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Quantification of hydrolytic degradation of cured urea-formaldehyde resin adhesives using confocal laser scanning microscopy

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ABSTRACT

This study reports a method of measuring the extent of hydrolytic degradation of cured urea-formaldehyde (UF) resins trapped in the lumen of softwood tracheids, using confocal laser scanning microscopy (CLSM) which enables quantitative determination of the area of a cured UF resin in the lumen as a function of acid etching time. Two formaldehyde/urea (F/U) mole ratios (1.6 and 1.0) and two hardener levels were employed to compare the extent of hydrolytic degradation of cured UF resins. For comparison, we also measured the mass loss of cured UF resin films after acid etching. Cured UF resins with a 1.6 F/U mole ratio resulted in greater hydrolytic degradation than those with a 1.0 F/U mole ratio. The hardener level also showed a clear influence on the extent of degradation with a limited consistency. These results indicate that cured UF resins with higher F/U mole ratios are more easily hydrolyzed than those with low F/U mole ratios, which could be ascribed to a more branched network structure of cured UF resins with a high F/U mole ratio.

1. Introduction

The hydrolytic degradation of cured urea-formaldehyde (UF) resins is responsible for long term formaldehyde emissions (FE) from wood-based composite panels bonded with UF resins. Thus, it is useful to quantify and visualize the hydrolytic degradation of the cured UF resin before and after acid etching at different intervals in order to provide information about FE from wood-based composite panels. The susceptibility of the cured UF resins to hydrolytic degradation depends on their chemical structure and the degree of cross-linking, and could be accelerated by high temperature and strong acidic conditions [1]. For instance, Hse et al. [2] studied the effect of reaction pH on the properties and performance of UF resins. Furthermore, Park et al. [3] reported that the amount of free formaldehyde present in UF resins contributed proportionately to the FE from particleboards, even after hot-pressing at relatively high temperatures.

In order to understand the mechanisms responsible for FE, various methods have been used to characterize the hydrolysis process of cured UF resins, for example using either acid or diffusion controls [4]. A conventional method of measuring hydrolytic degradation is gravimetric analysis by measuring mass loss of cured UF resins after intentional acid hydrolysis [5–7]. In addition, visualization using scanning electron microscopy (SEM) or atomic force microscopy (AFM) has also been employed to compare the hydrolytic degradation of UF resins without any quantitative information [5,8]. In this context, these microscopic methods could also be employed to quantitatively measure the hydrolytic degradation of cured UF resins.

On the other hand, imaging techniques have been employed in the investigation of wood-polymer interfaces involving UF resin based adhesives. For example, light microscopy, confocal laser scanning microscopy (CSLM), and SEM have been employed to examine the wood-coating interface [9] and penetration of UF resin into poplar wood in the tangential and radial directions [10]. Further, a single technique of image analysis has been established for detecting UF resin adhesives in both particle and fiberboards as well as on wood chips and fibers using CSLM [11–14], microcomputed tomography (μCT) [15–18], SEM [19,20], and confocal Raman microscopy [21]. Recently, a light microscope with visible and fluorescent stains was employed to detect UF resin penetration into softwood tissues [22] and industrial particleboard materials [23].

In spite of various attempts, it is still necessary to develop a method for quantifying the extent of hydrolytic degradation in cured UF resins. A combined method for quantifying and visualizing the hydrolytic degradation of the cured UF resin will be very useful in understanding the release of formaldehyde from wood products bonded using UF resins.

Here, we demonstrate a quantitative method of using a simple CLSM method to measure the hydrolytic degradation of cured UF

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Table 1
Non-volatile solids, viscosity, gel time, and pH of liquid UF resins with two different F/U mole ratios.

F/U mole ratio	Non-volatile solid (%)	Viscosity (mPa.s)	Gel time[a] (s)	pH
1.6	54.1	450	77	8.0
1.0	57.2	165	285	8.0

[a] Measured values at 3% NH_4Cl level.

resins that have been trapped in wood tissue before and after an intentional hydrolytic degradation using an acid, even though this method has been employed to quantify UF resin distribution in wood fiber [11,22,24–28].

