DIMENSIONAL STABILITY MEASUREMENTS OF THIN WOOD VENEERS USING THE WILHELMY PLATE TECHNIQUE

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ABSTRACT

The objective of this study was to investigate the effect of hydroxymethylated resorcinol (HMR) and a commercially available water repellent (WR) treatment on the dimensional stability and water uptake behavior of maple veneers. The Wilhelmy plate technique was used to assess the effects of the chemical treatments on the veneer by comparing the perimeter of the veneers before and after 24 h water immersion and by monitoring the initial water uptake behavior. The veneers were treated with the HMR and WR by dipping treatment at three different loadings: 5, 15, and 30 min of treatment time.

Water uptake into the untreated veneer increased dramatically during the 30 min of immersion time in water, compared with the HMR-treated veneer. Water uptake into the HMR-treated veneer, which was treated at the highest retention level (30 min), was limited during the initial stage of the water-immersion test.

The initial amount of water uptake into the veneer was lowered by 65% to 75% as a result of the HMR treatment, and the initial amount of water uptake into the water repellent-treated veneers was lower than that of the HMR-treated veneers depending on the HMR/WR treatment retention level. The initial amount of water uptake of the water repellent-treated veneers was lowered by 5 to 10%, compared with the HMR-treated veneers at the treatment time of 15 and 30 min.

HMR treatment improves the dimensional stability of wood as evidenced by the reduced swelling of the HMR-treated samples compared to the untreated samples in the water-immersion test.

The changes of sample perimeters measured by the Wilhelmy plate method were larger than those measured by digital calipers because the Wilhelmy plate method measures the perimeter change on the microscopic (cellular) level. It is hypothesized that the Wilhelmy plate method is a more effective tool than the caliper method for investigating the dimensional stability of small, thin, or nonrectangular samples in aqueous environments.

Keywords: hydroxymethylated resorcinol (HMR), water repellent, dimensional stability, perimeter, Wilhelmy plate method.

INTRODUCTION

The use of coupling agents is one of several surface modification methods that have become essential to enhancing the durability of adhesive bonds to metals, plastics, and advanced composites in aerospace and automotive industries. Such treatments are virtually nonexistent in the wood products industry. Surface modification can solve important adhesion problems in wood products (Vick 1996). Chemical modification of wood is used to improve undesirable characteristics such as dimensional instability, flammability, and biological and chemical degradation (Clemons

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et al. 1992; Kumar 1994; Rowell et al. 1988). In particular, most of these studies have focused on improving the dimensional stability of solid wood and composites through chemical modification (Nicholls et al. 1991; Rowell et al. 1989; Youngquist et al. 1986).

Hydroxymethylated resorcinol (HMR) is a wood surface treatment method that has achieved great success in promoting durable bonding of epoxy resin to wood (Vick 1995; Vick et al. 1995, 1996, 1998) and for bonding southern pine treated with chromated copper arsenate (CCA) preservative (Vick 1995). HMR treatment is also effective for enhancing adhesion of wood adhesives, such as phenol-resorcinol-formaldehyde, emulsion polymer/isocyanate, polymeric methylene diphenyl diisocyanate (PMDI), melamine-formaldehyde, and urea-formaldehyde resin (Hensley et al. 2000). A U.S. patent covering this invention has been assigned to the U.S. Department Agriculture (Vick et al. 1994).

It is evident that the effectiveness of HMR at improving adhesion is highly dependent on reaction time. Therefore, knowledge of HMR reactivity, as related to adhesion durability and measured after specific application rates or reaction time and drying time, is essential to maximizing adhesion and optimizing the bonding process.

One hypothesis for the improved durability of adhesives on HMR-treated wood is that the HMR treatment acts as a wood surface stabilizer i.e., increases the dimensional stability of the outer wood surface layer. Indeed, the HMR solution is comprised of low molecular weight molecules that can penetrate into the wood cell wall and chemically react with the cell wall constituents (Vick 1996).

In dimensional stabilization studies on wood, most researchers report using digital calipers to measure the change of dimensions before and after water-immersion tests regardless of the sample's appearance. More recently the application of linear variable displacement transducers (LVDTs) for measuring the swelling of strand-based panels has been reported (Oh et al. 2000). It is felt that more sensitive techniques to measure wood dimensional stability deserve some attention, and thus, the impetus for this work.

