Dynamic Sorption and Hygroexpansion of Wood Subjected to Cyclic Relative Humidity Changes.
II. Effect of Temperature

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To investigate the effect of temperature on the dynamic sorptive and hygroexpansive behavior of wood, poplar (*Populus euramericana* cv.) specimens, 20 mm in radial (R) and tangential (T) directions with two thicknesses of 4 mm and 10 mm along the grain, were exposed to a sinusoidally varying relative humidity between 45 and 75% for 1, 6, and 24 h at 25 and 40 °C. Moisture changes, as well as radial and tangential dimensional changes measured during cycling, produced the following results: moisture and dimensional changes in the specimens were generally sinusoidal, and an increase in temperature led to decreased moisture contents and transverse dimensions, accordingly. The amplitude of moisture and dimensional changes was in positive correlation with temperature, while the phase lag was inversely related to temperature. Sorption hysteresis and swelling hysteresis decreased as temperature increased. Both moisture sorption coefficient (MSC) and humidity expansion coefficient (HEC) were supposed to share the approximate value for different thick specimens if cyclic period is sufficiently long. Transverse anisotropy could be found under dynamic conditions, and the T/R was about 1.65 to 1.75, varying sinusoidally with a phase difference of about a half cycle to the imposed relative humidity.

Keywords: Dynamic sorption; Hygroexpansion; Nonequilibrium state; Temperature; Wood

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INTRODUCTION

As a porous material, wood's natural hygroscopic properties cause its sorptive and hygroexpansive behavior. As a result, wood products are easily subjected to deformation during daily use, *e.g.*, cracking and warping. This has a serious effect on the service lifetime of wood products.

Various studies have shown that the properties of wood sorption and hygroexpansion depend upon many factors, such as species, growth location, relative humidity (RH), and temperature (Liu and Zhao 2004; Ma and Zhao 2012). At a given RH, temperature increase generally results in a reduction in the equilibrium moisture content (MC) of wood. For example, a decrease of approximately 1% of equilibrium MC can be observed for every 10 °C increase between 20 and 100 °C (Stamm and Loughborough 1935; Kollmann 1959; Weichert 1963). Kelsey (1957) further investigated adsorption and desorption isotherms and the effect of temperature on the sorption hysteresis of Klinki pine. The results indicated that equilibrium MC and sorption hysteresis decreased with increasing temperature. Moreover, the White and Eyring sorption equation (Kelsey 1957) was applied, and the mechanism for the effect of temperature on wood hygroscopicity was found to be caused by a decrease in the amount of sorption sites with increasing temperature.

When temperature is higher than 100 °C, a primary factor causing the reduction in wood's hygroscopicity is the degradation of main components in the cell wall. Stamm (1964) reported that exposing wood to temperatures between 200 and 300 °C produced a permanent loss in hygroscopicity because of the thermal decomposition of hemicellulose, which is the most hydrophilic element in wood cell walls. Obataya and Tomita (2002) discussed the reversibility of hygroscopicity in wood by thermal treatment at different temperatures and discovered an irreversible decrease in MC when thermal treatment temperature was higher than 140 °C.

At the same time, temperature not only affects the sorption amount, but also the sorption rate of wood (Stamm 1964). It was reported that an increase in temperature could accelerate both moisture diffusion inside wood (Gong *et al.* 2001) as well as molecular structure relaxation (Engelund *et al.* 2013). The effect of temperature on moisture sorption, in turn, inevitably brings influence to bear on dimensional changes in wood. The shrinkage of wood increases with increasing temperature (Stevens 1963; Espenasl 1971). In addition, temperature was also shown to be linked with the linear range in the MC-dimension curve of wood (Stevens 1963).

It can be found that the effect of temperature on the sorption and hygroexpansion of wood under static conditions (constant RH and temperature) has been researched systematically. However, because atmospheric RH during wood processing and use is always changing and may be sinusoidal (Schniewind 1967), it is of great importance to understand wood sorption and deformation under this dynamic condition. Such work was first conducted by Chomcharn and Skaar (1983), who studied the dynamic sorption and hygroexpansion of wood wafers. Later in our previous studies (Ma *et al.* 2010; Yang and Ma 2013), the moisture and tangential (T) and radial (R) dimensional changes of wood subjected to a sinusoidally varying RH at a constant temperature was investigated.

