PROBING THE HYDROXYMETHYLATED RESORCINOL COUPLING MECHANISM WITH STRESS RELAXATION

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ABSTRACT

The isothermal stress relaxation of dry wood is well described by the Kohlrausch-Williams-Watts relationship. This provides a direct measurement of the relaxation time and cooperativity for amorphous wood-polymer segments. The insights afforded by this approach are demonstrated for wood treated with hydroxymethylated resorcinol, HMR, coupling agent. HMR significantly stiffens wood against stress relaxation as revealed by large increases in the measured relaxation time and coupling parameter. In contrast, phenol impregnation has no effect on the coupling parameter or the relaxation time. This reveals that the simple bulking of the wood cell wall does not explain the action of HMR. Instead, this suggests that HMR chemically crosslinks the cell wall. Consequently, one aspect of the HMR coupling mechanism may involve covalent crosslinking and stabilization of amorphous regions against water swelling and other mechanical stresses.

Keywords: HMR, adhesion, stress relaxation, cooperativity.

INTRODUCTION

It is well established that a dilute aqueous alkaline solution of hydroxymethylated resorcinol, HMR, is an outstanding coupling agent for wood adhesive bonds. As a preparative surface treatment, HMR provides remarkable durability enhancement for what would otherwise be troublesome wood bonds. This exceptional coupling action was first demonstrated with epoxy bonds to Sitka spruce (Vick et al. 1995). Since then, numerous examples of HMR effectiveness have been shown for other systems as in the case of: preservative-treated wood (Vick 1995; Vick et al. 1996), yellow cedar wood (Okkonen and Vick 1998), moisture-cure polyurethanes (Vick and Okkonen 2000), and bonds between wood and fiber-reinforced vinyl ester materials (Lopez-Anido et al. 2000)

Precisely how does HMR improve wood adhesive durability? Some important clues have been provided by Vick et al. (1998), who demonstrated that HMR efficacy has a molecular size and size distribution requirement. The coupling agent must possess a large quantity of methylolated monomers and dimers, in addition to higher molecular weight oligomers and polymers. Compounds such as phenol, resorcinol, and benzyl alcohol are known to preferentially adsorb and/or swell into the wood cell wall (Stamm 1964; Mantanis et al. 1994). Hydroxymethylated resorcinol monomers could be ex-

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pected to have a similar affinity for nanoscale wood penetration. Indeed, Son and Gardner's findings (2004) suggest that HMR cell-wall penetration is central to the coupling mechanism. They demonstrated that HMR stabilizes wood against water swelling, and not simply because of impaired wetting. In all likelihood, the question is not if HMR monomers enter the wood cell wall, but rather what happens once they get there. Once entering the cell wall, HMR monomers could stabilize wood in two ways: 1) by simple bulking, which blocks water adsorption sites, or 2) by crosslinking amorphous polymers which restricts segmental motions against stresses, whether from swelling or from mechanical inputs. Certainly, wood polymers contain ample nucleophilic and electrophilic sites for HMR reaction.

In an effort to determine if HMR crosslinks the wood cell wall, this work employs simple stress relaxation experiments to reveal the nature of cooperative relaxations and the relative time scale of same.

MATERIALS AND METHODS

Wood sample preparation

Yellow-poplar (*Liriodendron tulipifera*) sapwood was cut into samples with dimensions of 40 × 10 × 4 mm (respectively: longitudinal, tangential, and radial). All wood samples were water-impregnated by vacuum immersion (0.5–2 mm Hg) for 2 h, followed by soxhlet water extraction for 24 h; thereafter the samples were soaked in 95°C water for another 24 h, whereupon they were allowed to cool back to room temperature over a period of 6 h. These fully relaxed samples were then dried under ambient conditions for one day, and then completely dried to constant mass by storage over P_2O_5 for at least 2 days. This process removes most water solubles, but more importantly it relaxes all samples into a common hygrothermal history.

