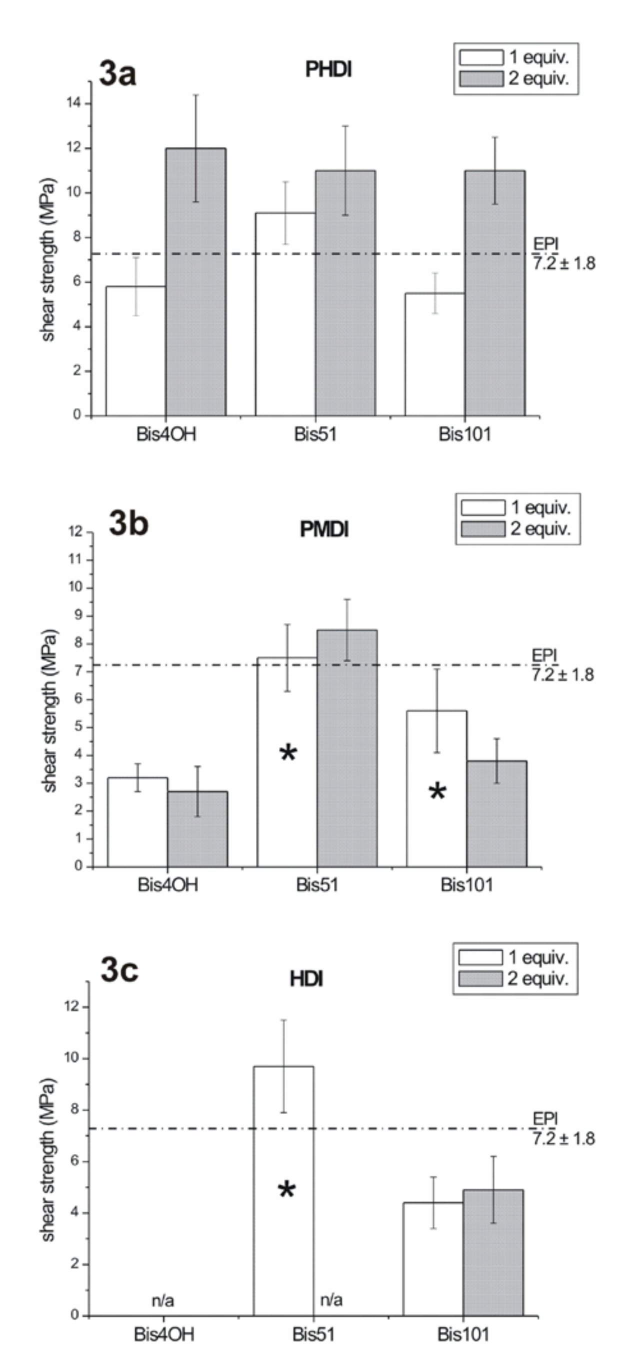

Fig. 3. Shear strengths of the adhesives cured with PHDI (3a), PMDI (3b) and HDI (3c). Asterisks denote unreacted NCO groups found in the cured adhesive

FTIR Spectroscopy

The FTIR analysis made for the cured adhesives of 1-to-1 components weight ratio revealed the presence of unreacted NCO groups in some formulations. The NCO band appearing in the respective spectrum is denoted in the columns of Fig. 3 with an asterisk. The isocyanate bands (*ca*. 2275 cm^{-1}) were found in the spectra of Bis51-HDI, Bis51-PMDI, and Bis101-PMDI systems. Suprisingly, the NCO/OH ratios in those formulations (0.65, 0.46, and 0.47, respectively) were below equimolar, which can be possibly explained by phase separation during curing process. The representative spectra are shown in Fig. 4.

The chemical bond theory of adhesion assumes that a slight excess of the isocyanate in the adhesive formulation contributes to the resultant strength of the joint by the formation of the covalent bonds toward a substrate. But the obtained results showed that the above mentioned condition was not necessary for achieving high joint quality, although the presence of the unreacted NCO groups was detected.

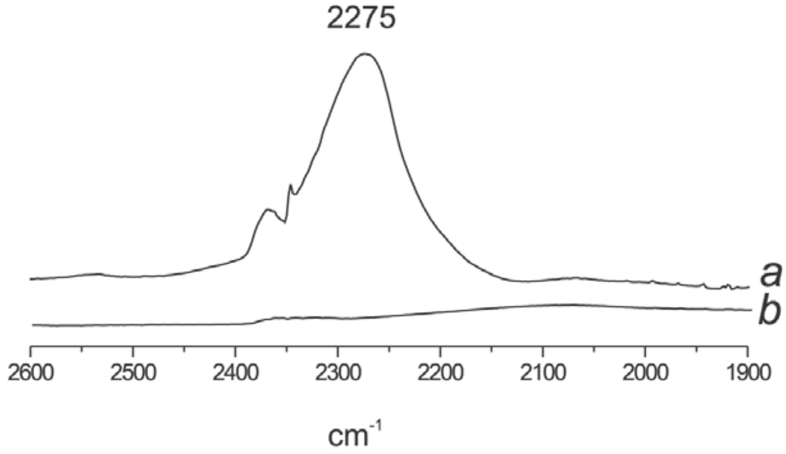

Fig. 4. Representative FTIR spectra of the NCO region of the cured adhesives: ***a*** – NCO band at 2275 cm^{-1}, ***b*** – NCO-free spectrum

CONCLUSIONS

1. The present studies showed that glycerol – an environmentally-friendly and renewable resource – could be coveniently transformed to hyperbranched polyglycerols (HBPGs) that might be substitutes for petroleum-based polyols.
2. The obtained results make it possible to conclude that hyperbranched polyglycerol-based polyols are feasible in application in wood adhesives. It was shown that polyglycerols bearing aromatic moieties within the core (i.e. bisphenol A) might be effective polyol components of 2-component polyurethane adhesives.
3. The observed tensile strengths of the best-performing joints exceed that of the substrate, which implies that satisfactory quality. Also, from the obtained results it can be concluded that hydroxyl functionality of the polyglycerol affects properties of the adhesive. It was shown that polyglycerol bearing 7 hydroxyl groups worked better, regardless of the isocyanate used, than polyglycerols bearing 4 or 12 hydroxyls, even when a below equimolar amount of the isocyanate was used.
4. Due to high viscosity of hyperbranched polyglycerols, some problems with miscibility with isocyanates may occur, but such problems can be overcome using diluents. Obviously, a reactive diluent, e.g glycerol, affects the performance of the

resultant adhesive joints; therefore further studies involving inert diluents or compounding neat HBPGs with isocyanate seem to be necessary.

5. The most promising systems based on Bis51 and PMDI – the most common industrial isocyanate – are to become a subject of further research and optimization.

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