The work presented here was conducted to investigate the effect of temperature on the dynamic sorption and hygroexpansion of wood. The results should be helpful in enriching the fundamental understanding of the sorptive and hygroexpansive behavior of wood under non-equilibrium conditions. The work also provides technical parameters for the moisture and dimensional stability control of wood products in service.

EXPERIMENTAL

Materials

Poplar (*Populus euramericana* cv.) from the Greater Khingan Mountains in China was chosen as the study species.

Methods

The specimens, cut into 20 mm in R and T directions with two thicknesses of 4 mm and 10 mm along the grain, were first boiled in distilled water for 15 min to remove their growth stress. Afterward, they were oven-dried at 105 °C for 48 h, and conditioned in 45% RH at 25 °C and 40 °C for 10 days. The humidity levels were controlled by saturated salt solutions of potassium carbonate and magnesium nitrate, respectively (Macromolecule Academy 1958). Then, the specimens were moved into a conditioning oven (DHS 225, YaShiLin, Beijing) to conduct the cyclic tests, where RH was changed sinusoidally between 45 and 75 ± 1.0%, cycled at three periods of 1, 6, and 24 h under 25 °C and 40 °C. The RH in the oven was programmed to vary in discrete steps according to a predetermined schedule, and a thermo recorder was placed near the specimens to monitor RH and temperature. During the process, weight changes, as well as R and T changes, were measured every 1, 5, or 15 min period for each of the three cycles, respectively, by an electronic analytical balance (sensitivity ± 0.1 mg) and a self-made 2-dimension measuring system made up of three CCD laser displacement sensors (sensitivity ± 1 μm) (Ma *et al.* 2010).

In addition, there were three end-matched replicates for each cyclic period, one for dimension and the other two for weight measurement. Each period was repeated three times, and average values of the three tests for weights and dimensions of the specimens were taken as the final result.

THEORETICAL

The moisture diffusion coefficient D was analyzed by the theoretical model for dynamic sorption (Ma *et al.* 2010) as follows,

$$m_i=m_{i-1}+a(h-exp(k_2k_1^{m_{i-1}}+k_3))\,\Delta t \tag{1}$$

$$K_1=1.0327-0.000674T \tag{2}$$

$$K_2=17.884-0.1432T+0.0002363T^2 \tag{3}$$

$$K_3=0.16 \tag{4}$$

$$D=1.48\times 10^{-8}exp(0.11m) \tag{5}$$

where m is MC (%), a is sorption rate constant (1/h), h is RH for the surrounding atmosphere (%), and T is temperature (K). K_1, K_2, and K_3 are given by the Bradley equation (Bramhall 1979). Their values were validated by experimental isotherm curves.

RESULTS AND DISCUSSION

General Moisture and Dimensional Responses

Moisture and dimensional responses of 10-mm thick poplar specimens to sinusoidally varying RH cycled for 6 h at 40 °C are shown in Fig. 1, in which dimensional changes are given in terms of swelling based on oven-dry dimensions. It is apparent that the moisture and dimensional changes are generally sinusoidal but lag behind the imposed RH. It also seems as if a repetitive “steady state” in the moisture and dimensional responses is reached in the third cycle, *i.e.*, between 720 and 1080 min.

Table 1 compares the moisture and R and T dimensional responses for 4 mm and 10 mm poplar wood at 25 and 40 °C. It is clear that both moisture and R and T dimensional changes were generally lower at 40 °C than at 25 °C, which is in accordance with static studies (Kelsey 1957). As mentioned above, this is because the hygroscopicity of wood decreased with increasing temperature as a result of losing sorption sites (Kelsey 1957) and the increased potential for moisture to evaporate (Willems 2014).

