

Glycerol as a renewable resource for wood adhesives

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Abstract. An approach allowing for conversion of renewable resource - glycerol to polyglycerols useful in polyurethane technology and cross-linking with isocyanates was presented. It was shown that hyperbranched polyglycerols could be substitutes for petroleum-based polyols and raw materials for polyurethane wood adhesives. The shear strengths of the resultant adhesive joints made on solid wood exceeded that of the substrate.

Keywords: adhesives, glycerol, polyglycerols, polyurethanes

1. Introduction

Constantly increasing production of bio-diesel from vegetable oils (triglycerides), mainly rape oil, generates considerable amounts of crude glycerol. Annual bio-diesel production is estimated on 12 Mt, which makes ca. 1.2 Mt of crude glycerol, since per each 1000 kg of bio-diesel 100 kg of by-product is yielded [1]. Additional amounts of glycerol are generated from saponification of fats and oils.

Such large supply of raw material entering the market induces a need for its efficient transforming into value-added products. Therefore, intense research in that field has been carried out for years, so that numerous approaches for glycerol transformation can be found in literature. Tang et al. [2] reported investigations of elastic polyesters derived from glycerol and aliphatic acid. Other ways of glycerol transformation are esters for detergents [3], cyclic acetals [4] or glycol [5]. Buhler et al. [6] reported the production of allyl alcohol, acetaldehyde and methanol from the treatment of glycerol under supercritical conditions. Watanabe et al. showed route from glycerol to acrolein [7].

Pyrolysis of glycerol to fuels was reported by Valliyappan et al. [8,9]. Catalytic transformation of glycerol to hydrogen was described by Hirai et al. [10] and Slinn et al. [11].

Also enzymatic approaches were reported by Papanikolau and co-workers [12,13] - citric acid and dimethyl carbonate were produced. As Velayutham et al. [14] reported that polyols from glycerol esterified with phthalic anhydride and oleic acid might be synthesized and subsequently used in polyurethanes.

In the present studies we have shown a short path from glycerol to polyurethanes via hyperbranched polyol intermediates (polyglycerols) and discussed properties and performance of the resultant adhesives.

Hyperbranched polyglycerols of various core and shell structures as well as various molecular weights were synthesized from glycerol using glycerol carbonate as intermediate. The obtained hyperbranched macromonomers were crosslinked with hexamethylene diisocyanate (HDI) and polymeric methylenediphenyl diisocyanate (PMDI). Properties of polyglycerols, adhesive formulations and the resultant polyurethane bond lines were investigated.

2. Materials and methods

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Glycerol was easily and conveniently transformed into the hyperbranched polyglycerols bearing polyether backbones using glycerol carbonate (GC) as an intermediate [15]. The route was shown in Fig. 1.

Three hyperbranched polyglycerols of various structures of core molecule and various inner sphere functionalities (Fig. 2) were used in this study: aliphatic molecule **1** with free hydroxyl groups, molecule **2** with hydroxyl groups partially blocked in the inner sphere with benzyls, molecule **3** with free hydroxyl groups and aromatic moiety in the core.

HBPGs, when thoroughly mixed with one weight equivalent of HDI or PMDI, were used as 2-component adhesives for beech wood bonding (30 min at 60°C under pressure 1.2 N/mm²). Samples for shear tests were prepared according to the respective European standard [16]. Reference series was bonded with commercial EPI adhesive under alike conditions.

Bond line densities were analyzed on a DA-X (GreCon) X-ray density profiler.