Since the CLSM system provides the same level of focus for all images, out-of-focus fluorescence can actually be eliminated [25]. Combined with a staining agent, UF resins become fluorescent and the wood fluorescence is quenched [24]. Thus, the presence of cured UF resins within the wood tracheids can be determined and quantified. In this way, the alteration of cured UF resins after acid hydrolysis can be evaluated. Therefore, the objective of this work was to develop a quantitative method of measuring and visualizing the extent of hydrolytic degradation of cured UF resin adhesives with different F/U mole ratios and hardener levels, using the CLSM method.

2. Materials and methods

UF resins with two extreme F/U mole ratios (1.6 and 1.0) were prepared in the laboratory, according to the published method, following a conventional alkaline-acid two-step reaction by adding the 2nd urea [7]. The properties of the UF resins are given in the Table 1.

The UF resin was mixed with NH_4Cl as hardener (0.1% and 3% based on the solid content of the UF resin). The mixture was poured into a petri dish, and pieces of radiata pine (*Pinus radiata*) veneer (10 mm x 5 mm x 2 mm) immersed and impregnated therein using 10 atm vacuum pressure for two days in order to remove excess of water from the resin condensation reactions. The samples were then cured in a convection oven at 60 °C for 24 hours. Further, thin cross-sections of approximately 20 µm thickness were obtained by dry sectioning with a sliding microtome (Yamato KOHKI, Japan). They were then immersed in the acid solution (1 N HCl) for different exposure periods such as 0, 1, 4, 8, and 24 hours in order to investigate the effect of acid etching time on the hydrolytic degradation of the cured UF resins trapped in the wood tracheids. Prior to examination using the CLSM method, the thin sections were stained with 0.05% aqueous toluidine blue for 20 seconds, washed and rinsed using glycerol so as to avoid hydrolysis affects to the UF resins.

The CLSM system used (LSM 700, Carl Zeiss, Germany) was equipped with an objective lens (EC Plan-Neofluar10x/0.30 M27) and a scanning module of fluorescence mode at two excitation wavelengths of 488 nm (green) and 555 nm (red) for the identification of cured UF resins and wood components, respectively, which had two emission wavelengths of 420–550 nm and 560 nm. Glycerol was used for mounting the sections, and 100 magnifications were set for taking microphotographs. The area measurement and calculation of cured UF resin area trapped within wood tracheids before and after acid etching, was carried out with the aid of image processing software (i-solution program, IMT solution, Vancouver, Canada) and Eq. (1), respectively.

$$\text{Cured UF resin Area}(\%)=\frac{\textit{total area of UF resin trapped in tracheids}}{\textit{total area of wood and resin (excludingrays)}}\times 100 \tag{1}$$

An average of four measurements of the area of cured UF resins trapped in tracheids from four different thin sections before and after acid etching for a certain period of time is presented in this work. Further, Duncan's multiple range tests (DMRT) were performed for all of the measurements from each of the treatment groups by analysis of variance (ANOVA) at a p value of 0.05.

In order to determine mass loss of cured UF resins after acid etching, the cured UF resin films were also prepared by mixing liquid UF resins with hardener at different levels such as 0.1, 1, 2, and 3% of NH_4Cl based on the solid content of liquid UF resin, and then cured at 50°C for 24 hours in a vacuum oven at 10 atm. The prepared films were cut into rectangular pieces about 2.5 mmx2.5 mm in size, weighed to determine the initial mass (m_O), and immersed in an acid solution (1 N HCl) over different exposure times (0, 1, 4, 8, and 24 hours) in order to mimic hydrolytic degradation under the types of conditions a wood-adhesive system would encounter in service. After the acid etching treatment, the films were blotted using tissue paper to remove remaining acid, and then air-dried for 24 hours. Subsequently, the films were re-weighed to obtain the film mass (m_1) after the acid etching treatment. The mass loss was calculated using Eq. (2):