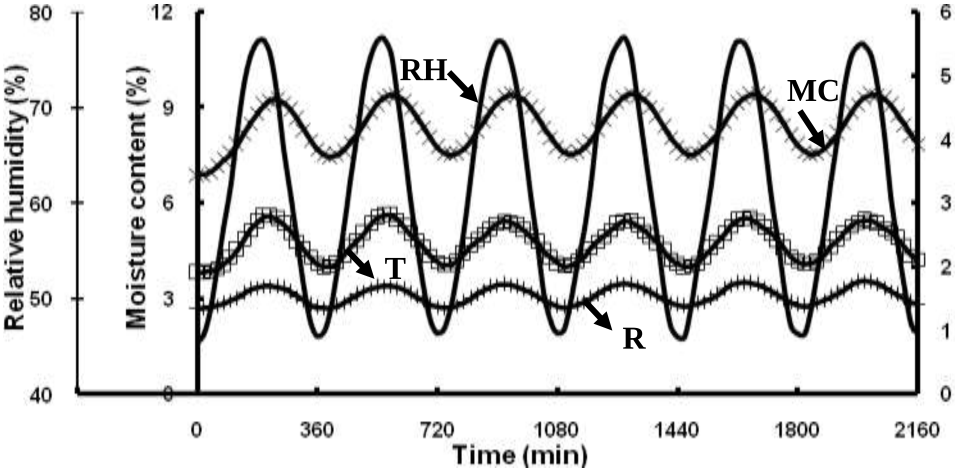

Fig. 1. Plots of RH, MC, and R and T dimensional changes against cyclic time for 10-mm thick poplar wood cycled at 6 h at 40 °C

Table 1. Comparison of Moisture and R and T Dimensional Responses for Poplar Wood between 25 and 40 °C

Thickness (mm)	Period (h)	MC (%)		T (%)		R (%)	
		25 °C	40 °C	25 °C	40 °C	25 °C	40 °C
4	1	8.15(0.254)	6.95(0.179)	2.90(0.084)	2.88(0.114)	1.89(0.032)	1.75(0.019)
	6	9.28(0.161)	8.56(0.100)	3.52(0.048)	3.17(0.044)	1.93(0.028)	1.81(0.028)
	24	8.45(0.244)	8.26(0.129)	3.55(0.006)	3.49(0.038)	2.52(0.018)	2.41(0.032)
10	1	7.73(0.227)	7.60(0.158)	1.82(0.050)	2.86(0.031)	1.23(0.039)	1.74(0.043)
	6	8.50(0.452)	8.39(0.157)	3.09(0.109)	2.38(0.019)	1.87(0.044)	1.54(0.024)
	24	9.11(0.043)	8.42(0.024)	2.51(0.020)	2.25(0.018)	1.76(0.013)	1.49(0.033)

Data provided as the average (standard deviation) per cycle from several replicate experiments

Amplitude and Phase Lag

The amplitude and phase lag of the moisture and R and T dimensional changes are two parameters characterizing wood's ability to respond to varying environments, which both depend on the reaction time of the wood-water system.

Table 2 presents the moisture and dimensional response amplitude and phase lag for poplar wood. It is evident that the amplitude is greater for the specimens exposed to longer cycles for both 4-mm and 10-mm thick specimens, which agrees with the results by Chomcharn and Skaar (1983). However, the values at 25 °C are lower than those at 40 °C, *i.e.*, there was a positive correlation between wood response amplitude and temperature. In addition, for thicker specimens, the moisture and dimensional amplitude were lower for all three cyclic periods. This was anticipated because there was not sufficient time for the thick specimens, especially their inner part, to respond to the RH changes.

On the other hand, it is obvious that as the cyclic period was increased, the phase lag decreased, which also confirms the results by Chomcharn and Skaar (1983). This was as expected, because with longer cyclic periods, the specimen response could more closely follow the RH changes (Ma *et al.* 2010). Moreover, It suggests that the phase lags at 40 °C are lower than those at 25 °C, *i.e.*, phase lag is inversely related to temperature at a given cyclic period and specimen thickness, which is supported by the fact that moisture diffusion (Gong *et al.* 2001) and structural relaxation (Engelund *et al*. 2013) could be promoted by higher temperature. In addition, phase lag increased with specimen thickness, or stated another way, thick specimens respond to RH changes more slowly. The moisture and R and T dimensional phase lags decrease in turn, demonstrating that the T dimension responded to dynamic conditions most rapidly, followed by the R dimension and moisture changes, which was attributed primarily to the ray restraint effect (Liu and Zhao 2004), causing R hygroexpansion to act later than T hygroexpansion; this supports our previous studies (Ma *et al.* 2010; Yang and Ma 2013).

