



ELSEVIER

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Wood adhesives derived from hyperbranched polyglycerol cross-linked with hexamethoxymethyl melamines

Mariusz Ł. Mamiński^{a,*}, Małgorzata Czarzasta^a, Paweł Parzuchowski^b

^a Faculty of Wood Technology, Warsaw University of Life Science—SGGW, 159 Nowoursynowska St., 02-776 Warsaw, Poland

^b Faculty of Chemistry, Warsaw University of Technology, 3 Noakowskiego St., 00-664 Warsaw, Poland

ARTICLE INFO

Article history:

Accepted 20 June 2011

Available online 1 July 2011

Keywords:

Adhesives for wood

Cure/hardening

Polyglycerol

ABSTRACT

Wood adhesive system based on hyperbranched polyglycerol cross-linked with hexamethoxymethyl melamines was described. The obtained results showed that it was possible to develop polyglycerol-based interior-grade adhesive exhibiting dry shear strengths of the joints exceeding that of the solid wood. Gelling times of the studied formulations were comparable to those of the industrial thermo-setting systems (60–80 s at 100 °C). It was also found that wet shear strengths depended on functionality and F/Me molar ratio in the cross-linking resin.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Fluctuating supplies and slowly increasing prices of oil, environmental policies and pressing on extending the area of use of renewable resources have become the engine for an intensified development of purely *green* adhesives and/or increasing the rate of substitution of oil-derived non-renewable components with renewable and environmentally benign ones. One of the twelve principles of *green chemistry* is that “synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment” [1]. Recent years have brought demand on technologies based on those principles [2,3].

To date, in the field of wood adhesives much work have been done on that. Carbohydrates and plant oils [4,5] were used in preparation of polyurethanes. Soy protein-based and protein-PMDI hybrid wood adhesives were also reported [6–8]. Pizzi widely discussed opportunities of using bio-based adhesives for wood [9]. Much attention was paid to tannins, which can be conveniently cross-linked with a number of compounds and be used as wood adhesives [10–12] or can substitute to some extent non-renewable synthetic resins and, in consequence, decrease the content of petrochemical component in an adhesive [13,14]. As it was reported in literature, lignin could be added to phenol–formaldehyde resin without significant affecting the bonding results [15,16] or be cured with i.e. glyoxal forming formaldehyde-free adhesives [17].

Not only are the mentioned above renewable resources useful in adhesive technology, but also glycerol (1,2,3-trihydroxypropane) – the resource that still remains underutilized, available annually in

amounts reaching 1.2 million tones [18]. Glycerol – through simple synthetic and environmentally friendly route – can easily be converted into hyperbranched polyglycerols (HBPGs) according to the procedures described by Rokicki et al. [19]. It was recently shown that these polyglycerols could be further used as modifying agents for urea–formaldehyde resins [20]. Moreover, it has been proposed that their high hydroxyl functionality makes them promising reactive components of other types of thermosetting adhesives for wood bonding.

The papers regarding using of hexamethoxymethyl melamines (HMMM) as cross-linkers for liquefied wood [21], polyurethanes [22] or starch-poly(vinyl alcohol) system [23] revealed usefulness of this type of compounds in wood bonding. Thus, it seemed interesting to investigate whether – taking into account high reactivity of methoxymethyl group toward hydroxyls in acidic conditions – hyperbranched polyglycerols are capable of undergoing cross-linking with methoxymethyl melamines and whether the resultant adhesive joints can exhibit satisfactory performance. In order to examine actual strengths of the bond lines, solid wood was used as the reference substrate, instead of veneers as reported by Imam et al. [23].

If the approach occurred efficient, it might be found that hyperbranched polyglycerols coming from renewable glycerol were convenient eco-friendly components of adhesives allowing to decrease petrochemicals utilization rate.

2. Materials and methods

All chemicals were purchased from Sigma-Aldrich and used as obtained. Three hexamethoxymethyl melamines (HMMMs) in the form of viscous resins were kindly donated by Cytec Industries

* Corresponding author. Tel.: +48 22 593 85 27; fax: +48 22 593 85 48.
E-mail address: mariusz_maminski@sggw.pl (M.Ł. Mamiński).

Inc. (Woodland Park, NJ, USA). Their trade names were as follows: Cymel 303 (C303): monomeric with primarily methoxymethyl functionality, free HCHO <0.25%, F/Me ratio 1.16. Cymel 328 (C328): oligomeric with main methoxymethyl and imino functionalities, HCHO <0.7%, F/Me 1.34. Cymel 373 (C373) mainly methoxymethyl and methylol functionalities; HCHO <1.5%, F/Me 2.0. Viscosities were 6.5, 7.1, 7.1 Pa s, respectively.

Viscosities were measured at 20 °C on a Brookfield DV II+ Pro viscometer equipped with a spindle no. 64. FTIR spectra were recorded on Bio-Rad FTS165 instrument. Each spectrum was taken as an average of 32 scans at a resolution of 4 cm⁻¹.

Size exclusion chromatography (SEC) measurements were made on GPC LabAlliance apparatus with a Jordi Gel DVB Mixed Bed (250 mm × 10 mm) column using water as an eluent at 35 °C and poly(ethylene oxide) for the calibration.

