

REDUCING MOISTURE SWELL OF DENSIFIED WOOD WITH POLYCARBOXYLIC ACID RESIN

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(Received November 1999)

ABSTRACT

A water-soluble polycarboxylic acid (PCA) resin was assessed for ability to limit moisture swelling of densified wood. Aspen flakes were treated in 0 (control), 1, 5, 10, and 20% PCA resin solutions and drained for 1, 10, and 20-min time periods. Following treatments, flakes were compressed to roughly 50% strain at 170°C. The PCA content of flakes significantly increased with increasing concentration and drain time. Water absorption and thickness swell of flakes decreased with increasing PCA content. Both water absorption and thickness swell of untreated flakes were over 100%; but for PCA-treated flakes, water absorption and thickness swell as low as 45% and 16%, respectively, were achieved. Irreversible thickness swell decreased with increasing PCA content, while reversible thickness swell remained relatively constant. The swelling coefficient decreased with increasing PCA content, a behavior that often is associated with bulking agents for treated, uncompressed wood. However, dynamic mechanical analysis further suggested that PCA resin acts as a cross-linking agent to stabilize the position of the collapsed cell walls.

Keywords: Dimensional stability, moisture, polycarboxylic acid, swelling, trimellitic anhydride, water, wood.

INTRODUCTION

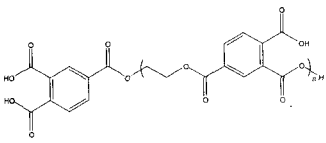
In many wood-based composites, the wood is densified during pressing, collapsing the hollow wood cells. Large amounts of swelling can occur when the original cell structure recovers after exposure to water. This swelling often results in internal stresses that can degrade the material structure and decrease the useful life of the composite. Some chemical treatments have reduced moisture swelling in wood by acting as bulking or cross-linking agents. Bulking agents, such as resins, anhydrides, and polyethylene glycol, lim-

it swelling by decreasing hydroxyl functionality and filling the free volume of wood where water would otherwise reside. Multifunctional reactive agents such as formaldehyde have also provided moisture stability for wood by acting as a cross-link agent for the wood polymers (Stamm 1964).

A polycarboxylic acid-based (PCA) resin was recently developed to act as a moisture inhibitor. The overall objective of this study was to assess the ability of PCA resin to reduce the moisture swelling of densified wood and determine whether PCA resin possesses bulking or cross-linking characteristics.

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TABLE 1. Physical and chemical properties of water-soluble polycarboxylic acid (PCA) resin used to treat aspen flakes.

Polycarboxylic Acid Characteristics		
Solids	50%	
Water	50%	
Acid number	250 mg KOH/gm	
PH	1.5	
Density	1.21 gm/cc	
Viscosity @ 25°C	50 cP	
Color	Pale yellow to amber	
Clarity	Clear	
		Oligomer analysis:
		n = 0; 5.5 wt. %
		n = 1; 30 wt. %
		n > 1; 14.5 wt. %

MATERIALS AND METHODS

Polycarboxylic acid resin

Aromatic polycarboxylic acid (PCA) resin (Table 1) was prepared from trimellitic anhydride and ethylene glycol according to the procedure of Anderson et al. (1998, 1999). Trimellitic anhydride and ethylene glycol were combined in the melt at a mole ratio of 2:1 and heated with removal of water. The molten reaction product was poured into hot water to hydrolyze the anhydride groups to carboxylic acids and provide a concentrated aqueous solution of the aromatic polycarboxylic resin. The trimellitic anhydride is a commercial product of BP Amoco Chemicals. The anhydrous resin contains about 11% mass trimellitic anhydride, 60% ethylene glycol bis[anhydrotrimellitate], and 29% trimellitic anhydride/ethylene glycol oligomers as identified by matrix-assisted laser desorption time of flight mass spectrometry. The resulting aromatic PCA resin is water-soluble and can be dissolved in water at 50% mass of solids to produce a stable aromatic polycarboxylic solution.

Specimen preparation

Aspen (*Populus tremuloides* Michx.) logs were quartered to produce sections with a radial face. Blocks cut from the quarters were submerged in distilled water under vacuum for 2 h. A microtome was used to slice 0.6-mm-thick flakes from the blocks. The flakes were

oven-dried between plate glass at 103°C to minimize warping and thermal degradation. The flakes were then sorted for defects, allowed to equilibrate at room temperature, and cut to roughly 12- × 24-mm dimensions. The moisture content of the flakes was approximately 6% prior to treatment.