BACKGROUND ON THE WILHELMY PLATE METHOD

Dynamic contact angle (DCA) analysis using the Wilhelmy plate principle represents a straightforward wettability assay. According to Wålinder and Ström (2001), the Wilhelmy theory can be described as follows:

The force F required to partially submerge a smooth plate in a liquid was given by Wilhelmy (1863) as:

$$F = P\gamma \cos\theta - \rho Ahg \qquad (1)$$

where P is the wetted perimeter of the plate, γ is the surface tension of the liquid, θ is the contact angle, ρ is the liquid density, A is the cross-sectional area of the plate, h is the depth of immersion, and g is the gravitational constant. If the force F is measured during the immersion in, and withdrawal from, a liquid and if F is plotted vs. the immersion depth h, a straight line is obtained where the slope is $-\rho Ag$, and the intercept on the F axis is $P\gamma \cos\theta$. In other words, if the surface tension of the liquid and the perimeter of the plate are known, Eq. (1) can be solved by linear regression of such plots to determine $\cos\theta$. The immersion and withdrawal of the plate correspond to the advancing and receding curve of the force vs. depth plot, which yield the advancing and receding contact angle, respectively. Equation (1) is linear only if $P\gamma \cos\theta$ = constant. Non-linearity would therefore indicate that γ, and/or θ are changing.

When porous and hygroscopic materials like wood are immersed in a liquid, a deviation from Eq. (1) is observed (Wålinder and Johansson 2001). This is due to wicking of the liquid along the wood surface and into void spaces in the wood structure. Polar liquids like water also absorb in the wood substance. Equation (1) may therefore be modified to:

$$F(h, t) = P\gamma \cos\theta + F_w(t) - \rho Ahg \qquad (2)$$

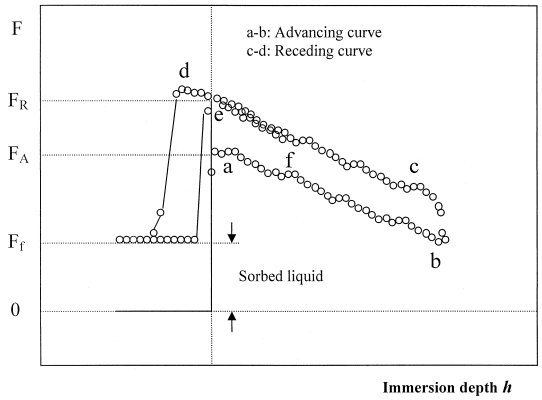

FIG. 1. The Wilhelmy plate method illustrated by a schematic plot of the recorded force F versus immersion depth *h* during a test cycle when a wood veneer is immersed in and withdrawn from a liquid.

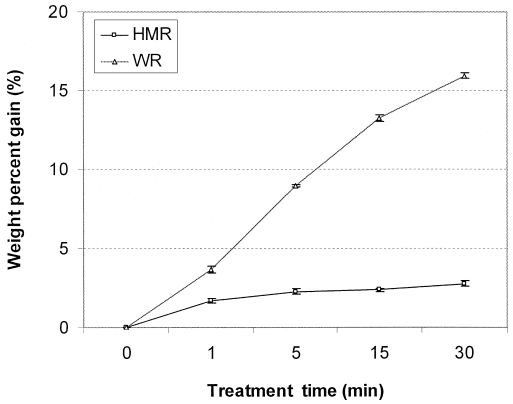

FIG. 2. Weight percent gain of maple veneers after treatment with HMR and WR for different treatment times.

where $F_w(t)$ represents the force due to wicking and sorption of the liquid at time *t.*

Figure 1 illustrates a plot of the recorded force F vs. immersion depth *h* during a test cycle when a wood veneer is immersed in, and withdrawn from, a liquid. No force is recorded until the veneer touches the liquid. The lower (stage a–b) and the upper (stage c–d) curves represent the advancing and receding situations, respectively. The slope of the advancing curve is uneven, which may be attributed mainly to the heterogeneous composition of the wood surface. The receding curve is less irregular presumably because the liquid 'wets out' the surface (resulting in zero contact angles). The intercepts F_A and F_R on the ordinate shown in Fig. 1 are obtained by linear regression of the advancing and the receding curves respectively. F_f is the final force, i.e., the weight of sorbed liquid during a test cycle equal to the term $F_w(t)$ in Eq. (2) at the time after the rupture of the meniscus (at $h \cong 0$). $F_w(t)$ is assumed to be zero when the veneer touches the liquid in the first test cycle (at $h \cong 0$). The intercepts for the advancing and receding curves are then given by

$$F_A = P\gamma \cos \theta_A \quad (3)$$

and

$$F_R = P\gamma \cos \theta_R + F_f \quad (4)$$

where θ_A and θ_R are the advancing and receding contact angles, respectively. When the veneer is immersed for the second time (see Fig. 1, stage e–f), the advancing and receding curves are approximately coincident, i.e., there is no hysteresis, which means that $\theta_A = \theta_R = 0°$. In the present study, the Wilhelmy method has been applied to calculate the perimeters of wood veneers when the veneers are immersed in and withdrawn from octane.