HMR treatment

HMR coupling agent was prepared as reported in Vick et al. (1995); the aqueous alkaline mixture of resorcinol and formaldehyde was reacted at room temperature for 4 h. The resulting HMR solution was then immediately used to impregnate the yellow-poplar samples (prepared as described above) by vacuum immersion (12–13 mm Hg) for 2 h. The HMR-impregnated samples were subsequently dried under ambient conditions for 1 day and then dried over P_2O_5 for no less than 48 h to obtain the fully dried, constant mass samples. This HMR treatment caused a sample mass increase of 2–3% based on dry wood.

Aqueous phenol treatment

The dry and water-relaxed yellow-poplar samples were impregnated with aqueous phenol (0.36 M) by vacuum immersion (12–13 mm Hg) for 2 h. The phenol concentration was the same mass concentration as resorcinol in the coupling agent recipe, meaning that the molar concentration was about 14% greater. The phenol-impregnated wood samples were subsequently dried under ambient conditions for 1 day and then dried over P_2O_5 for no less than 48 h to obtain the fully dried, constant mass samples. Phenol impregnation caused a sample mass increase of about 4% based on dry wood.

Stress relaxation analysis

Stress relaxation tests were conducted on a TA Instruments DMA 2980 in single cantilever bending along the longitudinal sample axis. Prior to the stress relaxation, all samples were isothermally equilibrated in the DMA furnace for 40 min. A 0.03% static strain was then imposed for a 3-h period while the modulus was monitored. Following the initial 3-h relaxation, the static strain was released (by returning to the original zero displacement point) and the sample recovered isothermally in the DMA furnace for 40 min; whereafter the relaxation measurement was repeated. Each sample was subjected to five cycles of this sequential relaxation analysis, excepting the phenol-impregnated samples, which experienced four cycles. All stress relaxation experiments were conducted at various tempera-

tures on dry samples. The data analysis is described in the discussion.

RESULTS AND DISCUSSION

More than 20 years ago, a theoretical model was developed that effectively describes relaxations in glass-forming materials, both polymeric and nonpolymeric (Ngai et al. 1986). The model characterizes two distinctly different motional regimes. In the regime of rapid motion, for example far above a polymer's glass transition temperature, the time (t)-dependent relaxation is well described by a linear exponential:

$$\phi(t) = \exp[-(t/\tau_o)] \qquad (1)$$

where τ_o is the "primitive" relaxation time, which is characteristic of polymer motions, which are a function only of conformational energy barriers, independent from neighboring chains. Upon cooling, a critical point is reached where polymer relaxations become restricted. In this slower regime, the motions of adjacent polymer segments are coordinated or cooperative, for example, at temperatures near the glass transition. The relaxation function for these cooperative segmental motions is best described by a fractional exponential:

$$\phi(t) = \exp[-(t/\tau)^{1-n}] \qquad 0 < n < 1 \qquad (2)$$

where τ is the effective relaxation time and is a function of τ_o (Ngai et al. 1986); n is the so-called coupling parameter and it describes the degree to which the relaxation distribution is broadened by segmental interactions. Higher values of n indicate broader relaxation distributions, or increased segmental coupling. In other words, the temperature-dependence of segmental relaxations near the glass transition reveals the coupling parameter, which reflects the local environment and/or chemical structure. Determination of the coupling parameter can therefore provide structural and morphological insights. For example, Laborie et al. have measured segmental coupling in ethylene glycol plasticized wood (2004), and how this is affected by cured phenol-formaldehyde (2005). In those efforts, Laborie et al. evaluated the temperature-dependence of wood softening with the principle of time/temperature equivalence. In contrast, the present work uses isothermal stress relaxation to evaluate the coupling parameter in dry wood. Equation (2) (which is known as the Kohlrausch-Williams-Watts relationship) takes the following form in the stress relaxation experiment:

$$E(t) = E_r + \Delta E e^{-(t/\tau)^{(1-n)}} \qquad (3)$$

where E(t) is the time-dependent modulus; E_r is the fully relaxed modulus, ΔE is the change in modulus occurring during the relaxation. Relaxations in polymeric glasses are well described by Eq. (3) (Yee et al. 1988; Han et al. 1995; Chang et al. 1997), meaning that the effective relaxation time and the coupling parameter may be obtained by fitting Eq. (3) to the experimental data. Indeed, we have found that the stress relaxation of dry wood (over a temperature range of from 25° to 115°C) is well described by this equation. In this work a linearization method (Yee et al. 1988) was first applied to the data in order to obtain an estimate of n; whereafter this estimate was used to conduct a least squares fit of the data to Eq. (3). A nonzero value of E_r (~5% of the initial unrelaxed modulus) was fixed during the fitting procedure in order to optimize the goodness of fit and to reduce the error in estimates of n and τ.