Flakes were soaked for 2 min in 100-ml solutions of PCA resin prepared at 0 (control), 1, 5, 10, and 20% concentrations, removed, and drained for 1, 10, and 20 min to allow for PCA adsorption into the wood. Flakes were not blotted dry after draining. Six flakes were assigned to each treatment. The PCA content was determined as the percent mass increase from the oven-dry mass. The influences of percent concentration and drain time on PCA content in the flakes were investigated using a two-way analysis of variance.

Compression tests

Following treatment in solution and draining, flakes were immediately compressed using a universal testing machine. The compression device consisted of upper and lower heated aluminum platens securely attached to the crosshead and base of the testing machine via stud bolts (Fig. 1). Four cartridge heaters embedded into each platen provided heat, and on/off controls maintained the temperature through feedback from thermocouples. Cold water circulated between the individual platens and the testing machine. The flakes were compressed to a thickness of 0.3 mm, corre-

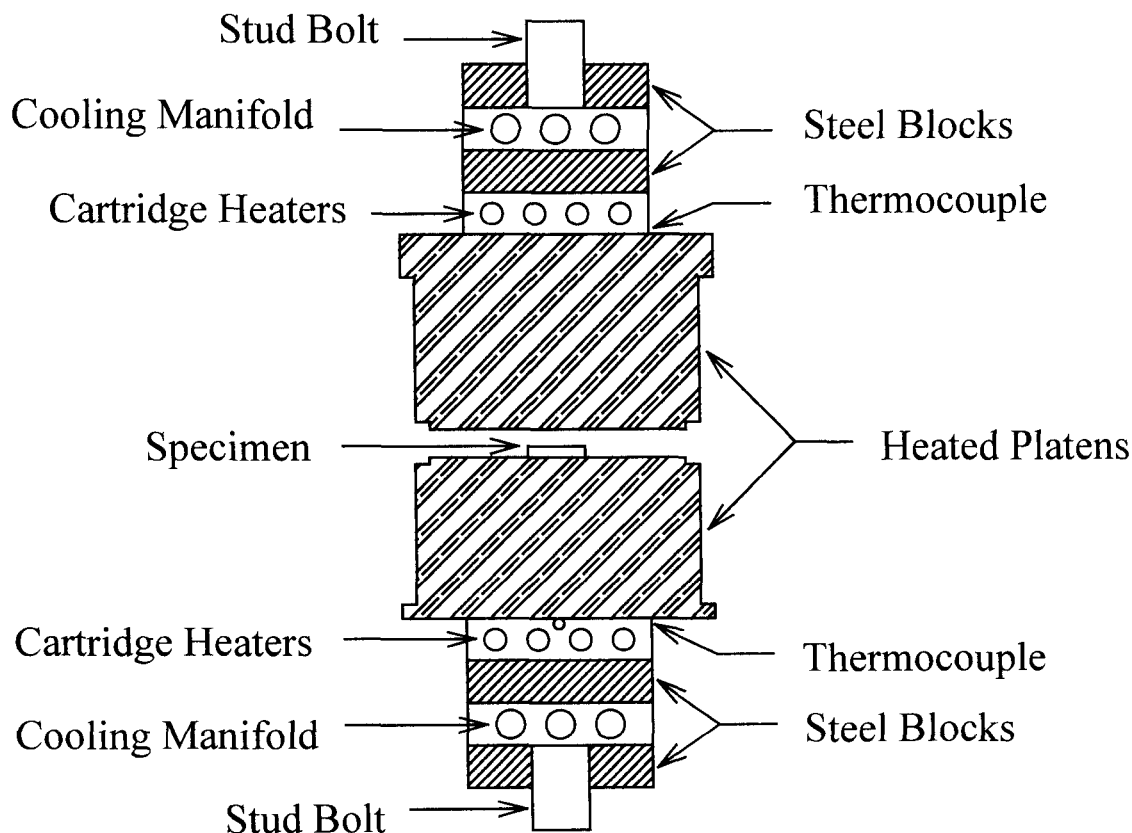


FIG. 1. Test device used to compress control and PCA-treated aspen flakes.

sponding to approximately 50% strain, for 5 min at 170°C.

