Elastic Properties of Adhesive Polymers. III. Adhesive Polymer Films Under Dry and Wet Conditions Characterized by Means of Nanoindentation

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ABSTRACT: The mechanical properties of cured wood-adhesive films were tested in dry and wet states by means of nanoindentation. A fluid cell was used to monitor possible property changes as a function of changing moisture content. Under wet conditions, the elastic modulus and hardness of all tested adhesives (i.e., urea formaldehyde, melamine urea formaldehyde, phenol resorcinol formaldehyde, and one-component polyurethane) were reduced to about half of their values in the dry state. After renewed drying, all adhesives largely recovered their initial mechanical properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1331–1334, 2010

Key words: adhesives; films; indentation; mechanical properties; resins

INTRODUCTION

Wood-composite structural elements are often exposed to temperature and humidity variation in service. For the wood-adhesive bonds in structural parts, this means that in addition to structural loads, loads due to the swelling and shrinkage of wood have to be sustained with changing moisture levels. Several studies have determined the influence of various moisture conditions on bond performance.[1–3] These studies have found that adhesives perform quite differently under similar conditions, with this depending on the type of adhesive used. Test setups for international standards[4,5] therefore consider a variety of moisture treatments for the testing of wood-adhesive bonds. These standardized tests usually examine the performance of the entire bond, which is determined by both the performance of the adherent wood and the adhesive itself. For wood, a strong dependence of the mechanical properties on the moisture content is well known.[6] With respect to the performance of cured adhesive polymers under wet conditions, a lack of information is evident, and this is in part due to experimental limitations. For instance, in a simulation of the hygroelastic behavior of wood-based composites for construction, the simplification of assuming that the cured adhesive was insensitive to moisture was made.[7] Irle and Bolton[8,9] were among the first who tried to characterize the physical properties of formaldehyde-based adhesives films. They found urea formaldehyde (UF) adhesives to be much more rigid than phenol formaldehyde (PF) adhesives under dry conditions. PF was found to be extremely hygroscopic, and high humidity had a stronger effect on the mechanical properties of the PF adhesive versus the UF adhesive. Bond performance, in contrast, was better for PF-bonded particleboards under both dry and wet conditions. Muszynski et al.[10] found the mechanical properties of phenol resorcinol formaldehyde (PRF) adhesive films to be highly sensitive to changing moisture contents in comparison with other adhesives. The high durability of PRF bonds was explained by the fact that the hygromechanical properties of the adhesive and wood were at comparable levels in the case of PRF. Furthermore, Muszynski et al. stated that tests with pure adhesive films are difficult and are associated with potential error because of problems encountered in the production of uniformly thin, completely cured, and reproducible films.

In the first part of this study,[11] we presented methods of preparing thin adhesive films and methods of determining basic mechanical properties (elastic modulus and Poisson ratio) of different adhesives typically used in wood bonding. In the second part of this study, nanoindentation was