$$\text{Mass loss}(\%)=\frac{(m_0-m_1)}{m_0}\times 100\% \tag{2}$$

3. Results and discussion

3.1. The area of cured UF resins trapped in tracheid lumens before acid etching

Fig. 1 shows images of cured UF resin trapped in the lumens of tracheids before and after the acid etching. The CLSM microphotographs taken before acid etching clearly shows the cured UF resins trapped in the lumens of many tracheids (Fig. 1, a and b), indicating that the UF resin has penetrated deeply into the wood tissues. However, the CLSM microphotographs after the acid etching show the presence of the cured UF resin inside a limited number of trachieds lumens (Fig. 1, c and d). These images in the cross section plane made it possible to quantitatively measure the area of the cured UF resins in the lumens, which enabled us to investigate the process of hydrolytic degradation of the cured UF resins with different F/U mole ratios and hardener levels as a function of the acid etching time. In addition, we also reported quantitative measurements of the penetration behavior of UF resins using both light microscope and CLSM method [22].

Table 2 shows the area of cured UF resins in the lumens and corresponding statistical analysis for UF resins with two F/U mole ratios and two hardener levels. When two different F/U mole ratios (*i.e.*, 1.6 and 1.0) at 0.1% hardener level were compared, the area of cured UF resin of 1.6 F/U mole ratio was much less, which could be due to the viscosity differences between the two liquid UF resins. In other words, a greater viscosity of the UF resin of high F/U mole ratio penetrates slowly into the tracheid lumens while the low F/U mole ratio UF resin goes quickly into the tracheid lumens. As a result, the total area of cured UF resin in the tracheid lumens at 0.1% hardener level is smaller for high F/U mole ratio UF resin. But it is opposite for low F/U mole ratio UF resin with low viscosity.

By contrast, the areas of cured UF resins trapped in wood tracheids lumen at 3% hardener level were 25.5% and 30.89% for 1.6 and 1.0 F/U mole ratio UF resins, respectively. These values were not significantly different in the statistical analysis. This finding was quite similar for both UF resins as shown in Table 2. This could be due to two different effects of the hardener addition. Firstly, the addition of 3% hardener solution (*i.e.* 20% NH_4Cl) might cause the dilution effect of the water in the hardener solution. A higher level of hardener results in a greater concentration of water into the liquid UF resin, which dilutes the resin to a lower viscosity. Secondly, a 3% hardener level accelerated the cure of the two UF resins to a greater extent than observed with the 0.1% hardener level under the same impregnation condition. The lower