OBJECTIVES

The main objective of this work was to investigate the effect of HMR and a commercially available water repellent (WR) treatment on the dimensional stability and water uptake of maple veneers. This paper also discusses the differences observed in the measurement of dimensional stability of HMR and WR-treated maple wood veneer using either digital calipers or the Wilhelmy plate method.

EXPERIMENTAL METHODS

Materials

HMR (Vick et al. 1994) was prepared from the following ingredients: 3.34 weight percent of resorcinol, 2.44 weight percent of 3 molar sodium hydroxide solution, 90.43 percent of deionized water, and 3.79 weight percent of a 37%-aqueous solution of formaldehyde. The

TABLE 1. *Statistical analysis (Tukey's test, $\alpha = 0.05$) for weighted percent gain (WPG) of HMR- and WR-treated maple veneer as a function of treatment time.*

Comparison	Diff. of means	*P*	q	*P**	$P < 0.050$
WPG (HMR-treated) vs. treatment time					
30 min vs. 1 min	1.102	4	15.622	<0.001	Yes
30 min vs. 5 min	0.518	4	7.343	<0.001	Yes
30 min vs. 15 min	0.424	4	6.011	0.003	Yes
15 min vs. 1 min	0.678	4	9.611	<0.001	Yes
15 min vs. 5 min	0.094	4	1.333	0.783	No
5 min vs. 1 min	0.584	4	8.279	<0.001	Yes
WPG (WR-treated) vs. treatment time					
30 min vs. 1 min	12.288	4	158.704	<0.001	Yes
30 min vs. 5 min	6.990	4	90.278	<0.001	Yes
30 min vs. 15 min	2.638	4	34.071	<0.001	Yes
15 min vs. 1 min	9.650	4	124.633	<0.001	Yes
15 min vs. 5 min	4.352	4	56.208	<0.001	Yes
5 min vs. 1 min	5.298	4	68.425	<0.001	Yes

* The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference ($P \leq 0.001$).

solution was allowed to react for 4 h at 20°C. A commercial water repellent, Thompson's Waterseal, manufactured by Thompson's company (Cleveland, OH) was also used to compare with the HMR treatment. Hard maple (*Acer saccharum*) veneer was obtained from Northern Michigan Veneer (Gladstone, MI), a decorative veneer manufacturer. To calculate the perimeters of each wood veneer sample before and after 24 h water immersion, octane (surface tension = 21.76 mN/m) was used as a probe liquid in the DCA test.

Sample preparation

The veneers were equilibrated to 10% moisture content in an environmental chamber. After equilibration, the veneers were cut to approximately 6-mm (width) by 34-mm (length) by 0.58-mm (thickness) for the Wilhelmy plate experiments and digital caliper measurements. Before the HMR and WR treatments, all veneer samples were dried in an oven. The veneers were then treated with HMR and the water-repellent solution by soaking at various treatment times of 5, 15, and 30 min. The weight percent gain of the veneer samples after treatment was determined using the following equation.

$$\text{weight percent gain (\%)} = \frac{W_H - W_O}{W_O} \times 100 \quad (5)$$

W_O: oven-dry basis weight of veneer before soaking (g)

W_H: oven-dry basis weight of veneer after soaking (g)

Five specimens of each treatment type were tested, and the weight percent gain values were averaged. After soaking treatment, all treated samples were conditioned in an environmental chamber (20°C, 65%) for a month.