2.1. Polyglycerol HBPG

Polyglycerol used in the studies was synthesized from TMP (1,1,1-tris(hydroxymethyl)propane) as the core of molecule and glycerol carbonate (GC) according to the procedure previously described elsewhere [19]. In a 0.5 L three-neck flask equipped with a magnetic stirrer, thermometer, dropping funnel and a bubble meter TMP (22.8 g, 0.17 mol) of was placed followed by 0.28 g (2 mmol) of potassium carbonate. The reaction mixture was heated at 160 °C. Glycerol carbonate (200 g, 1.69 mol) was added drop wise during 17 h at 160 °C. Then the reaction mixture was heated for additional 8 h until a characteristic cyclic carbonate band at 1786 cm⁻¹ disappeared completely in the FTIR spectrum. The crude product was obtained as a viscous dark yellow liquid. It was dissolved in 500 mL of water and potassium carbonate was neutralized with concentrated HCl. Water was removed under reduced pressure followed by an azeotropic distillation with toluene. The polymer was dried at 100 °C (0.05 Tor) for 6 h. Dark yellow oil of viscosity 9.5 Pa s at 20 °C was obtained. Yield 141.3 g (95%). Hydroxyl functionality was 13 based on ¹H NMR.

¹H NMR (400 MHz, D₂O), δ (ppm): 4.79 (H₂O, OH), 4.12–3.07 (m, 56H, polyether backbone), 1.38 (bs, 2H, CH₂CH₃), 0.93 (bs, 3H, CH₂CH₃); FTIR (KBr); cm⁻¹=3380, 2870, 1070; SEC: M_n=736, M_w=1268, D=1.72.

2.2. Adhesive preparation and bonding

Adhesive unit formulation: 1 part by weight of HBPG was thoroughly mixed with 1 or 2 parts by weight of the respective HMMM and 0.02 part by weight of 40% aqueous solution of p-toluenesulphonic acid (TSA). Viscosities and gel times of the formulations were shown in Table 1. The adhesive was applied (120 g/m²) onto the solid beech wood specimens (moisture content 5.2%, density 697 ± 15 kg/m³) prepared according to EN 205 standard and subjected to 240 s bonding in a hot press (180 °C) under pressure of 1.5 N/mm². The bonded samples were

Table 1

Characteristics of the studied adhesive formulations.

Components	Weight ratio	Gel time at 100 °C (s)	Viscosity at 20 °C (Pa s)	Pot-life (h)
C303 HBPG	1:1	70	7.42	12
C328 HBPG	1:1	60	8.61	8
C373 HBPG	1:1	75	8.77	8
C303 HBPG	1:2	80	8.75	12
C328 HBPG	1:2	60	9.12	8
C373 HBPG	1:2	70	9.10	8

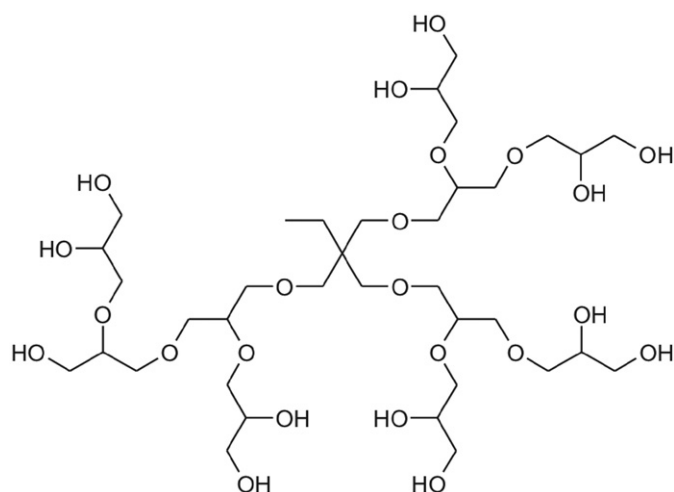


Fig. 1. Theoretical structure of the HBPG used in the studies.

conditioned at 20 ± 2 °C and 65 ± 5% relative humidity for 7 days. Pressing time and platen temperature were not optimized upon these investigations.

2.3. Shear strength of the joints

Test samples (150 × 20 × 5 mm³) of the lap area ca. 200 mm² were subjected to shear strength tests. The reference samples were bonded with pure HMMM cured with 0.02 part by weight of TSA under alike bonding conditions. Twenty samples were tested in each series (Fig. 1).

3. Results and discussion

3.1. Shear strengths

In order to investigate applicability of hyperbranched polyglycerols as components of adhesives, formulations containing various amount of cross-linkers (i.e. methoxymethyl melamines) were prepared. From the data in Table 1, it is apparent that regardless of the components weight ratio, gel times of the formulations remain within the range typical for thermosetting systems in wood bonding. Thus, the reactivity of the adhesives was found to be appropriate for the bonding tests.

In Fig. 3 bond line shear strengths for neat HMMMs were presented. The series was mentioned as reference. As the data in Fig. 2 indicate, it is possible to perform bonding with neat HMMMs. The obtained strengths regardless of the HMMM type were satisfactory. In all cases, when dry, cohesive failure in wood was observed. Differences between means for C303 (7.3 ± 1.2 N/mm²) and C328 (9.0 ± 1.7 N/mm²) were not significant, but the differences between C303 and C373 (10.8 ± 1.0 N/mm²) were significant. The strengths for wet series after 24 h water soaking were lowered by 32%, 46% and 69%, respectively.

In order to decrease content of a synthetic component in the adhesive system, some part of methoxymethyl melamine was substituted by hyperbranched polyglycerol (HBPG). In Fig. 3 shear strengths of the adhesives containing 50 wt% of HBPG were shown. It is apparent that for the dry bond lines strengths were not affected and remained at high level—above the strength of the substrate (100% wood failure). All three series exhibited comparable values 8–8.6 N/mm². After 24 h water soaking, the specimens were subjected to shear strength tests. It was found that 50 wt% addition of HBPG did not alter strength of the bond

Download English Version:

<https://daneshyari.com/en/article/773449>

Download Persian Version:

<https://daneshyari.com/article/773449>

[Daneshyari.com](https://daneshyari.com)