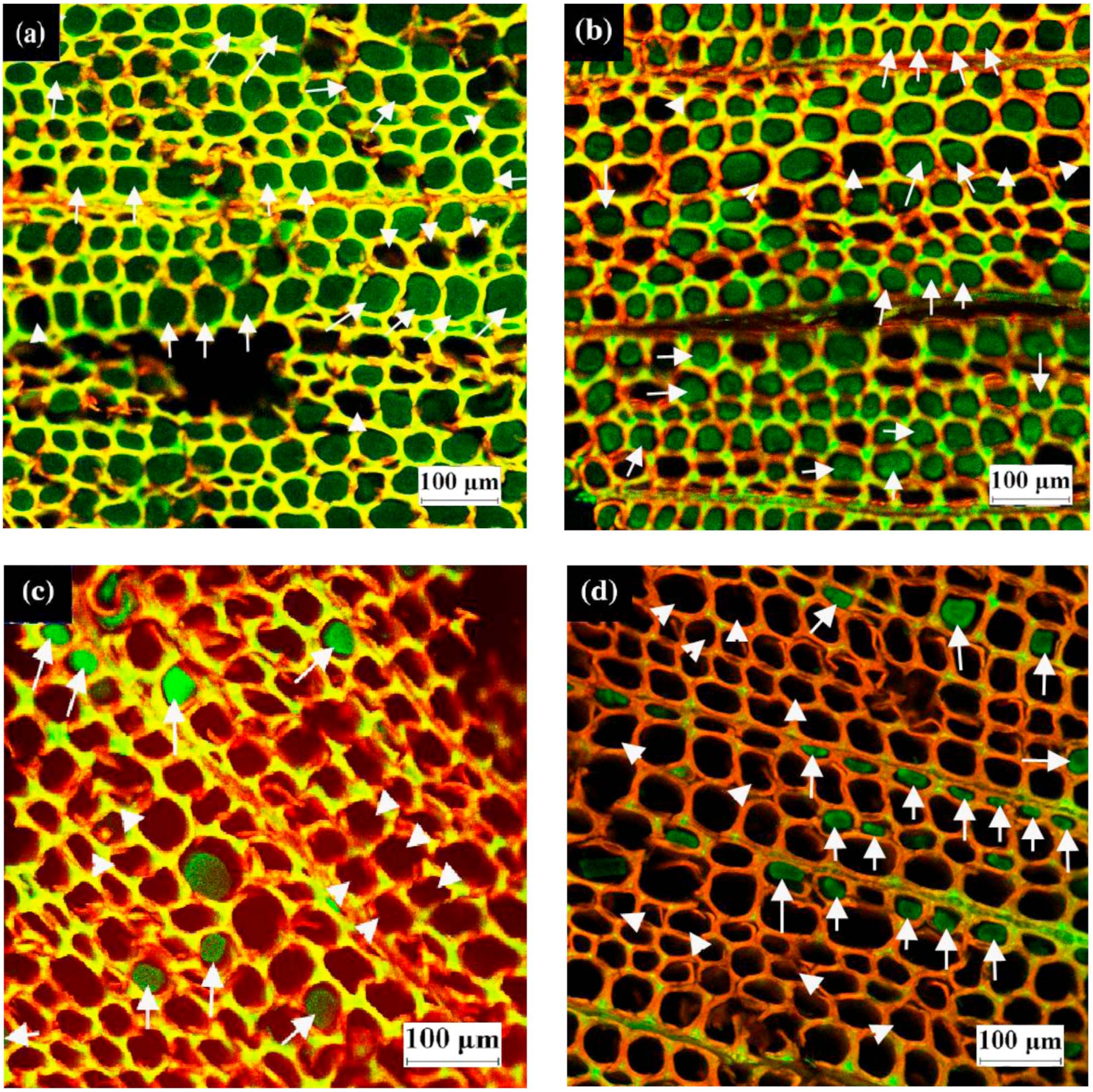

Fig. 1. Typical CLSM microphotographs of the cured UF resins trapped in the softwood tracheids with 3% of the hardener addition: (a) 1.6 F/U mole ratio UF resin before the acid etching, (b) 1.0 F/U mole ratio UF resin before the acid etching, (c) 1.6 F/U mole ratio UF resin after 1 hour acid etching, and (d) 1.0 F/U mole ratio UF resin after 1 hour acid etching. Cured UF resins in the lumen of tracheids are showed in green color (arrows), while the empty tracheids are showed in black color (arrow heads).

Table 2
The area of cured UF resins in the tracheid lumens and its statistical analysis for different F/U mole ratios and hardener levels.

F/U mole ratio	1.6		1.0	
Hardener levels (%)	0.1	3.0	0.1	3.0
Area of cured UF resins (%)[a]	8.21	25.50	46.98	30.89
Group[b]	a	b	d	bc

[a] Values are calculated by Eq. (1) based on an average of four measurements.
[b] The groups with the same letters are not statistically significant at a p value of 0.05.

viscosity and the greater cure acceleration of UF resin at 3% hardener level might result in similar values in the area of cured UF resin in lumen.

3.2. The area of cured UF resins trapped in tracheid lumens after the acid etching

Fig. 2 shows quantitative measurement results of the cured UF resin area trapped in the lumen of tracheids at two F/U mole ratios and two hardener levels as a function of the acid etching time. The results obtained after 24 hours etching were not included in Fig. 2 because the UF resin area was minimal, with its range from 0.1 to 0.2%. Moreover, the results of the area measurements after 24 hours were not statisti-

