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Cure chemistry of wood/polymeric isocyanate (PMDI) bonds: Effect of wood species

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Abstract

The wood-species dependent performance of polymeric isocyanate resin (PMDI) was investigated by fracture analysis and solid-state NMR. The fracture performance of two different woods (yellow-poplar and southern yellow pine) bonded with PMDI was evaluated using mode-I cleavage. The fracture toughness of pine samples was significantly greater than the corresponding yellow-poplar samples. Separately, the cure chemistry of wood/PMDI bondlines was investigated by solid-state NMR with nitrogen-labeled (N^{15}) resin, and by employing spectral decomposition of the complex resonance arising from protonated nuclei. A small but statistically significant species effect was found in both the cure chemistry and in the proton rotating-frame relaxation for samples cured at lower temperatures. These differences were not found at higher cure temperatures. This suggested that a species effect might arise in the core of commercial wood-based composite panels, where lower cure temperatures are found. Wood acetylation altered the wood-PMDI cure chemistry by reducing the relative signal intensity in the urethane spectral region by 35%. However acetylated wood specimens still exhibited significant N^{15} signal in the urethane spectral region. Since little or no urethane was expected from acetylated samples, an unequivocal urethane detection remains elusive, and if it is detected its occurrence was grossly overestimated by the spectral decomposition employed in this work.

Keywords: A-adhesives for wood; S-wood; M-fracture mechanics; Solid-state NMR

1. Introduction

Polymeric diphenylmethane diisocyanate (PMDI) is an important adhesive for the manufacture of oriented strand board (OSB) and similar particulate wood-based composites. This wood binder polymerizes into a polyurea/polybiuret network through a rapid reaction with adsorbed wood moisture [1]. The adhesive is also capable of forming covalent urethane bonds with wood [2], which serve to enhance bondline durability. The general nature of PMDI cure chemistry with wood is depicted in Fig. 1.

PMDI resins are known to exhibit a wood species-dependent performance [3–5]. This is of great practical significance because the wood species mixture in OSB manufacture will vary daily as a function of timber availability; resin performance and composite properties will vary accordingly. This work attempts to reveal the nature of the species-dependent performance of PMDI resins. In this case, resin performance is compared by means of mode-I fracture testing of southern yellow pine and yellow-poplar, two woods that are commonly used for OSB manufacture in the southeastern United States. Aspects of the cure chemistry and morphology of pine and poplar bondlines are compared by means of solid-state NMR of magnetically labeled PMDI resins cured with these two woods.

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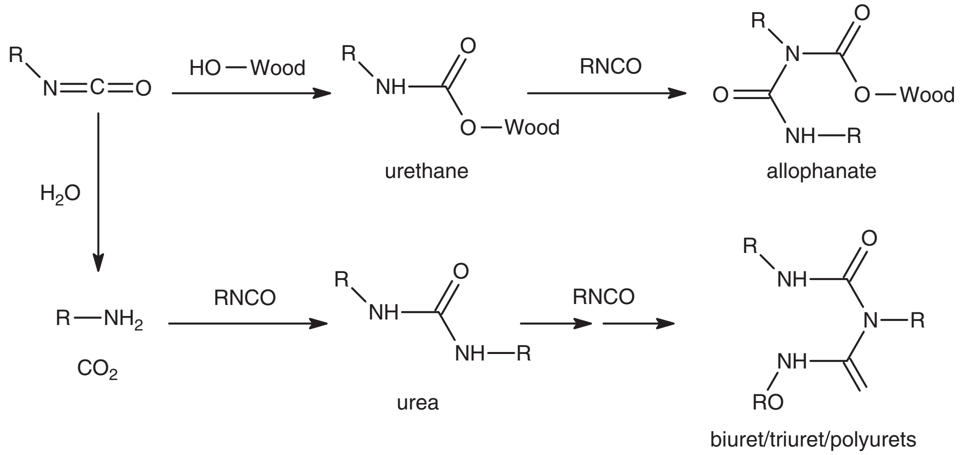

Fig. 1. Generalized reaction of PMDI resin with wood.