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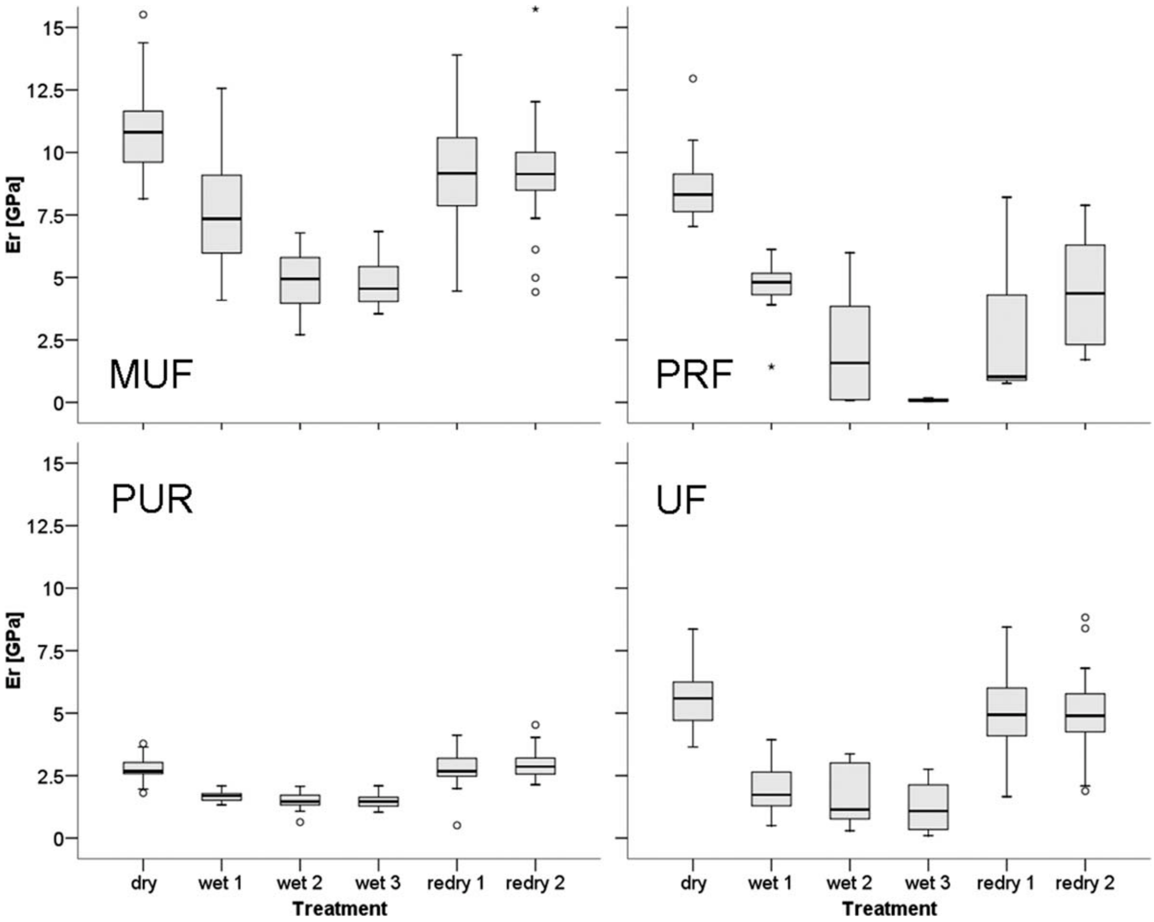

Figure 1 Reduced elastic modulus (E_r) for different wood adhesives in a dry state and at different points of time in wet and redried states.

identified as a proper tool for directly characterizing mechanical properties (elastic modulus, hardness, and creep behavior) of thin adhesive films as well as cured adhesive present in the bond line.[12] Also, the influence of temperature on the mechanical properties of adhesive films was measured by nanoindentation.[13] With respect to moisture, Bell at al.[14] introduced nanoindentation as a tool for measuring the mechanical properties of nylon 6 in an ambient fluid. Clear differences in the mechanical properties and an effect on the glass-transition temperature were found after 24 h of water impregnation, and this was attributed to a decrease in hydrogen bonding in the amorphous regions of the polymer.

In this study, we examined the influence of water on the mechanical performance of different typical wood adhesives in the form of polymer films with a known wide range of properties in the dry state.[12] With nanoindentation used as a tool for determining the mechanical behavior under dry and wet conditions, specimen preparation was simple as only small pieces of cured adhesive were necessary for the nanoindentation tests. The results should contribute to a better understanding of the different performances of wood-adhesive bonds under dry and wet conditions.

EXPERIMENTAL

Adhesive-film preparation

Thin adhesive films were prepared as described in detail in a previous article[11] from four different wood adhesives: UF (W-Leim Spezial, Dynea Austria GmbH, Krems, Austria), melamine urea formaldehyde (MUF; Dynomel L-435 with the hardener H469, Dynea Austria), PRF (Aerodux 185 with the hardener HR150, Synthesa Chemie GmbH, Perg, Austria), and one-component polyurethane (1K PUR, Purbond HB110, Collano AG, Sempach, Switzerland). UF is designed for interior use, MUF and 1K PUR fulfill standards for load-bearing engineered wood products, and PRF is approved for the bonding of aircraft wood structures (German Federal Air Authority). Pieces of adhesive films with dimensions of approximately 5 × 5 mm^2 and a thickness of 0.2–0.5 mm were cut from cast adhesive films and glued to metal discs with epoxy resin.