It is instructive to observe how n and τ influence the relaxation response according to Eq. (3). Figure 1 demonstrates that the short-term response involves two stages: an initial slow relaxation, followed by a more rapid relaxation. When n is fixed, changes in τ affect the onset of the rapid relaxation stage; but notice that the respective slopes of the rapid stage are equivalent. On the other hand, when τ is fixed, variations in n impact the slope of the rapid relaxation stage.

Figure 2 compares the 25°C sequential stress relaxation response of the water-relaxed (control) samples to that of the HMR-treated samples. For each sample, recall that five 3-h stress relaxation experiments were conducted sequentially with 40-min intervening recovery pe-

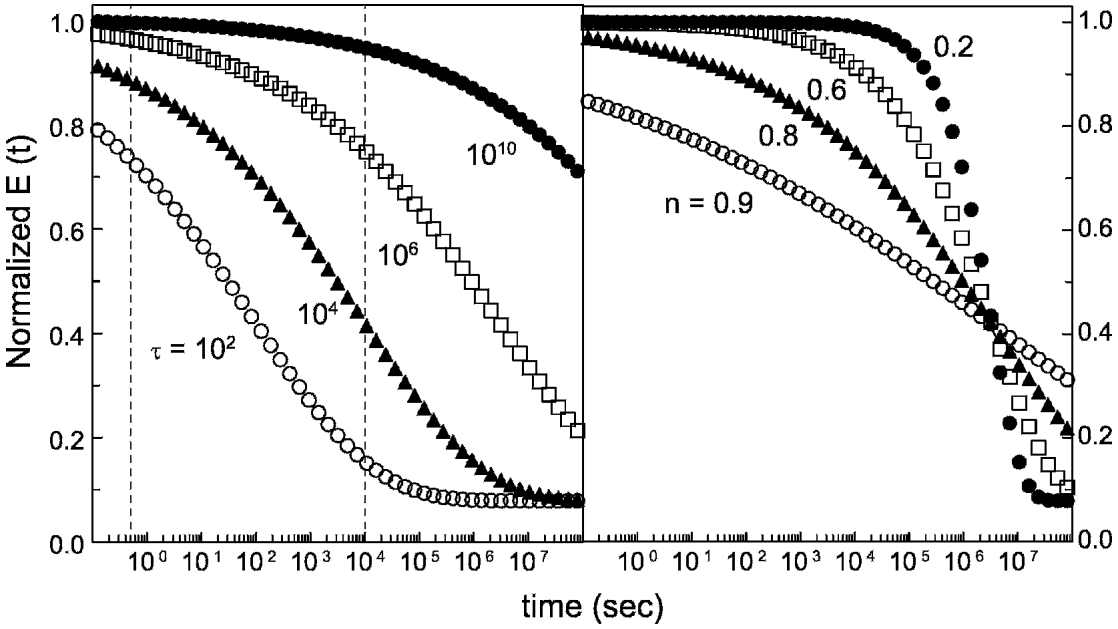

FIG. 1. Demonstration of how the effective relaxation time and the coupling parameter (respectively τ and n from Eq. (3)) influence the stress relaxation response. Left: n is fixed at 0.8 and τ varies as indicated. Right: τ is fixed at 3×10^6 and n varies as indicated. The dotted lines in the left panel indicate the experimental times used in this study.