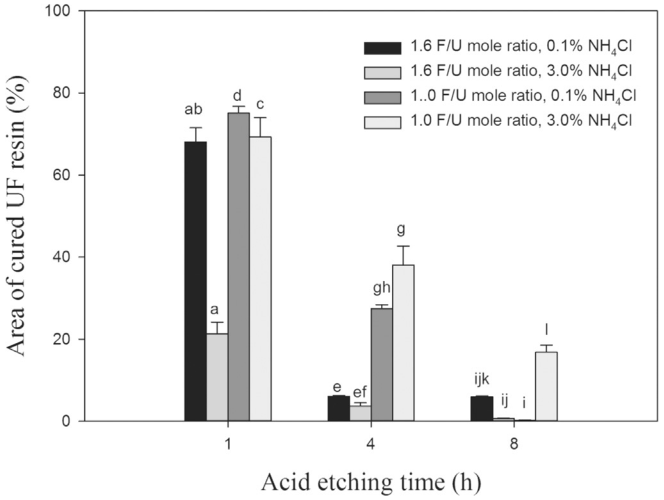

Fig. 2. Changes of the area of cured UF resins trapped in tracheid lumens at different F/U mole ratios and hardener levels as a function of the acid etching time including the statistical analysis results. The same letters are not statistically different at the *p* value of 0.05.

cally different between the F/U mole ratios and the hardener levels.

As expected, the area of cured UF resin in the cross section decreased with an increase in the acid etching time, although there were some fluctuations in the measurements as indicated by the standard deviations. The results also showed that UF resins with 1.6 F/U mole ratios were more susceptible to acid hydrolysis than those with 1.0 F/U mole ratios. This is quite compatible with the reported results [7]. In other words, high F/U mole ratio UF resins possess much more branched network structures that those of low F/U mole ratios [29]. A more branched UF resin has more pendant hydroxymethyl groups which were easily hydrolyzed by the acid [29]. And the fact that UF resins with high F/U mole ratios contain more methylene-ether linkages is also expected to contribute to more hydrolytic degradation of high F/U mole ratio UF resins [30].

The area of cured UF resin in the tracheid lumens decreased after acid etching because the acid hydrolyzed the cured UF resin with an increase in the acid exposure time. It was previously reported that hydrolysis of the cured UF resin under acidic conditions resulted in the splitting of ether bridges or terminal hydroxymethyl groups, which have been known to contribute to FE from UF resin-bonded wood panels [31–33]. Microscopic inspection of these samples combined with a statistical analysis showed that different patterns of cured UF resin remained within the wood tracheids, depending on F/U mole ratio and acid exposure time. For example, for 1 and 4 h of exposure to acid, the hydrolysis was significantly different for F/U mole ratios of 1.6 and 1.0. As mentioned above, the high F/U mole ratio was more susceptible to acid hydrolysis compared to the low F/U mole ratio UF resin. It was also reported that the linear structures in UF resins had greater hydrolytic stability compared with those of the branched structures in UF resins [7,30].

As shown in Fig. 2, the areas of the cured UF resins with 1.6 F/U mole ratio after 1 hour of acid etching were about 68% and 21%, at hardener levels of 0.1% and 3% respectively. This result was quite consistent with the previous report [8] which showed that the mass loss of cured UF resin was greater with the higher level of hardener. As expected, a higher level of hardener also influences the network structure of the cured UF resin. The higher hardener level for the UF resin with higher F/U mole ratio increases the rate of resin polymerization, which results in a greater degree of branching within the network structure of the cured resin. Thus more branched UF resin structures are more susceptible to acid hydrolysis. In other words, higher hardener levels result in a higher extent of hydrolytic degradation. Furthermore, it was reported that formaldehyde release in particleboards could result from free formaldehyde, which was previously bound to the wood cellulose during the curing or hardening stage, slowly hydrolyzing under the influence of the acidic condition in the wood [4]. Therefore, it was concluded that diffusion control was likely predominant in the formaldehyde release system, resulting in an increase in susceptibility to acidic hydrolysis.