Water absorption and thickness swell measurements

Immediately following compression, the mass and thickness of the flakes were recorded and used as the baseline for water absorption and thickness swell calculations. The PCA content in the flakes was determined. Thickness was measured at four locations on each flake, roughly 4 mm from the edges, and averaged. All flakes were then submerged in distilled water and subjected to a series of wet-dry cycles, being soaked for 24 h and dried at 103°C for 3 h. Cycles were continued until the thickness of the wet flakes remained nearly constant for two consecutive cycles. A total of six cycles were conducted. After the sixth cy-

cle, final percent water absorption and thickness swell were assessed. Percentage water absorption and thickness swell values were calculated using the compressed mass and thickness of each flake as an oven-dried basis. Reversible and irreversible thickness swell, two components of the total thickness swell of compressed wood, were also determined. Reversible swelling is the recurring component with repeated wet-dry cycles. In contrast, irreversible swelling is the component that swells when wetted, but does not shrink upon drying. In addition, the swelling coefficient, defined as swelling strain divided by fractional water absorption, was determined.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was conducted on 12.8- × 54.0- × 1.6-mm bass-

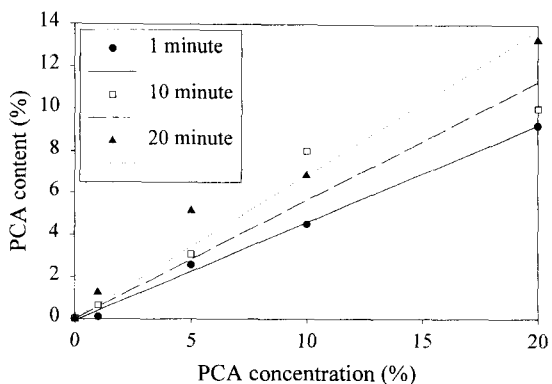


FIG. 2. The PCA content in compressed aspen flakes increased with increasing PCA concentration for 1, 10, and 20-min drain times. Regression lines were fitted to the overall data for each drain time. Individual symbols represent the average of six flakes for each PCA concentration.

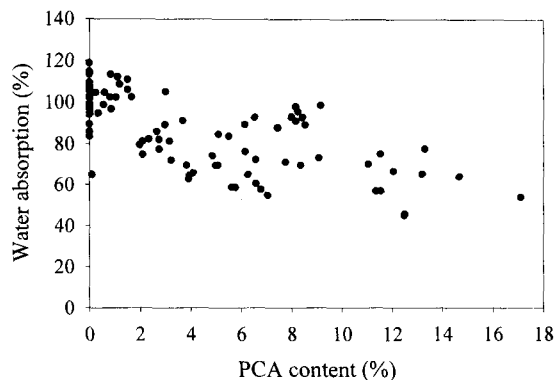


FIG. 3. Water absorption of compressed aspen flakes decreased as PCA content increased.

wood (*Tilia spp.*) specimens. Samples were treated as described previously except the 20% PCA concentration and 10-min drain time were the only treatments used. Control samples were used for comparison. Three replicate tests were conducted. All samples were placed in an oven for 5 min at 170°C. Samples were not subjected to compression. The oven-dried samples were then sealed in aluminum foil to maintain environmental conditions. Dynamic mechanical analysis was conducted on samples under three-point bending with a span of 48 mm. Samples were subjected to a constant frequency of 1 Hz and strain of 5×10^{-4} . The temperature was decreased quickly to -40°C , held for 15 min to allow the sample temperature to equilibrate, and increased to 200°C at a rate of $5^{\circ}\text{C}/\text{min}$.

Both the storage modulus (E') and $\tan \delta$ were recorded with changing temperature. The storage modulus, E' , is a measure of the vibration energy stored in the material and is similar to the static Young's modulus. $\tan \delta$ is defined as the ratio between the loss (E'') and storage moduli ($\tan \delta = E''/E'$) and is a measure of the vibration energy dissipated by the material. Changes that occur in $\tan \delta$ are indicative of molecular rearrangements taking place in the sample (Menard 1999). A $\tan \delta$

peak is often indicative of phase transitions in material components.