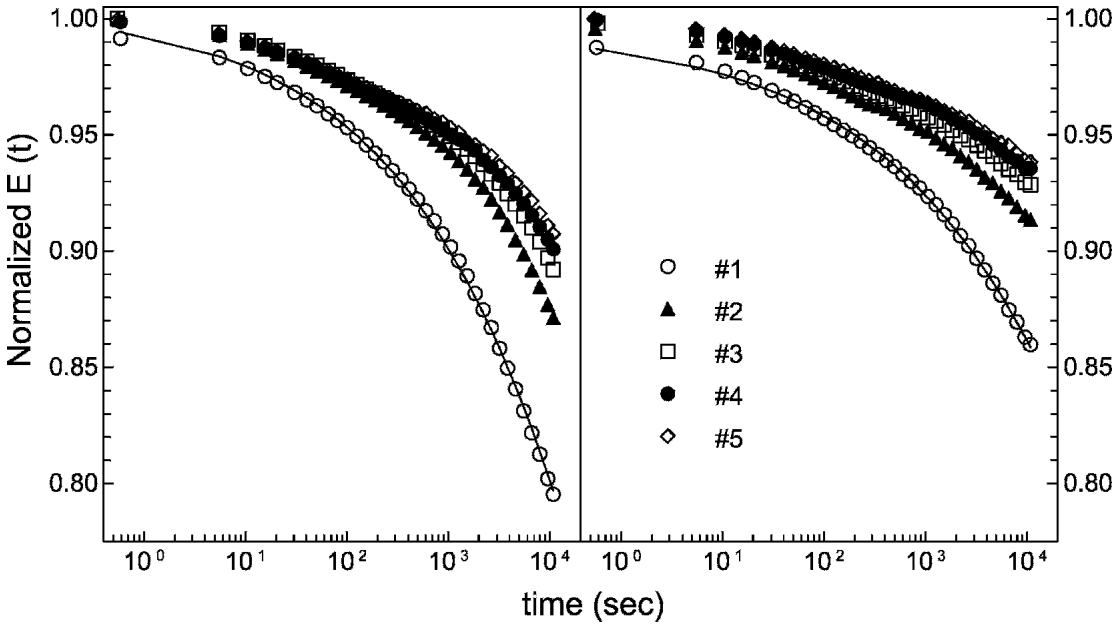

FIG. 2. Typical 25°C sequential stress relaxation response of water-relaxed control samples (left) and HMR-treated samples (right). The solid lines show the fit of Eq. (3) to the initial relaxation. At right, the legend indicates the experimental sequence for both samples.

riods. It is apparent that the HMR treatment effectively stiffens the yellow-poplar samples against stress relaxation, the detailed discussion of which will be deferred until later. For the present discussion, it is interesting to note that each stress relaxation alters the subsequent sample response; this can be seen in the succeeding relaxations, which differ markedly from the initial response. Stated another way, the 40-min interval between stress relaxations does not allow for complete sample recovery. Be aware that the strain level used in this work was 0.03%, which is well within the linear response according to a 1 Hz dynamic strain sweep experiment. Figure 3 plots the mean n and τ values, which were averaged across five different control samples (25°C), but for the same relaxation within the experimental sequence. The coupling parameter shows a slight increase over the sequence of 5 measurements; however, analysis of variance indicates that the increase is not significant ($p = 0.31$). In contrast, the effective relaxation time increases dramatically during the experimental sequence. This implies that the strain history has little or no effect on the cooperativity of a given sample, but it clearly increases the time required for these coordinated motions. In other words, for a single sample the breadth of the relaxation distribution is not altered by the strain history, but the distribution itself is displaced into longer relaxation times. Table 1 summarizes the coupling parameters measured for all samples, and it demonstrates that the coupling parameter exhibits no significant changes across the experimental relaxation sequence. Occasionally, a sample exhibited an atypical response in any one of the series of relaxations; those results were thrown out and they are noted as the omissions in Table 1. In the subsequent discussion, we have elected to represent individual samples by the simple average of n and τ, respectively calculated over the five sequential relaxation measurements. Likewise, subgroupings are represented by the simple grand averages. Figure 4 compares the average coupling parameters for control and HMR-treated samples measured at three different temperatures; Figure 5 shows a similar plot of the average effective relaxation times. Figures 4 and 5 demonstrate that both the coupling parameter and the effective relaxation time are temperature-dependent, as would be expected. Furthermore, relative to the control the following points should be noted: 1) HMR treatment significantly stiffens the wood against stress relaxation; the effective time and cooperativity of the relaxation increases; 2) HMR treatment increases the temperature sensitivity of n and τ; and 3) related to the previous point, the HMR influence on stress relaxation is greatest at 25°C; it becomes less significant at higher temperatures. Unfortunately, we cannot know which wood polymers are most affected by HMR; this is one of the drawbacks of the isothermal stress relaxation experiment. However, we can surmise that HMR appears to affect a more mobile component of the wood cell wall. At high temperatures, the HMR effect is reduced, presumably because the mobile chain segments sampled at 25°C are largely relaxed at the higher experimental temperatures. Given the reactivity of HMR, it is reasonable to suspect that the effects summarized above are caused by chemical crosslinking within the wood cell wall. Furthermore, the "mobile" components of the cell wall are likely the hemicelluloses and lignin.