2. Experimental

2.1. Materials

Commercial PMDI resin (Huntsman Rubinate 1840) was obtained from Hunstman Polyurethanes and was used as received. ^{13}C-Carbon monoxide (99% ^{13}C) and ^{15}N-aniline (98% ^{15}N) were purchased from Cambridge Isotope Laboratories and used as received. All other chemicals were purchased from Aldrich Chemical Company and used as received.

Two different wood species were tested: yellow-poplar (*Liriodendron tulipifera*) and southern yellow pine *(Pinus* spp.). Blocks of yellow-poplar and southern yellow pine were softened by soaking in distilled water. Flakes (5.1 cm × 5.1 cm × 0.6 mm) were sliced from the radial wood surface with a disk flaker. Flakes were dried at 105 °C for 24 h to determine dry weights and were equilibrated at ambient conditions to achieve 6–7% moisture content (MC).

2.2. Methods

2.2.1. Doubly labeled PMDI (^{15}N, ^{13}C) synthesis

Synthesis of doubly labeled PMDI resin was conducted as described previously [1,2] with the following modifications. The acid catalyzed condensation of formaldehyde with ^{15}N-aniline was conducted with aniline to formaldehyde molar ratio of 4:1 and aniline to HCl molar ratio of 1:1.5.

The synthesis of ^{13}C-phosgene was conducted by reacting chlorine (3.58 g, 50.4 mmol) with ^{13}C-carbon monoxide (1.22 L, 50.4 g) in 1,2-dichlorobenzene (ODCB) [2]. ODCB (75 mL) was transferred into a sealed, dry 100-mL graduated cylinder with a canula. Chlorine gas was bubbled into the ODCB until the desired amount (3.58 g) was obtained. The Cl_2/ODCB solution was transferred to a 200-mL flask fitted with two stopcock valves. One stopcock opening was sealed with a rubber septum, while the other was connected to the reaction vessel through chemical-resistant tubing. The reactor was a five-necked, 1-L, glass reactor vessel (1-L Ace Glass medium-pressure, glass reactor), which was initially evacuated to a pressure of 0.5 mmHg and then cycled with dry nitrogen and vacuum twice before it was filled with ^{13}C-carbon monoxide. The Cl_2/ODCB solution was then forced into the reactor with compressed nitrogen. The reactor was sealed off and the reaction was allowed to proceed at 55 °C for 36–48 h under vigorous agitation. The reactor was then cooled to room temperature and excess chlorine was removed by the addition of 0.5 mL of 1-phenyl-1-cyclohexene. Phosgene was purified by transferring it to a cold trap (immersed in liquid nitrogen) by means of intermittent application of vacuum to the cold trap. After the phosgene purification/transfer was complete, ODCB (100 mL) was added to the cold trap through a canula. The phosgene/ODCB solution was then allowed to warm to room temperature. The phosgene yield (57%) was determined by iodometric titration [6].

The phosgenation was conducted in a separate 5-necked, 1-L, glass reactor vessel (1-L Ace Glass medium-pressure, glass reactor). ^{15}N-polyamine was vacuum-dried (60 °C, 0.6 mmHg) for 2 h in a 50-mL double-necked flask. ODCB (25 mL) was transferred into the flask through a canula and the solution was allowed to cool to room temperature. A dark brown polyamine/ODCB solution was obtained. Phosgene/ODCB solution was transferred into the evacuated (0.5 mmHg) five-necked glass reaction kettle submerged in an ice water bath. The polyamine/ODCB solution was then transferred into the reactor through a canula, while vigorous agitation was maintained. The reactor was sealed off and slowly heated to 180 °C, followed by reaction at that temperature for 20 min. During reaction, the gas pressure inside the reactor was released twice, at 10 and 20 min, after the reaction temperature (180 °C) was attained. After phosgenation, the reaction mixture was filtered through a Buchner glass filter under a nitrogen blanket into a 250-mL round-bottomed flask. The reaction mixture was vacuum-distilled at 0.3 mmHg and 60 °C to remove ODCB. The doubly