Dimensional stability measurements

Digital caliper measurements.—To measure the perimeters of each veneer sample before and after a 24 h water-immersion test, the thickness and width of each sample were measured using digital calipers.

$$\text{perimeter} = 2 \times (\text{thickness} + \text{width}) \quad (6)$$

$$\text{change of perimeter (\%)} = \frac{P_w - P_a}{P_a} \times 100 \quad (7)$$

P_w: perimeter after 24 h water immersion (mm)
P_a: perimeter before 24 h water immersion (mm)

Wilhelmy plate method for perimeter measurements.—The Wilhelmy plate analysis was carried out using a Cahn model DCA-322 Dynamic Contact Angle Analyzer. The probe solvent used was octane, which meets the American Chemical Society (ACS) grade of over 99% purity. Veneers were immersed in a small beaker filled with octane at a speed of 200 μm/s. The veneers were immersed in the octane along the grain, i.e., in the fiber direction, to a depth of 10 mm and were then withdrawn above the liquid. The force exerted on the veneer was automatically recorded from the DCA balance and recorded every second. The perimeter P of the veneers was then calculated using Eq. (4) and the known value of γ for octane and assuming $\theta = 0$. The measurements were performed at the temperature of 20°C and relative humidity of 50%.

Water absorption by DCA analyzer.—The veneers were immersed to a depth of 34 mm in a small beaker filled with water. The force (weight gain of samples) exerted on the veneer was automatically recorded from the DCA as a function of time.

Statistical analysis.—Statistical analysis of the data included performing a pairwise multiple comparison procedure, Tukey's test ($\alpha = 0.05$) between weight percent gain of HMR- or WR-treated maple veneer and treatment time. Statistical analysis was performed using Sigma Stat software.

RESULTS AND DISCUSSION

HMR and water-repellent treatment on the veneer.—Figure 2 shows the weight percent gain (WPG) of the HMR-treated and water repellent-treated maple veneer as a function of treatment time. As shown in Table 1, Tukey's test showed significant differences among the WPG of HMR-treated veneers and treatment time except for between 5 and 15 min of treatment time and also showed significant differences among the WPG of WR-treated veneers and treatment time at $\alpha = 0.05$.

The Tukey's test is a statistical technique, which is good at detecting real treatment effects and is ideally used with a limited number of comparisons or in small experiments where few means are compared (Steele and Torrie 1980). As can be seen in Fig. 2 and Table 1, the weight percent gain of HMR increased significantly in the range from 1.7 to 2.8% as the treatment time increased from 1 to 5 min and from 15 to 30 min. The weight percent gain of the commercial water repellent also increased significantly in the range from 3.7 to 15.9% as the treatment time was increased from 1 to 30 min. The uptake of water repellent in the maple veneer was much higher than that of the HMR solution for the treatment times examined in the study. An explanation for this observed difference in weight uptake can be attributed to the solids content of HMR solution at 5%, being much lower than the water repellent solids content of about 90%.

Measurement of water absorption and dimensional stability.—The water uptake measured during 30 min of water immersion on the HMR-treated and untreated maple veneer is plotted in Fig. 3. It can be observed that the water uptake on the untreated veneer increases dramatically during 30 min of water immersion compared to the HMR-treated veneers. The uptake of water on the HMR-treated veneers increased very slowly in the water immersion test. The initial uptake of water was lowered as a result of the HMR treatment. Here it is important to note that generalizations about the water uptake of veneer are made on short duration immersion times (30 min).

The uptake of water on the water repellent-treated and untreated maple veneer is plotted in Fig. 4. It can be observed that the uptake of water on the untreated veneer increased to a larger extent for 30 min of water immersion compared to the water repellent-treated veneers. The initial water uptake (0 to 5 s) of the water repellent-treated veneer was relatively lower than that of the HMR-treated ve-

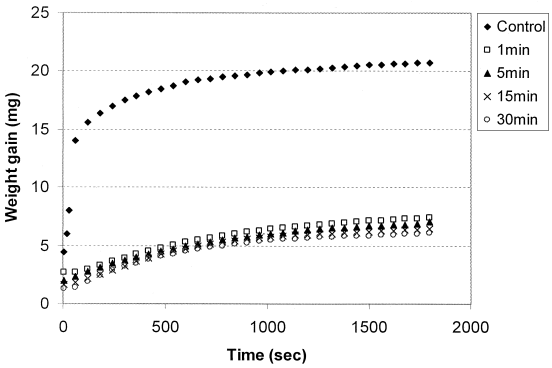

FIG. 3. Uptake of water on the HMR-treated and untreated maple veneer for 30 min.