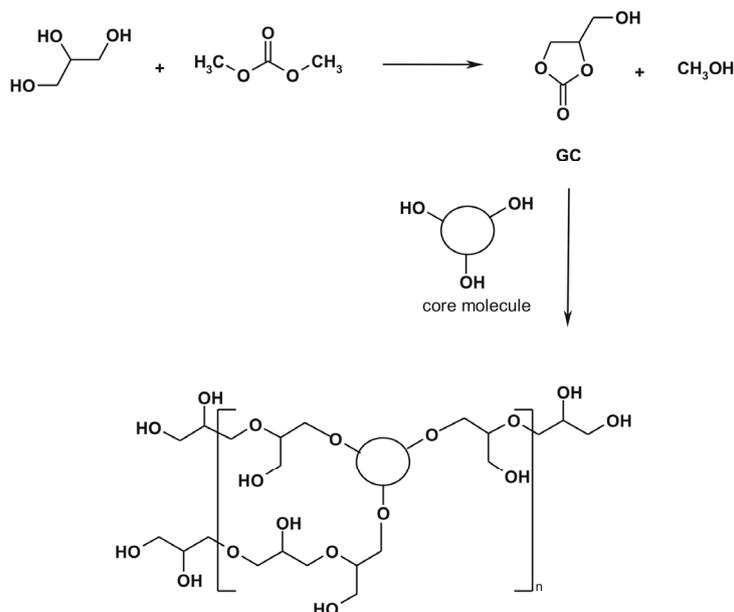


Fig. 1: Synthetic path to hyperbranched polyglycerol

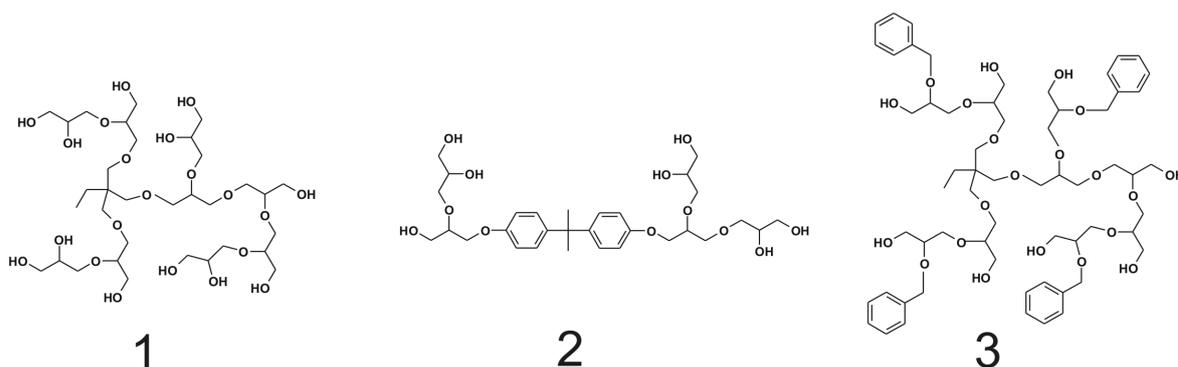


Fig. 2: Structures of the studied polyglycerols.

3. Results and discussion

As data in Table 1 indicate, used hyperbranched polyol components allowed for fast gelation of the adhesive systems, due to their high hydroxyl functionality. However, high viscosities of HBPGs **1** and **2** caused by abundance of hydrogen bonds are a drawback affecting ease of compounding.

Table 1. Viscosities of neat HBPGs and gelation times of adhesive formulation

HBPG	Viscosity [Pa s]	Gelation time at 20°C [min]	
		HDI	PMDI

1	29.0 (50°C)	— ^a	5
2	505 (50°C)	2	15
3	4.2 (20°C)	90	5.5

^a – immiscible

The resultant shear strengths of the adhesive joints were shown in Fig. 3. As the data indicate polyglycerols **2** and **3** when compounded with HDI or PMDI provide adhesives of excellent mechanical performance exceeding that of the substrate (100% wood failure) as well as bond line strengths exceeding that of commercial EPI bond lines. The lowest strength values were observed for fully aliphatic polyglycerol **1**, which can be explained by its poor mechanical properties as well as by high density of crosslinking caused by high hydroxyl functionality and subsequent brittleness of the polymer. On the other hand, lower hydroxyl functionalities of **2** and **3** accompanied by presence of rigid aromatic structures provided excellent performance of the polyurethane adhesive.