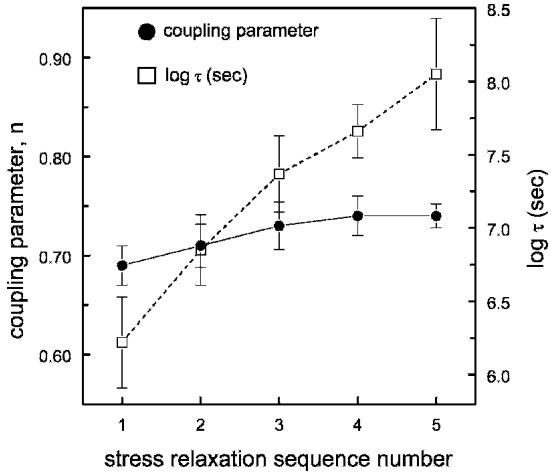

FIG. 3. Mean coupling parameter and effective relaxation times per relaxation test for all control samples analyzed at 25°C. Each mean was calculated across samples for each of the five relaxations within the typical sequence.

TABLE 1. *Coupling parameters obtained for all samples analyzed in this work. The "mean" is the simple average across the experimental sequence for one sample. The "Grand" is the grand average of the means for sample groupings as indicated.*

Treatment	Sample #	1	2	3	4	5	Mean	Grand
				Experimental sequence at 25°C				
Water-relaxed control	1	—*	0.74	0.78	0.79	—	0.77	
	2	0.73	0.73	0.73	0.74	0.74	0.73	
	3	—	0.71	0.74	0.74	0.74	0.73	0.73
	4	0.68	0.67	0.68	0.69	0.70	0.68	
	5	0.68	0.70	0.72	0.74	0.76	0.72	
HMR-treated	1	0.84	0.85	0.86	0.86	0.86	0.85	
	2	0.85	0.85	0.87	0.88	0.88	0.87	
	3	—	0.85	0.85	0.85	0.84	0.85	0.85
	4	0.84	0.84	0.87	0.88	—	0.86	
	5	0.78	0.79	0.81	0.82	0.83	0.81	
				Experimental sequence at 65°C				
Water-relaxed control	1	—	0.68	0.70	0.70	0.71	0.70	
	2	—	0.70	0.70	0.71	0.72	0.71	
	3	0.68	0.65	0.68	0.68	0.70	0.68	0.71
	4	0.72	0.73	0.73	0.74	0.75	0.73	
	5	0.70	0.72	0.72	0.72	0.73	0.72	
HMR-treated	1	—	0.88	0.88	0.88	0.88	0.88	
	2	0.75	0.78	0.79	0.80	0.80	0.78	
	3	0.75	0.76	0.77	0.77	0.77	0.76	0.79
	4	0.75	0.75	0.76	0.76	0.76	0.76	
	5	0.74	0.75	0.76	0.77	0.77	0.76	
				Experimental sequence at 115°C				
Water-relaxed control	1	0.64	0.63	0.64	0.64	0.64	0.64	
	2	0.65	0.65	0.67	0.68	0.68	0.67	
	3	0.70	0.71	0.73	0.74	0.76	0.73	0.66
	4	0.63	0.64	0.64	0.63	0.65	0.64	
	5	0.63	0.62	0.64	0.64	0.65	0.64	
HMR-treated	1	0.70	0.67	0.69	0.69	0.69	0.69	
	2	0.73	0.75	0.75	0.75	0.78	0.75	
	3	0.74	0.72	0.73	0.76	—	0.74	0.71
	4	0.67	0.69	0.70	0.70	0.69	0.69	
	5	0.66	0.67	0.69	0.69	0.71	0.68	
				Experimental sequence at 25°C				
Phenol-treated	1	0.73	0.76	0.77	—		0.75	
	2	0.73	0.76	0.76	0.76		0.75	
	3	0.71	0.74	0.74	0.76		0.74	0.74
	4	0.73	0.74	0.72	0.72		0.73	
	5	0.74	0.73	0.72	0.74		0.73	