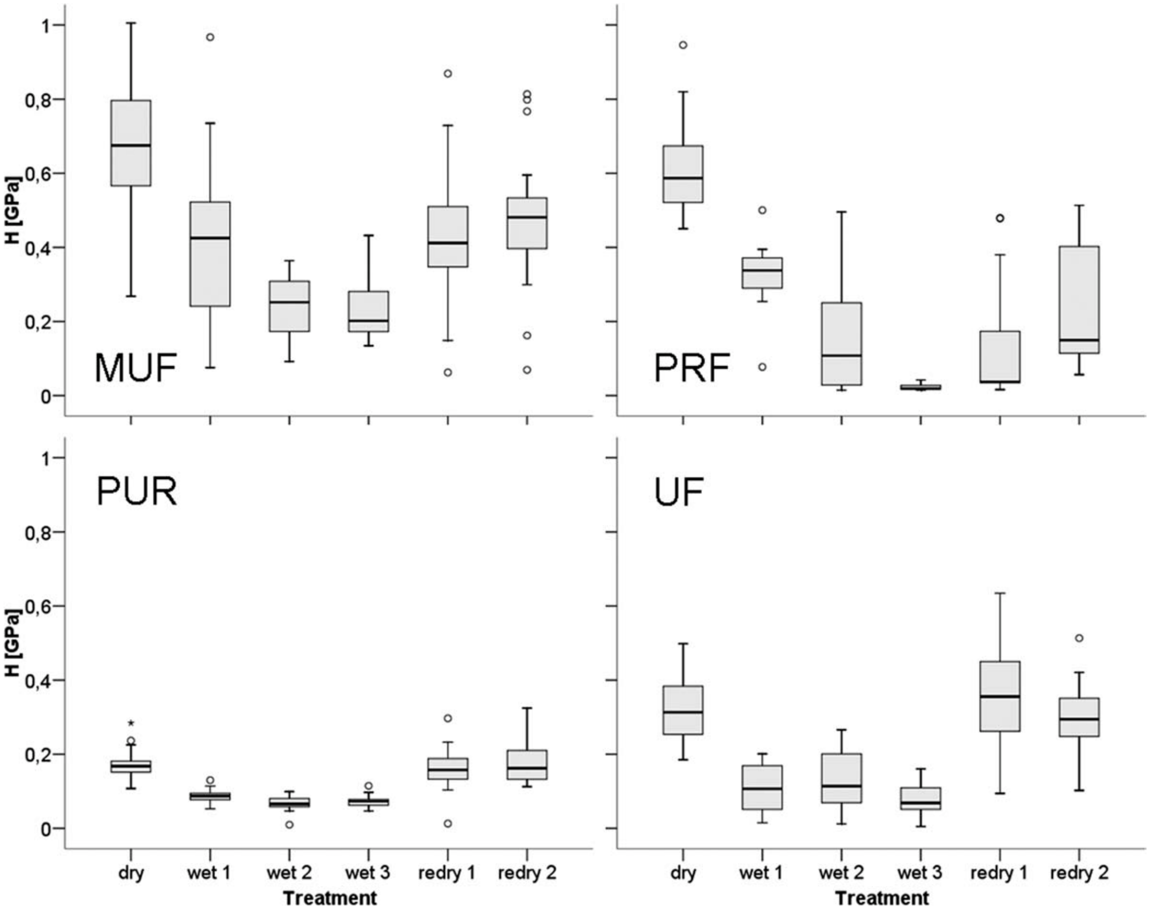

Figure 2 Indentation hardness (*H*) for different wood adhesives in a dry state and at different points of time in wet and redried states.

Mass change due to water exposure

Water loss was measured as an indicator for the absorption of water by the polymer. It was assumed that there was an insignificant difference between water uptake and water loss due to redrying.

Five pieces of adhesive film [ca. 5×5 mm^2 and 2×2 mm^2 in the case of polyurethane (PUR)] per adhesive type were stored in deionized water for 3 days at room temperature to examine the water uptake. The mass loss of the water-saturated films was measured after 18 h of vacuum drying at 40°C and was assumed to correspond to the water loss.