Table 2. Amplitude and Phase Lag of Moisture and T and R Dimensional Responses for Poplar Wood

	Thickness (mm)	Cyclic period (h)	MC		T		R	
			25 °C	40 °C	25 °C	40 °C	25 °C	40 °C
Amplitude (%)	4	1	1.73(0.056)	1.78(0.056)	0.60(0.014)	0.95(0.021)	0.32(0.023)	0.50(0.013)
		6	2.49(0.069)	3.02(0.130)	0.89(0.008)	0.96(0.025)	0.57(0.007)	0.58(0.022)
		24	3.29(0.019)	3.43(0.056)	0.95(0.239)	1.04(0.035)	0.77(0.059)	0.80(0.041)
	10	1	0.84(0.014)	1.01(0.034)	0.45(0.007)	0.63(0.014)	0.22(0.004)	0.33(0.003)
		6	2.08(0.057)	2.14(0.021)	0.75(0.016)	0.77(0.007)	0.48(0.025)	0.39(0.023)
		24	2.61(0.051)	2.75(0.057)	0.87(0.040)	0.92(0.035)	0.72(0.026)	0.78(0.048)
Phase Lag (radians)	4	1	0.65(0.045)	0.63(0.054)	0.52(0)	0.5(0)	0.61(0.032)	0.55(0.050)
		6	0.47(0.044)	0.42(0.044)	0.31(0.050)	0.16(0.010)	0.33(0.044)	0.23(0.021)
		24	0.43(0.032)	0.31(0.031)	0.23(0.022)	0.08(0.084)	0.26(0)	0.16(0)
	10	1	1.14(0.092)	1.06(0.102)	0.72(0.031)	0.69(0.056)	0.99(0.028)	0.96(0.094)
		6	0.81(0.053)	0.54(0.038)	0.49(0.046)	0.29(0.017)	0.51(0.049)	0.36(0.029)
		24	0.5(0.038)	0.36(0.038)	0.26(0)	0.11(0)	0.29(0.027)	0.18(0.006)

Data provided as the average (standard deviation)

As suggested in Table 2, amplitude and phase responses should be strong functions of the cyclic frequency. Figure 2 further takes the 10 mm thick specimen at 25 °C as an example to present this relation. It is evident that the amplitude and phase lag were both linear to the frequency of cyclings, which could be described as the typical linear equation of $y=ax+b$ with high R^2 values.

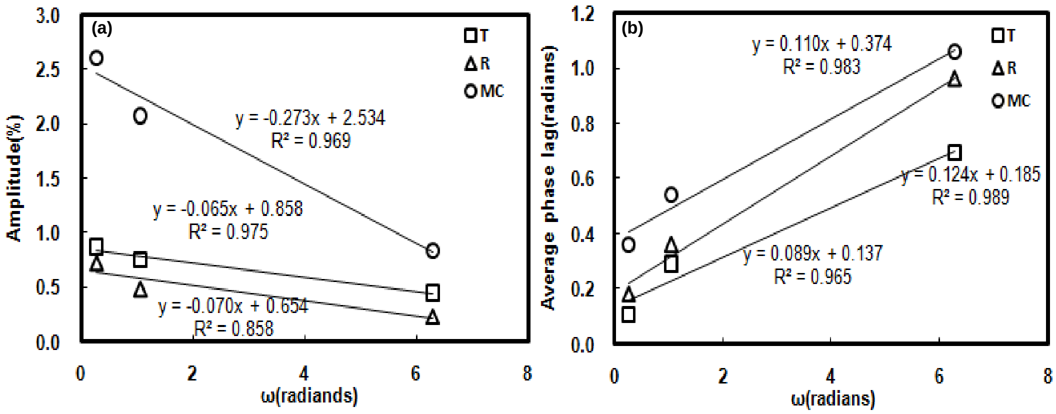

Fig. 2. Plots of amplitude (a) and phase lag (b) responses against angular frequency of RH cyclings (25 °C, 10 mm)

Sorption and Swelling Hysteresis

Dynamic sorption isotherms and tangential dimensional changes against relative humidity for 10-mm thick poplar wood at the cyclic period of 6 h, for example, are shown in Fig. 3(a) and Fig. 3(b), respectively. Sorption hysteresis in dynamic condition, which mainly relates to fast diffusion-rates rather than slow wood structure relaxation-rates for long equalization times compared with static state, can be observed in Fig. 3(a), and it is more obvious at 25 °C. This suggests that sorption hysteresis decreases as temperature increases, which was also the case under static conditions (Kelsey 1957). And it is clear that the wood displays swelling hysteresis caused by sorption hysteresis under dynamic conditions in Fig. 3(b).