* Data excluded because of atypical response.

We speculate that lignin is the most probable target for HMR reaction since lignin contains a large number of nucleophilic and electrophilic sites.

While chemical crosslinking might explain the results discussed above, one may also consider the possible effects of the simple bulking caused by HMR monomers that enter the amorphous regions of the cell wall. Could cell-wall bulking, in the absence of chemical crosslinking, explain the HMR effect exhibited above? This hypothesis was tested with samples impregnated

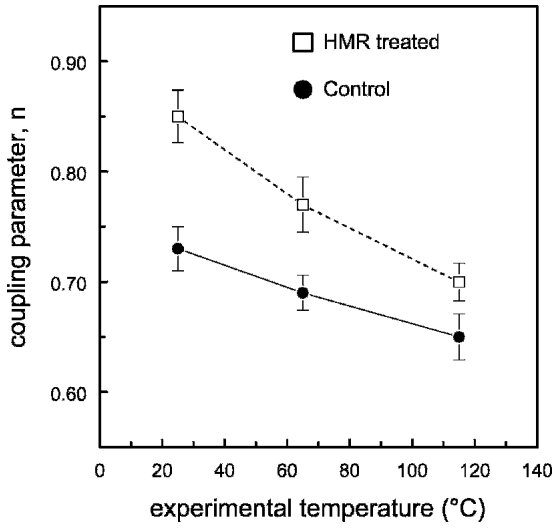

FIG. 4. Mean coupling parameter as a function of experimental temperature for HMR-treated and control samples as indicated.

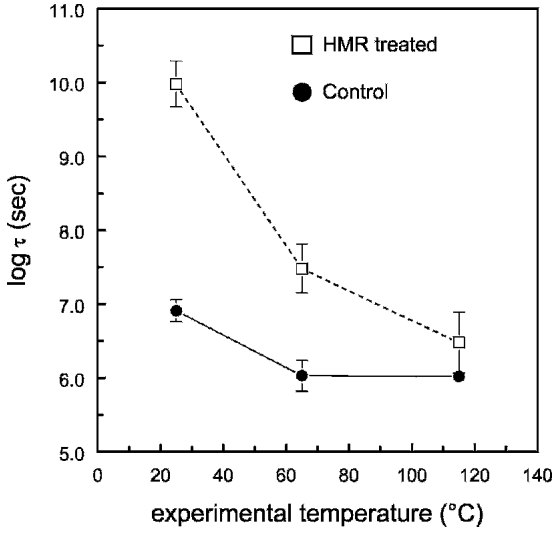

FIG. 5. Mean effective relaxation time (τ) as a function of experimental temperature for HMR-treated and control samples as indicated.

with aqueous phenol. The wood cell wall is known to preferentially adsorb phenol from aqueous phenol solutions (Stamm 1964). And since phenol is much less reactive than resorcinol, bulking wood with aqueous phenol is not expected to promote crosslinking at 25°C. Yellow-poplar samples were impregnated with phenol and then subjected to stress relaxation experiments at 25°C as before (except that these samples were subjected only to four stress relaxation cycles). Figure 6 demonstrates that phenol impregnation has no effect on the coupling parameter; in this case, the comparison is based upon the means calculated across samples for each experimental cycle. Figure 7 suggests that phenol impregnation may have slightly increased the effective relaxation time; however, the effect shown has little if any significance. Summarizing, unreactive phenol enters the cell wall and has little if any effect on the stress relaxation of wood. In contrast, the highly reactive HMR monomers dramatically stiffen the cell wall against stress relaxation as seen from the significant increase in relaxation time and cooperativity.