RESULTS AND DISCUSSION

Polycarboxylic acid resin content

The PCA content in the flakes increased with increasing concentration and drain time (Fig. 2). Individual symbols in Fig. 2 represent the average of six flakes for each PCA concentration. Both concentration and drain time significantly influenced the PCA content, and there was a significant interaction between concentration and drain time as determined using a two-way analysis of variance ($P < 0.001$). Following treatment and compression, flakes became progressively darker in color as PCA content increased. The polarity of the PCA molecule makes it highly attracted to the water molecules within the PCA solution. Thus as the PCA solution diffused into the wood, flakes treated with higher solution concentrations resulted in higher PCA contents in the wood.

Water absorption and thickness swell

As PCA content increased, both water absorption (Fig. 3) and thickness swell (Fig. 4) decreased. Whereas water absorption and thickness swell over 100% resulted with control flakes, water absorption and thickness swell as low as 45% and 16%, respectively, were achieved with PCA-treated flakes. The

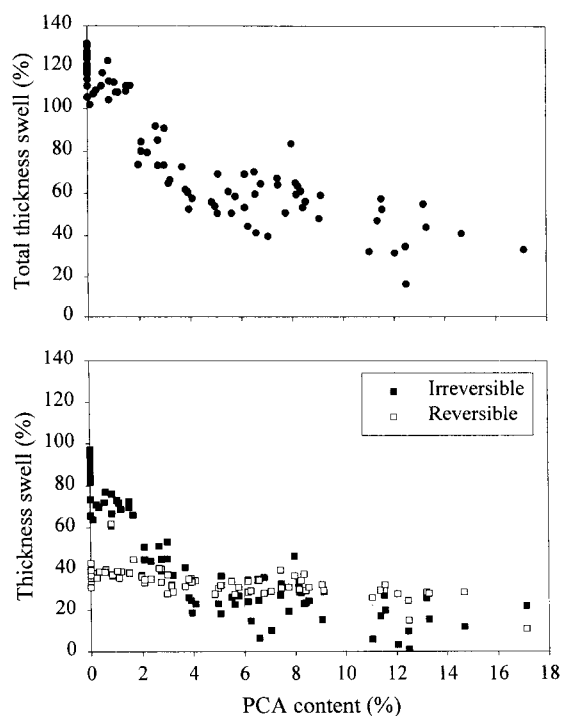


FIG. 4. Total thickness swell of compressed aspen flakes decreased nonlinearly with increasing PCA content. Irreversible swell decreased and reversible swell was relatively constant with increasing PCA content.

decrease in thickness swell was nonlinear, having diminishing reductions as PCA content increased. For instance, total thickness swell decreased by over 60% with the addition of only 5% PCA content. However, between 5% and over 10% PCA content, thickness swell decreased by only 17%.

The PCA content reduced total thickness swell primarily by reducing the irreversible component. Irreversible swell decreased as PCA content increased, while the reversible swell remained relatively constant (Fig. 4). At 0% PCA content (control), irreversible swell was 89% and reversible swell was 34%. In contrast, above 10% PCA content, irreversible swell was 15% and reversible swell was 26%. Clemons et al. (1992) report similar behavior with the irreversible swell of acetylated (acetic, maleic, and succinic anhydrides) fiberboards. The irreversible swell of fiberboards

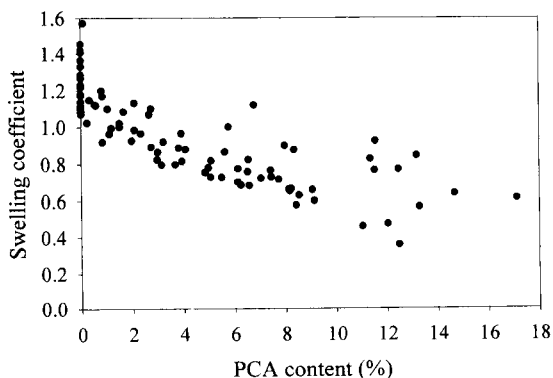


FIG. 5. Swelling coefficient, defined as the swelling strain divided by fractional water absorption, of compressed aspen flakes decreased with increasing PCA content.

treated with acetic anhydride was less than half that of untreated fiberboards. For fiberboards treated with maleic and succinic anhydrides, the irreversible swell was virtually removed. Hsu et al. (1988) noted that the irreversible swell of densified wood composites is higher than the natural swelling of wood. Thus, by reducing the irreversible component of thickness swell, PCA resin can likely reduce a substantial percentage of the total thickness swell in densified wood composites.