To investigate the sorption hysteresis of wood under dynamic conditions quantitatively, the maximum hysteresis ratio A/D (adsorption MC/desorption MC) for each cycle was calculated and summarized in Table 3.

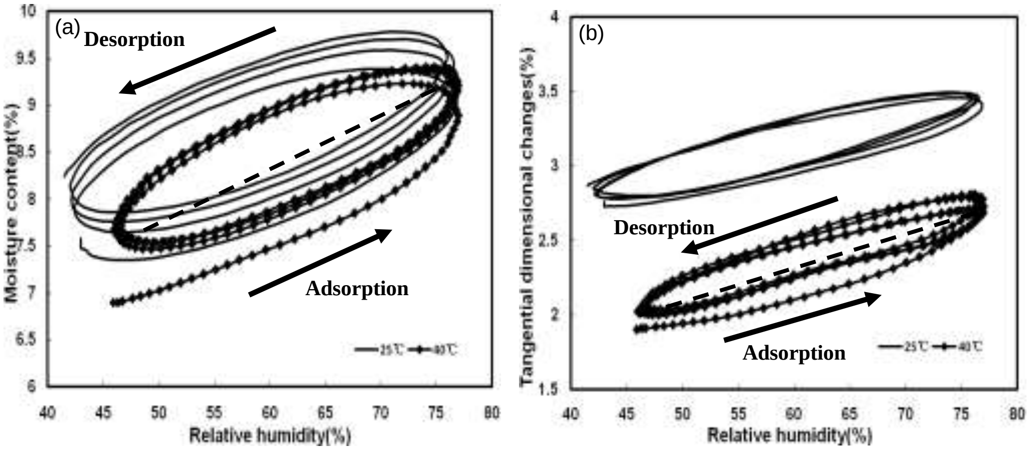

Fig. 3. Plots of dynamic sorption isotherms (a) and tangential dimensional changes against relative humidity (b) for 10-mm thick poplar wood cycled for 6 h

As shown in Table 3, the A/D ratio was found to be about 0.88, with no consistent effect of cyclic period and specimen thickness. Compared with the A/D ratio at 25 °C, the values under 40 °C increased slightly, that is, the A/D ratio rose as temperature was raised, which was observed by Weichert (1963) under static conditions.

Table 3. A/D Ratio for Poplar Wood under Dynamic Conditions

Thickness (mm)	Cyclic Period (h)	25 °C		40 °C	
		A/D	Average	A/D	Average
4	1	0.888(0.004)	0.868	0.876(0.006)	0.887
	6	0.890(0.004)		0.906(0.007)	
	24	0.825(0.005)		0.880(0.007)	
10	1	0.915(0.002)	0.880	0.861(0.001)	0.884
	6	0.854(0.005)		0.880(0.008)	
	24	0.872(0.006)		0.912(0.006)	

Data provided as the average (standard deviation)

It also can be seen in Fig. 3 (a) that the dynamic sorption isotherms of each cycle behaved like overlapped ellipses. The ellipses at 40 °C quickly converged to a stable one, while those at 25 °C continued to shift, owing to the fact that higher temperature could accelerate the moisture diffusion and structural relaxation rate. The slope of their long axis represents variation in MC per RH change, which is known as the moisture sorption coefficient (MSC) (Skaar 1988), an index used to evaluate wood hygroscopicity. Similarly, the slope of the long axis of the ellipses in Fig. 3 (b) indicates variation in dimension per RH change, which is called the humidity expansion coefficient (HEC) (Skaar 1988), an index used to evaluate the dimensional stability of wood.

