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Influence of N,N-dimethylformamide on one-component moisture-curing polyurethane wood adhesives

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ABSTRACT

The influence of the solvent N,N-dimethylformamide (DMF) on one-component moisture-curing polyurethane (1C-PUR) bonded wooden specimens was investigated. The applied methods were ATR-IR spectroscopy, VIS-NIR spectroscopy, FT-IR microscopy, UV Fluorescence microscopy, Nanoindentation, and AFM imaging. Findings reveal that DMF influences the curing kinetics of the 1C-PUR, supporting its thorough conversion by affecting the morphology and mechanical properties of the cured adhesive. Furthermore, DMF partially dissolves the wood's lignin and seems to make bound wood moisture more available for reaction with the adhesive. The outcomes confirm that 1C-PUR enters neither the wood cell walls nor the wood rays. The vessel system of the early wood represents the major pathway for the penetration of 1C-PUR into the beech wood.

1. Introduction

N,N-dimethylformamide (DMF) is an organic, polar, toxic and hygroscopic solvent. It is used in polyurethane synthesis, because it promotes sufficient solubility of reactants such as diisocyanate and catalysts [1]. This contributes to a homogeneous reaction and to comparatively high yields in polyurethane production. When used as a primer, DMF is capable of improving wood failure percentage (WFP) and tensile shear strength (TSS) of moisture-curing one-component polyurethane (1C-PUR) bonded wooden joints in the dry and wet states [2]. Within this work it was also found that DMF greatly enhances the wettability of the wooden adherend, thus supporting the joints' performance. Another explanatory approach for the effect of DMF on the performance of such joints was given by implementing the outcomes into the Swelling Strain Model described by Frihart [3]. However, various questions are still open. Therefore the current work intends to contribute to the basic understanding on how DMF affects the 1C-PUR adhesive (fluid or hardened) and the wooden substrate. The most reactive compounds of 1C-PUR wood adhesives are isocyanates, such as polymeric diphenyl methane diisocyanate (pMDI). The reaction of DMF with arylisocyanates at boiling temperature was investigated by Weiner [4] and Jovtscheff [5]. They found that aromatic isocyanates like phenylisocyanate or naphthylisocyanate react with DMF, emitting carbon dioxide and forming dimethylformamidine. However DMF did not react with aliphatic isocyanates under these conditions, demonstrating that reactions between DMF and isocyanates are highly dependent on the isocyanates' molecular structure. Joel et al. [6] also dealt with reactions between phenylisocyanate and DMF. They proclaimed that at 20 °C and in the presence of water the isocyanate is initially hydrolyzed during the first 24 h, leading to the formation of diphenylurea. However no conversion of the aryl isocyanate with the solvent could be found up to 120 h reaction time at 20 °C, but after about 48 h reaction time the isocyanate and the urea slowly started to convert into triphenylbiuret. In the presence of polyurethane catalysts, substantial amounts of these biuret structures were already found after 24 h at 20 °C. A temperature rise to above 60 °C was required before the phenylisocyanate and the DMF reacted with each other without catalysts, thereby liberating CO_2 gas and forming phenylformamidine. This is consistent with reactions described by [4,5]. As Ulrich [7] summarized the interactions between polar solvents (or their impurities) and diisocyanate at elevated temperatures can also cause undesired side reactions in PUR production, leading to chain termination or undesired additional crosslinking. Both reactions disturb the homogeneous molecular

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weight distribution in the final polyurethane. Ulrich assumes that the lower the temperature during polymerization, the less the undesired side reactions that occur. Summing up, no evidence in the literature was found for any substantial direct reactions between DMF and the isocyanates present in 1C-PUR adhesives at 20 °C in the presence of (wood-) moisture. Nonetheless DMF is basically capable of influencing the morphology of PUR polymers after curing, which is characterized by content and distribution of dispersed hard segments in the soft segment matrix. As Oprea [8] concluded, such a variation in morphology is accompanied by an alteration of hydrogen bond interactions within the hard segments and between hard and soft segments. He found accordant changes in tensile strength and Young's modulus by means of tensile tests. In addition to its influence on the polyurethane, the solvent DMF also interacts with wood. Ashton [9] described the fast swelling of hardwood after immersion in DMF at room temperature and concluded that DMF has even more swelling potential than water. This corresponds with Mantanis et al. [10], who added that the comparatively low molecular weight and the high basicity of this amide support its wood swelling potential. Based on results by Nayer [11] Mantanis et al. [12] also stress the DMF's high capability to establish hydrogen bonds to the OH groups of the cellulose, thus enhancing the wood's swelling. However DMF does not dissolve the cellulose itself, not even after prolonged heating [13]. Therefore DMF was used for the Soxhlet extraction of wood chips, leading to polar extracts [14]. The present work investigates the influence of DMF on the curing process at 20 °C and the resulting properties of 1C-PUR bonded wooden joints.

2. Materials and methods

2.1. Adhesive

The commercial 1C-PUR wood adhesive HB S 309 (Purbond AG, Switzerland) was used for all the experiments (Viscosity Brookfield ca. 24,000 mPa s). It is approved for glulam production in Europe.