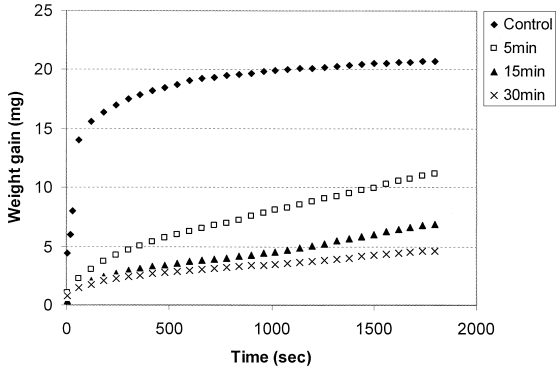

FIG. 4. Uptake of water on the water repellent (WR)-treated and untreated maple veneer for 30 min.

neers (Fig. 3). This might be attributed to the greater initial hydrophobicity of the commercial water repellent treated wood. While it is well known that oil-based water repellent treatments increase the hydrophobicity of wood, HMR treatment has been shown not to change the surface free energy of wood (Gardner et al. 2001). In addition, the water contact angle on HMR treated wood is lower than on untreated wood (Gardner et al. 2001), which may partially explain the difference in the initial wetting behavior between HMR- and the commercial water repellent-treated wood.

A digital caliper was used to measure the dimensional changes of HMR-treated veneer before and after the water immersion test. Wilhelmy plate measurements were also used to determine the perimeter of the HMR-treated veneer in both the swelled and dry state. It can be assumed that the probe liquid (octane) completely 'wets out' the veneer in the receding mode, i.e., the receding contact angle, $\theta_{R,}$ is equal to zero and cos θ in Eq. (4) is equal to 1. The perimeter, P (mm), can easily be calculated by dividing the mean value of the force, F (mN) (as shown in Fig. 5), which is registered during the wetting cycle with the surface tension, (mN/m), of the test liquid.

Figure 5 presents two examples of immersion and withdrawal of untreated maple veneer (before and after the 24 h water-immersion test) in octane. As shown in this figure, there is little or no hysteresis between the advancing and receding curves for a test in octane. This implies that octane completely 'wets out' the wood surface resulting in zero advancing and receding contact angles. The receding force is related to the perimeter length, i.e., a larger sample perimeter after swelling results in a higher absolute value of the calculated force from the DCA measurement.

Figure 6 shows the effect of soaking treatment time on the dimensional stability of HMR and WR treated maple veneers. As can be seen in Fig. 6, the experimental results indicate that the HMR treatment improves the dimensional stability as evidenced by the smaller perimeter change from both analyses. The dimensional stabilization efficiencies (DSE) of the three loadings of HMR treatment (5, 15, and 30 min of treatment time) were about 21, 42, and 79%, respectively. That is to say, the highest loading of HMR treatment result in a highly efficient decrease in the swelling of the veneers from 7.8% to 1.6% compared with the untreated veneers. The corresponding DSE values for the WR treated veneers were about 8, 33, and 37%. A possible explanation for the HMR treatment improving dimensional stability could be that the treatment blocks liquid penetration into the wood cell wall. This explanation supports the postulation of Vick (1996) that the small HMR molecules penetrate into the wood cell walls causing high-density hydrogen bonding with the hydroxyls of wood polymer chains or