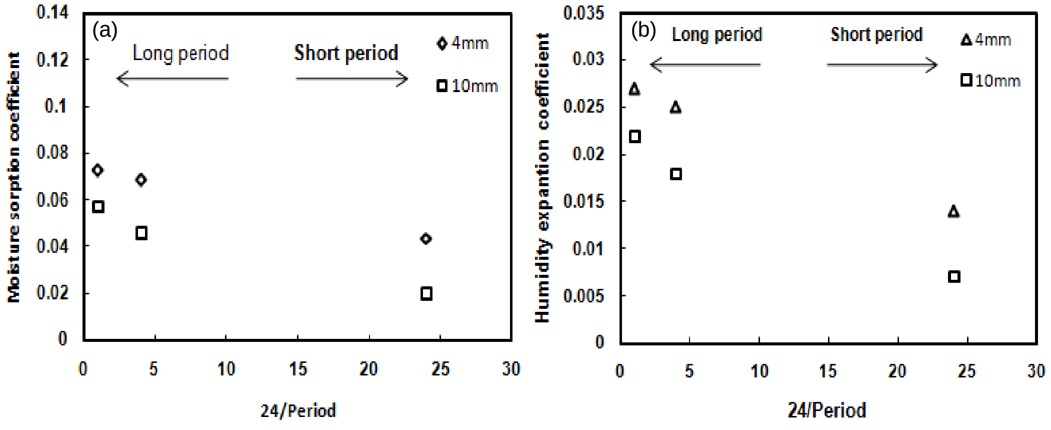

Fig. 4. Dynamic moisture sorption coefficient (a) and humidity expansion coefficient (b) at different cyclic periods for poplar wood (40 °C)

Figure 4 shows the dynamic moisture sorption coefficient (a) and humidity expansion coefficient (b) against different cyclic periods. A negative relation was observed between the MSC/HEC and specimen thickness at a given cyclic period. For specimens with the same thickness, both the two coefficients increased with increasing cyclic durations. The intercepts of the Y-axis from the data tendency, corresponding to the values expected if the cyclic period is sufficiently long that moisture inside the specimens changes uniformly without gradient, are supposed to share the approximate value for both 4 mm and 10 mm thick specimens. In addition, the MSC and HEC values were all less than the static value (Noack *et al*. 1973) but not much far from the corresponding dynamic values by Chomcharn and Skaar (1983).

Dynamic Sorption Modeling

Figure 5 shows a comparison of theoretical curves with experimental results of dynamic sorption cycled at 1 h at 40 °C as an example. The plot suggests that the theoretical curves calculated by the mathematical model (Ma *et al.* 2010) agree with the experimental data.

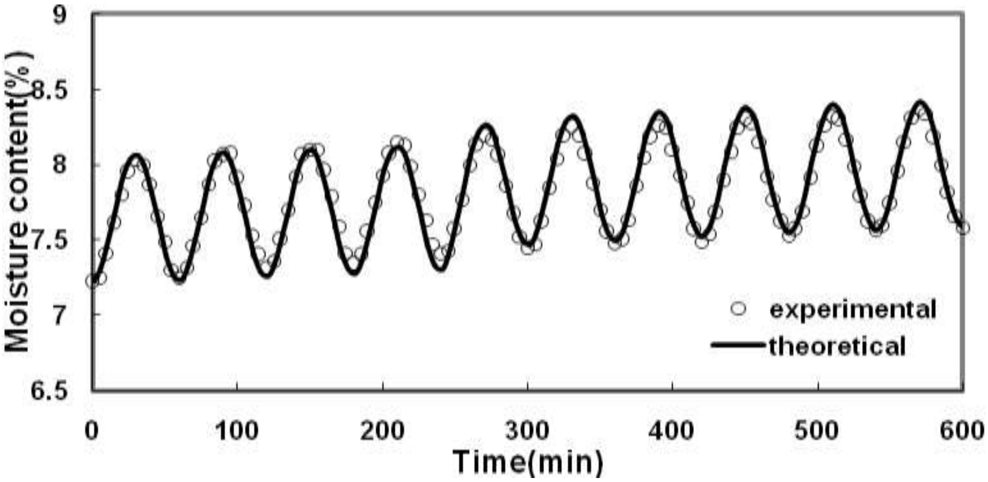

Fig. 5. Comparison of theoretical curves with experimental results of dynamic sorption for 10-mm thick poplar wood cycled at 1 h (40 °C)

Table 4. Diffusion Coefficient *D* for Poplar Wood Calculated from Moisture Content under Dynamic Conditions

Thickness (mm)	Period (h)	D×10^{-3} (m^2/s) 25 °C	D×10^{-3} (m^2/s) 40 °C
4	1	0.047	0.900
	6	2.232	4.680
	24	2.520	5.400
10	1	0.013	0.025
	6	0.432	1.620
	24	1.800	2.844

Table 4 summarizes the diffusion coefficient *D* used in dynamic sorption modeling for 4 mm and 10 mm thick specimen cycled at three periods at both 25 °C and 40 °C. It is apparent that the coefficient increased as the cyclic period was increased or the specimen thickness was decreased. Moreover, there was a positive relation between *D* and temperature, which agrees with the static results (Ma and Zhao 2012).