In contrast, the higher hardener content in low F/U mole ratio UF resin-wood systems made this resin more resistant to acid hydrolysis. The area of cured UF resin remaining in the tracheid lumens was 75% and 69%, respectively, at 0.1% and 3% hardener level for UF resins with a 1.0 F/U mole ratio. These values indicated that the 1.0 F/U mole ratio UF resin was more resistant to acid hydrolysis than the 1.6 F/U mole ratio UF resin. In addition, a higher hardener level for the 1.0 F/U mole ratio UF resins also decreased hydrolytic degradation. This result supports previous reports that the crystallinity and crystal domain size increased with an increase in NH_4Cl level [34,35]. With a greater proportion of crystalline regions, cured UF resin of 1.0 F/U mole ratio was more resistant to acid hydrolysis. The crystalline parts in the UF resin provide a barrier for moisture to attack the cured UF resin [36]. Furthermore, the crystalline regions in cured UF resins did not alter even in contact with wood [37].

3.3. The influence of the hardener level to the mass loss upon the acid etching

In order to support the obtained results on the hydrolytic degradation of the UF resins with different hardener levels and F/U mole ratios, we have measured the mass loss for cured UF resin films after certain periods of acid exposure time. Table 3 presents the mass loss of UF resin films with different F/U mole ratios and hardener levels after acid etching for different periods of time. The longer period of etching, resulted in a higher mass loss of the cured UF films, particularly for the high F/U mole ratio UF resins, which have showed the higher mass loss. UF resin films with 1.6 F/U mole ratio were mostly amorphous, and therefore easier to hydrolytically degrade in comparison to the 1.0 F/U mole ratio resin which contained crystalline structures in its cured state in contact with wood [37].

Apparently, UF resin films with lower levels of hardener showed a higher mass loss, particularly for the high F/U mole ratio resin. This result indicated that a 0.1% level of hardener could possibly result in incomplete cross-linking of the UF resins during cure. In other words, UF resin films cured by adding 0.1% hardener were classified as partially cured [38].

When the films were exposed to the acid, the acid attacks partially cured or incompletely cured parts of the UF resin film at 0.1% hardener level. This resulted in a higher mass loss by releasing hydrolyzed components. This finding is consistent with the work of Grigsby et al. [39], where incompletely cured resin condensation products were consequently more susceptible to loss by water extraction. Therefore, this experiment definitively proves that the hardener influences the hydrolytic degradation of the cured UF resins.

Table 3
Mass loss of cured UF resin films with different F/U mole ratios and hardener levels after the acid etching for different times.

F/U mole ratio	Hardener level (%)	Mass loss after the acid etching time (%)			
		1 h	4 h	8 h	24 h
1.6	0.1	3.83±0.81	12.93±3.86	20.23±4.38	26.91±7.61
	1	0.03±0.07	1.05±0.50	1.22±0.59	11.27±3.45
	2	0.09±0.18	0.93±0.73	0.92±0.50	7.52±2.80
	3	0.27±0.34	0.36±0.38	0.76±0.25	3.58±2.64
1.0	0.1	1.48±0.73	2.01±1.50	4.04±1.77	3.53±2.66
	1	0.14±0.17	0.33±0.15	1.36±0.40	2.30±1.41
	2	0.06±0.11	0.41±0.27	1.30±0.56	1.85±1.70
	3	0.67±0.95	0.81±0.78	0.78±0.54	0.41±0.28

4. Conclusions

The influence of F/U mole ratios and hardener levels on the hydrolytic stability of cured UF resin within wood tracheids was investigated. Hydrolytic degradation was determined quantitatively by measuring the area of cured UF resin trapped in the lumens of softwood tracheids. High F/U mole ratio resin trapped in the tracheid lumens showed greater hydrolytic degradation after acid etching. However, low F/U mole ratio resins showed greater resistance to acid etching than those of high F/U mole ratio resin, which was believed to be due to the presence of crystalline structures in the low F/U mole ratio resin. The hardener level also showed a clear influence on the degree of degradation with a limited consistency, depending on the F/U mole ratio. In addition mass loss measurements along with statistical analysis showed that the F/U mole ratio and hardener level clearly influenced acid hydrolytic degradation of the cured UF resin. These results demonstrated that the influence of F/U mole ratio and hardener level on the hydrolytic degradation of cured UF resin trapped in the lumens of softwood tracheids was successfully quantified by the CLSM method. Measurements of mass loss and statistical analysis also supported the results by CLSM.

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