SUMMARY AND CONCLUSIONS

The isothermal stress relaxation response of wood (from 25 to 115°C) is well described by

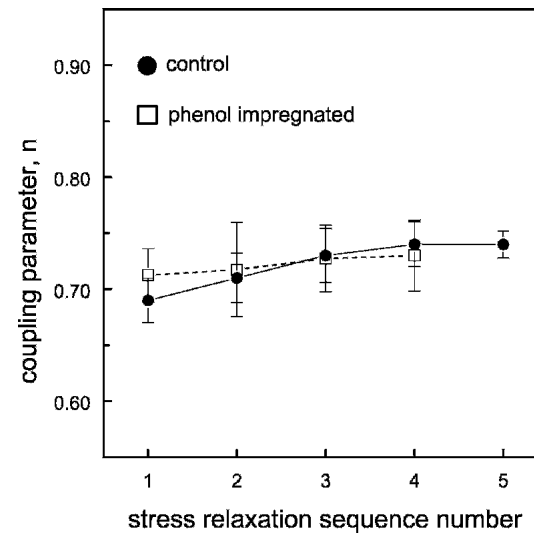

FIG. 6. Mean coupling parameter for all control and phenol-impregnated samples analyzed at 25°C. Each mean was calculated across samples for each of the relaxations within the typical sequence; each mean based upon 3–5 observations.

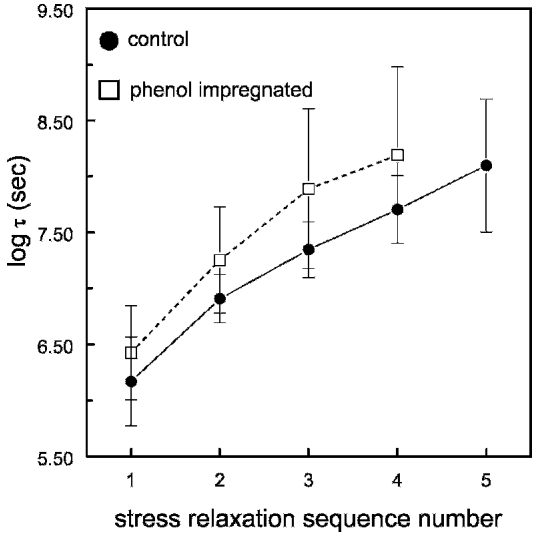

FIG. 7. Mean effective relaxation time (τ) for all control and phenol-impregnated samples analyzed at 25°C. Each mean was calculated across samples for each of the relaxations within the typical sequence; each mean based upon 3–5 observations.

the fractional exponential relationship known as the KWW equation. This provides a direct evaluation of the relaxation time and of the Ngai coupling parameter; the latter describes the cooperativity of segmental motions. The analysis demonstrates that HMR significantly increases the time and cooperativity of wood cell-wall relaxations. This stiffening against the imposed strain is suspected to arise from chemical crosslinking of a mobile cell-wall component, speculated to be lignin. The effects caused by HMR are not explained by the simpler effects of cell-wall bulking (or swelling). These findings suggest that one aspect of the HMR coupling mechanism may be related to wood cell-wall crosslinking. Under this scenario, HMR crosslinking will stabilize wood in and around the adhesive interphase against the damaging effects of water swelling (Son and Gardner 2004) and other mechanical stresses. These findings say nothing about the potential chemical reaction between HMR and the adhesive; and so this possibility must also be considered for adhesives having the appropriate reactivity.

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