2.2. DMF and acetone

The DMF (C_3H_7NO, MW 73.09 g/mol) used for the current work is a high boiling, polar aprotic, hygroscopic and toxic organic solvent with a comparatively high dipole moment of 3.24 D [9,15,16] produced by Sigma-Aldrich, puriss p.a., ACS reagent, reag. Ph. Eur. ≥ 99.8% (GC), vapor pressure at 2.7 mmHg (20 °C). The acetone used (puriss ≥ 99.9%) was produced by Azelis GmbH, Germany.

2.3. Wood

The diffuse porous European beech wood (*Fagus sylvatica* L.) with a measured average raw density of 0.67 g/ cm^3 was used as the adherend for the bonding processes. Before further experimental processing the wood was cut into slats of 8 mm thickness and stored in 20 °C/65% relative humidity (RH) climate for at least 2 weeks, resulting in a 12.5% average wood moisture content. Slats with discolorations, wavy direction of grain or other flaws were sorted out. Consequently the slats were mixed to randomly scatter influences of the wood over the whole sampling.

2.4. Manufacturing of bonded samples

Within 1 h after planing the conditioned slats underwent the gluing procedure according to [17]. An amount of 180 g/m^2 1C-PUR adhesive was applied (to one side) by means of a toothed spatula. Consecutively the pressing was performed over 75 min at a specific pressure of 0.8 MPa using a jig in a calibrated press. Afterward the pressed parts were stored at 20 °C/65% RH for at least 3 days in order to assure sufficient hardening of the adhesive. DMF was used as a primer on some specimens before application of the 1C-PUR. The accordant adherends underwent the priming process within 30 min after planning; 40 g/ m^2 DMF was applied onto a metal sheet using a paintbrush, avoiding a spray mist. Subsequently, the surfaces to be bonded were covered with the sheets. This technique provided a more homogeneous liquid spread than direct brushing onto the wood. The adhesive was applied 30 min after the DMF treatment.

2.5. IR-ATR investigation on fluid 1C-PUR droplets

Recent studies used FT-IR and IR-ATR for analysis of adhesive droplets and reaction kinetics [18–20], since this method is accurate, swift and comparatively easy to perform. In the current study, spectra of the 1C-PUR adhesive droplets (Figs. 1–3, 5) were collected whilst hardening by means of a Nicolet Avatar 320 FT-IR-ATR spectrometer with a resolution of about 4 μm in combination with Omnic software. The device was equipped with a diamond crystal, leading to an average light penetration depth of ca. 5 μm. The measured bands of the highly reactive isocyanate (NCO) groups served as a reference for the progress of the hardening reaction in accordance with [19]. In addition to the 1C-PUR adhesive, three mixtures were prepared in total (1C-PUR: DMF = 10:1 and 10:5; 1C-PUR:acetone = 10:5). A droplet of each

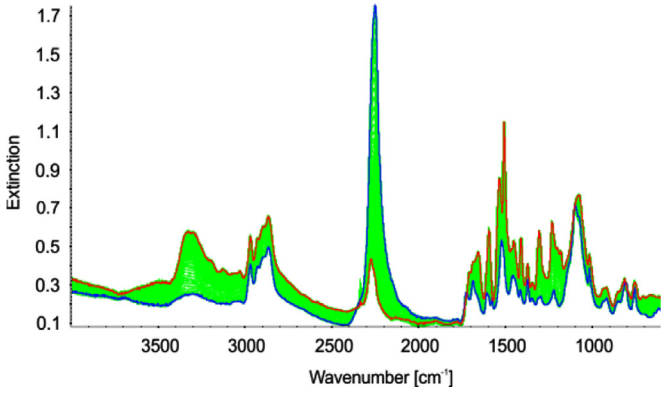

Fig. 1. ATR spectrum of a fluid 1C-PUR droplet during hardening. Blue spectrum collected after 10 min, red spectrum collected after 24 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

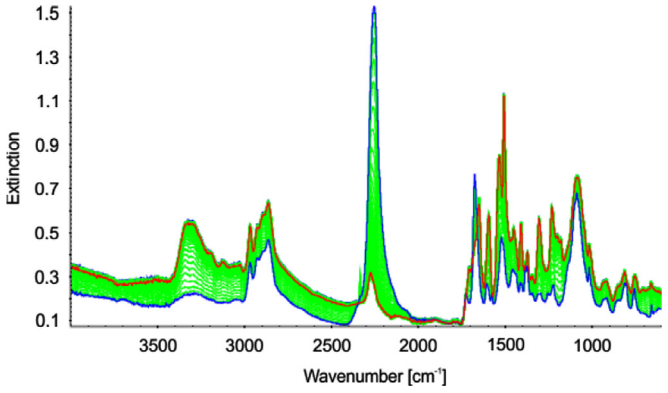

Fig. 2. ATR spectrum of a fluid droplet during hardening. Droplet mixture 1C-PUR: DMF = 10:1. Blue spectrum collected after 10 min, red spectrum collected after 24 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)