The swelling coefficient decreased as PCA content increased (Fig. 5), suggesting that the reduction in thickness swell was greater than the reduction in hygroscopicity. Stamm (1964) found similar behavior for a number of stabilizing treatments (e.g., acetylation, penetrating resins, salts, etc.) for solid wood that are deemed to act as bulking agents. It is not clear whether similar behavior for compressed wood suggests a bulking action for PCA treatments.

Dynamic mechanical analysis

Dynamic mechanical analysis was used to assess the possible molecular changes that may have occurred within the PCA-treated wood flakes. Evidence to discern between bulking and cross-linking actions of the PCA resin was of particular interest. Basswood

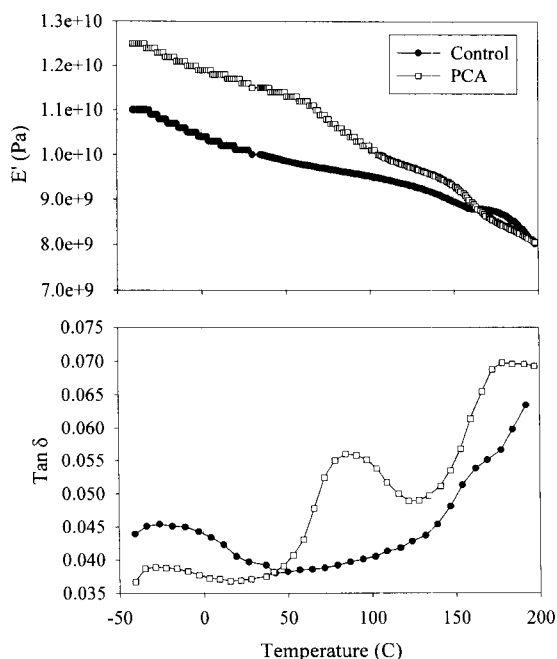


FIG. 6. Dynamic mechanical spectra of representative uncompressed control and PCA-treated basswood samples.

samples treated with PCA resin displayed higher storage modulus, E' , than control samples. Representative curves are shown in Fig. 6. The increased E' of the PCA-treated samples indicated a stiffening in the material. This evidence of stiffening may support the presence of increased cross-link density in the wood polymers. A thermal transition was noted at ca. 85°C for PCA-treated samples. The transition is marked by a large broad $\tan \delta$ peak and a corresponding decrease in E' characteristic of glass transitions in amorphous polymers. The absence of this transition combined with the lower E' in the control samples suggests that motion of cross-linking chains of the PCA-treated samples began at this point. This hypothesis is further supported by the fact that E' of the PCA-treated and control samples merged after this transition. In addition, the dried PCA-treated samples were the same dimensions as the untreated controls. The lack of permanent swelling from the treat-

ment is consistent with known cross-linking agents such as formaldehydes (Stamm 1964).

A second, less prominent transition is evidenced by a shoulder in $\tan \delta$ and a corresponding decrease in E' in both control and PCA-treated samples at 155°C and 170°C, respectively. Kelley et al. (1987) noted that the glass transition of lignin and hemicellulose approached 200°C as moisture content approached zero. The PCA-treated samples displayed a more prominent transition that might be attributed to some degree of bulking of the PCA chain, thereby increasing free volume. However, any bulking effect is likely to be limited because the transition is not decreased in temperature.

CONCLUSIONS

Polycarboxylic acid resin appears to be a promising treatment for limiting moisture swelling of densified wood. Thickness swell decreased nonlinearly with increasing PCA content in the flakes. The primary reduction in thickness swell was due to a decrease in irreversible, not reversible swell. A decrease in the swelling coefficient with increasing PCA content is similar to known bulking agents for uncompressed wood. Using DMA, the PCA treatment was found to increase stiffness and alter phase transitions in the treated wood. Interpretation of these results suggests that the resin could act as a cross-linking agent. The potential stiffness improvements from PCA-treated wood and the water-soluble nature of PCA may be beneficial over acetylation, which has been found to decrease certain mechanical properties (Rowell et al. 1995, Chow et al. 1996).

ACKNOWLEDGMENTS

The authors gratefully acknowledge BP Amoco for partial financial support for this research, Ron Anderson for his helpful comments and contributions, and David Harper for assisting with some experimental aspects of this study.

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