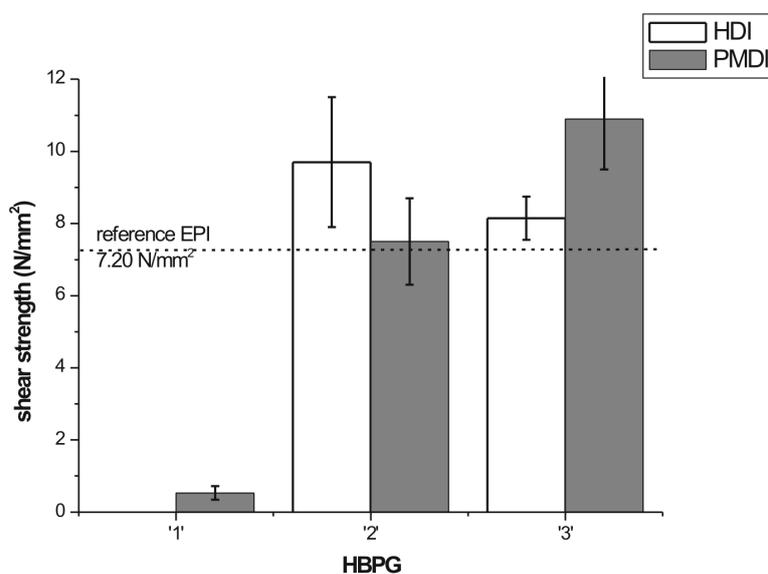


Fig. 3: Shear strengths of the studied joints made in solid wood

Thus, the presented results clearly showed that glycerol – a renewable raw material generated in bio-diesel production as a by-product – might be successfully transformed into polyol components of polyurethane adhesives. It was also proved that performance of polyglycerol-based polyurethanes was comparable and even exceeded that of some commercial systems. Measurements of bond line density profiles revealed that densities of the studied bond lines (980 kg/m³) were lower than those of reference commercial EPI (1090 kg/m³) (Fig. 4). The phenomenon may be explained by slight foaming of polyurethane, so that resultant density of the bond line was decreased.

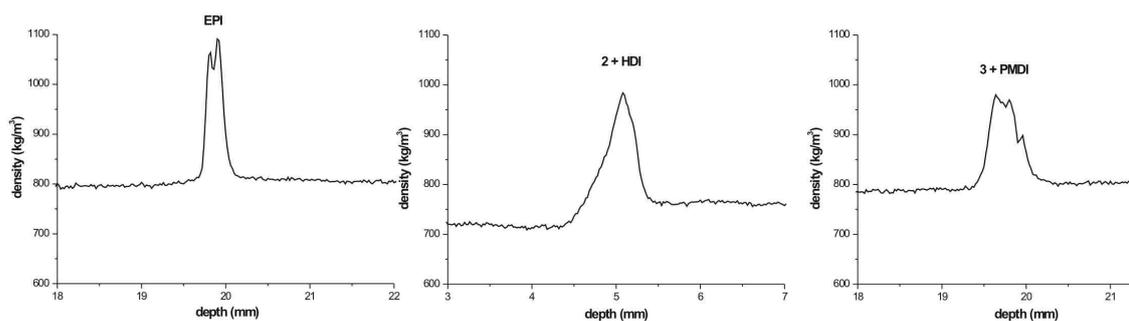


Fig. 4: Studied bond line density profiles.

4. Conclusions

It seems that hyperbranched polyglycerols derived from glycerol can be a convenient platform for development of environmentally friendly polyols and – in future – substitute or even replace petroleum-based ones. That approach should be considered as one of the alternative ways to novel, green adhesives derived from renewable resources. However, the presented results clearly showed that properly designed structure of a hyperbranched polyol was a factor strongly affecting performance of the bond lines.

5. Acknowledgements

This work was supported by grant no. N N209 032938 from The Ministry of Science and Higher Education to M. Mamiński.

6. References

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