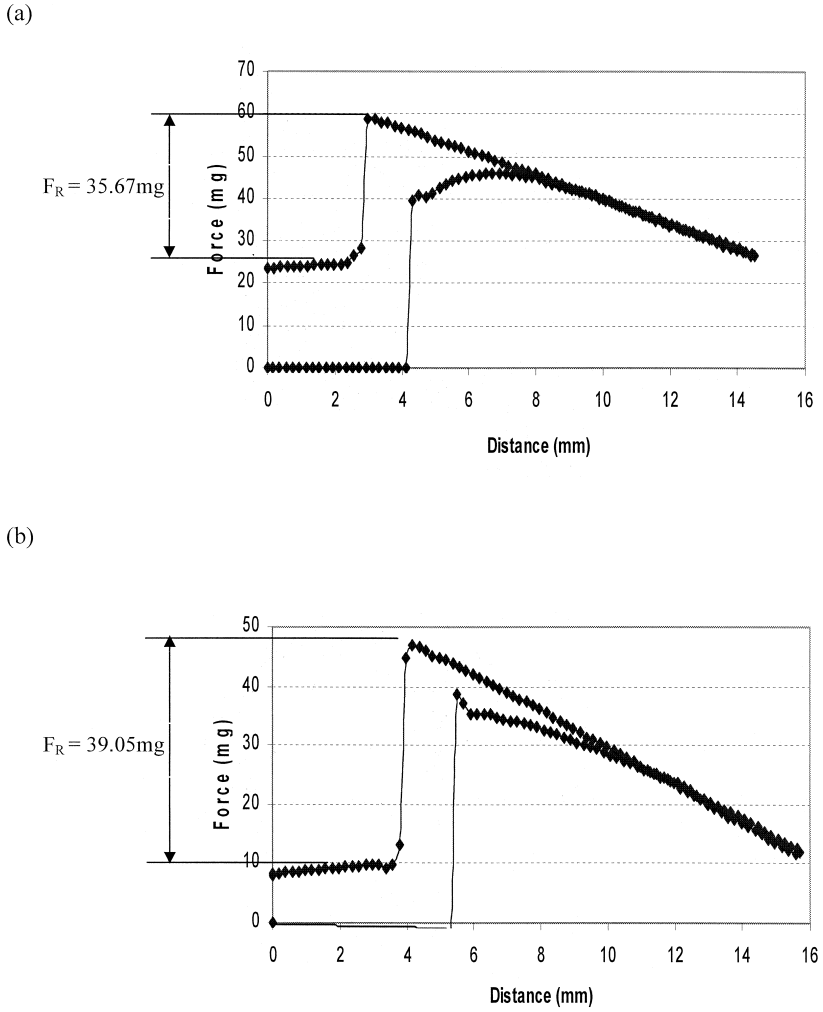

FIG. 5. Examples of DCA test in octane for untreated maple veneer. (a) before water immersion (b) after water immersion.

chemical crosslinking between wood cell-wall constituents. More work is needed to confirm this hypothesis.

Figure 7 shows the differences observed in the dimensional stability of HMR and water repellent-treated maple wood veneer as measured by digital calipers and the Wilhelmy plate method, and this figure demonstrates that the changes of perimeter measured by the Wilhelmy plate method were larger than those determined by the digital caliper. When the perimeter of veneer is measured using the digital calipers, it is assumed that the veneer is perfectly rectangular. The perimeter of veneer is actually not rectangular on the microscopic scale. For this reason, the measurements using the Wilhelmy plate method are more sensitive in detecting perimeter changes in the veneer sample. The Wilhelmy plate method is therefore shown to be effective technique for investigating the dimensional stability of small, thin or nonrectangular samples.

CONCLUSIONS

Based on the research presented in this paper, we can draw the following conclusions:

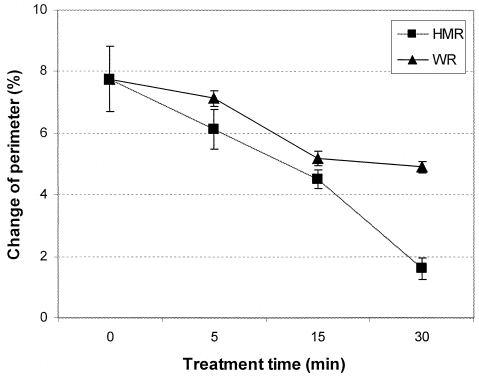

FIG. 6. The change of veneer perimeter measured by DCA after 24 h soaking in water for different treatment times.

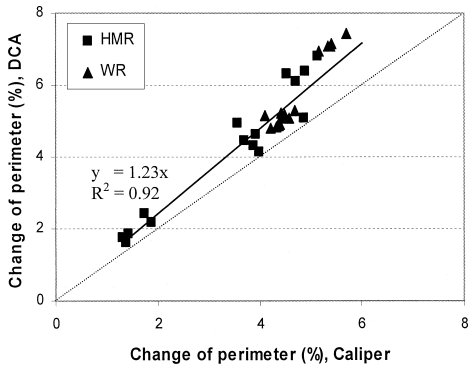

FIG. 7. Relationship between the change of veneer perimeter measured by DCA and the veneer perimeter measured using digital calipers.

1. HMR treatment improves the dimensional stability of veneer as evidenced by the smaller perimeter change in the water-immersion tests. The dimensional stabilization efficiencies (DSE) for the three loadings of HMR treatment were about 21, 42, and 79%, respectively. The highest loading of HMR treatment resulted in a highly efficient decrease in veneer swelling from 7.8% to 1.6% compared with the untreated veneers. The corresponding DSE values for the WR-treated veneers were about 8, 33, and 37%.
2. The changes in veneer perimeters determined using the Wilhelmy plate method were larger than those determined using the digital calipers because the Wilhelmy plate method measures perimeter changes on the microscopic (cellular) level. Therefore, the Wilhelmy plate method is more sensitive for measuring dimensional changes on small, thin, or nonrectangular samples.

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