Nanoindentation

Nanoindentation was chosen for the mechanical characterization of the adhesive films. All nanoindentation experiments were performed with a Hysitron TriboIndenter system (Hysitron, Inc., Minneapolis, MN) equipped with a fluid cell and a three-sided pyramidal diamond fluid cell indenter tip (Berkovich type). The previously specified samples were clamped magnetically to the indenter stage. Two different specimens for each adhesive film were examined with 15 indents under dry conditions and 8 indents under wet conditions. Measurements were performed first in the dry state for reference (24°C and 35% relative humidity). Afterwards, specimens were immersed in deionized water, and measurements were performed after 2, 24, and 30 h of immersion. Thereafter, the specimens were allowed to dry under the ambient conditions (24°C and 35% relative humidity) and were tested twice in the dry state after drying times of approximately 12 and 26 h. Experiments were performed in a load-controlled mode with a preforce of 2.5 μN and a three-segment load ramp: load application within 3 s, a hold time of 20 s, and an unloading time of 3 s. The peak load was 600 μN for all indents performed. The load–depth curves were evaluated according to the Oliver–Pharr method,[15] and this resulted in the hardness and reduced elastic modulus as described in more detail in a previous study.[12]

RESULTS AND DISCUSSION

Absolute values for the reduced elastic modulus for all sets of measurements performed in dry and wet

TABLE I
Water Content of Adhesive Films After Storage in Water for 3 Days

	Mass loss (%)	
Adhesive	Mean	Standard deviation
MUF	8.16	2.68
UF	29.74	2.18
PRF	25.35	1.55
PUR	6.38	6.94

The water content was evaluated from the mass loss of the adhesive films after vacuum drying at 40°C.

states are shown in Figure 1. In their initial dry condition, the mechanical properties of all four adhesives were significantly different, as already known from earlier studies.[11,12] For both the reduced elastic modulus and the hardness (Fig. 2), the highest values were found for MUF, which was followed by PRF, UF, and PUR. Because both the hardness and the reduced modulus of elasticity reacted in an almost identical manner to wetting and redrying, the two properties are addressed together with the term *mechanical performance* in the following discussion. Already after 2 h of immersion in water, all adhesives showed a highly significant loss in mechanical performance; this was moderate for PUR and MUF (-40%) and more pronounced for PRF and UF (-50 to -60%). In general, the loss in mechanical performance was intensified by continued immersion in water. After 30 h of immersion, the most striking loss in performance was found for PRF (-90%) and UF (-80%), whereas PUR and MUF remained relatively stable with losses of 40% and 60%, respectively. The difference in behavior between PRF and UF on the one hand and PUR and MUF on the other hand corresponded well to the highly significant mass change due to water loss measured for PRF (25%) and UF (30%). Also, for MUF, a less substantial but still significant mass change of 8% due to water loss was observed, whereas the water loss of 6% determined for PUR was not significant in a statistical sense because of the very high variability associated with these measurements (Table I). It thus seems reasonable to assume that the water taken up by the polymer acts as a softener and leads to a loss in mechanical performance. Apparently, the PRF and UF studied here disposed of a significant capacity for absorbing water, and this made them susceptible to a sorption-induced loss in mechanical performance. In contrast, MUF seemed to be much less accessible to water and therefore more stable in a wet environment. Finally, PUR, the least hydrophilic polymer, showed the smallest change in mechanical performance after water storage (Figs. 1 and 2).

After the nanoindentation tests under wet conditions, the water was removed, and the specimens were allowed to dry under the ambient conditions for 12 and 26 h. Because of drying, all the adhesives regained the mechanical performance lost in a wet environment. This recovery was clearest for PUR, which already regained its original performance after 12 h. A similar recovery to 80–90% of the original values in the dry state was observed for UF and MUF. In a statistical sense, the reference values and values after redrying were similar (t test analysis, $P = 0.05$) in the case of UF, and this led us to the assumption that UF also fully recovered, but MUF marginally did not. In contrast, the recovery was very slow for PRF, and even after 26 h of drying, it reached only a level of 50% with respect to the initial dry performance. As there was a clear trend of increasing performance from 12 h of drying to 26 h of drying for PRF (Figs. 1 and 2), it can be assumed that recovery would have continued to higher levels after prolonged drying, but no further measurements were performed.

CONCLUSIONS

This study demonstrates that nanoindentation is capable of characterizing changes in mechanical properties of adhesives due to water uptake *in situ*. All the characterized adhesives showed a very significant loss in mechanical properties due to uptake water, which was largely recovered after drying. This fact being established, future studies will concentrate on the effect of the moisture sensitivity of adhesives on the performance of wood-adhesive bonds in the wet state.

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