Transverse Anisotropy

The ratio of tangential dimensional change to radial dimensional change (T/R) during the cyclic process was worked out to discuss transverse anisotropy under dynamic conditions. Figure 6 takes 10-mm thick poplar cycled at 1 h as an example. The T/R ratio was about 1.65 to 1.75, lower than the static results (Liu and Zhao 2004). At the beginning of the cycle, T/R decreased sharply and changed sinusoidally in general, but lagged about a half cycle to the varying RH. This is probably because the wood ray restraint effect was hindered when moisture content increased; as a result, T/R decreased during adsorption and increased during desorption.

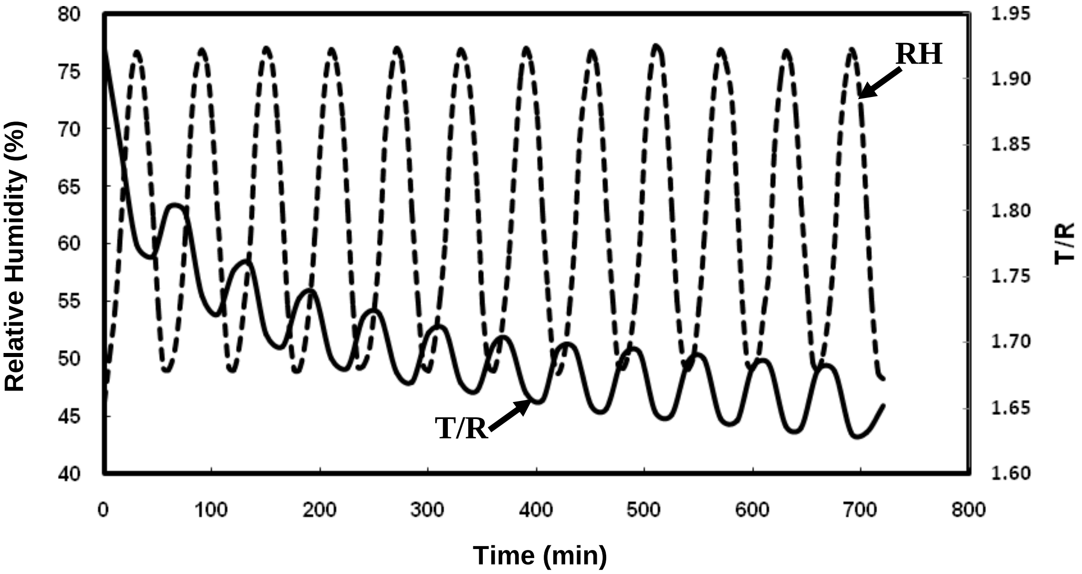

Fig. 6. Transverse anisotropy for 10-mm thick poplar wood cycled at 1 h (40 °C).

CONCLUSIONS

1. Moisture and dimensional changes of the specimens were generally sinusoidal, and an increase in temperature led to decreased MC and transverse dimensions, accordingly.
2. Amplitude of moisture content and dimension was in positive correlation with temperature, while phase lag was inversely correlated with temperature.
3. Both sorption hysteresis and swelling hysteresis decreased as temperature increased. In addition, both MSC and HEC were supposed to share the same approximate value for the specimens of different thicknesses if cyclic period is sufficiently long.
4. The theoretical curves calculated by the mathematical model agreed satisfactorily with the experimental data. Moisture diffusion coefficient increased with increasing cyclic period and temperature, but was reduced with a decrease in specimen thickness.
5. Transverse anisotropy could be found in the specimens under dynamic conditions, and the ratio of T changing rate to R changing rate (T/R) was about 1.65 to 1.75, changing sinusoidally with a phase difference of about a half cycle to the imposed RH.

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