The Mechanical Strength Change of Wood Modified with DMDHEU

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1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) was used to enhance the dimensional stability, fungal resistance, and weathering of wood. The mechanical strength of wood treated with DMDHEU and different catalysts at different treating temperatures was studied. With increasing temperature, the modulus of rupture (MOR) and modulus of elasticity (MOE) of DMDHEU-treated wood first increased and then decreased. Different catalysts exhibited different effects on the MOR and MOE. In the context of SEM, EDAX, and FTIR analyses, the mechanism of strength loss resulting from the treatment with DMDHEU is discussed. In addition, the relationship between strength and pore size distribution determined by DSC was studied. The filling effect of the cured DMDHEU in wood pores reduced the pore size of the samples and may provide mechanical support to the cell wall, which prevents strength loss of the treated wood when the curing temperature is relatively low (90˚C). But at higher curing temperatures (150˚C), the mechanical strength properties of DMDHEU-treated wood decreased greatly.

Keywords: DMDHEU; DSC; FTIR; Mechanical strength; Pore size; SEM; Wood modification

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INTRODUCTION

The modification of wood with use of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) has attracted increasing attention over the past years (Hill 2006). Modification of wood with DMDHEU improves the dimensional stability and induces high resistance against fungi and insects by depositing the chemical into the cell wall (*i.e.* a bulking effect) and by reacting with the functional groups of wood polymers (*e.g.*, mostly hydroxyl groups of cellulose, hemicelluloses, and lignin) (Videlov 1989; Militz 1993; Yusuf *et al.* 1994, 1995; Yasuda and Minato 1994; Simonsen 1998; Van der Zee *et al.* 1998; Verma *et al.* 2009, 2010).

Due to the partial filling of the pores with chemicals and to cell wall bulking, a reduction in fibre saturation point of wood has been shown in modified wood (Hill 2008). DMDHEU-modified wood has a higher number of pores smaller than 30 nm and a lower fraction of bound water. This helps to explain why DMDHEU-treated material exhibits limits water uptake and increases resistance to biological attack (Dieste and Kraus 2009). Besides, it was found that wood treated with DMDHEU has good performance to resist weathering (Pfeffer *et al.* 2012). DMDHEU treatment of wood strips partially reduces the degradation of lignin and cellulose and stabilizes the wood cell walls during artificial weathering (Xie *et al.* 2005, 2008). The modification reduces the UV sunlight absorbed by the lignin. Lignin absorbs 80% to 95% of the UV component of sunlight due to its phenolic nature; holocellulose (5% to 20%) and extractives (2%) absorb the remainder (Norrström 1969).

Although many advantages result from DMDHEU modification, some degree of strength loss of the treated wood is induced during the modification. Different preservatives have different reactivity with wood and have different effects on the mechanical properties of wood. DMDHEU is a waterborne agent; it can penetrate into the cell walls of wood, reacting with the cell walls and influencing the mechanical properties of the wood. A reduction in the bending strength of DMDHEU-treated wood has been previously reported (Nicholas and Williams 1987; Ashaari *et al.* 1990).

Three reasons are considered to explain the strength loss of wood modified with DMDHEU at some curing temperatures.

- The first reason is due to the deposition of chemical agents within the cell wall, which reduces the freedom of movement among the polysaccharides and imparts a more rigid structure to the cell wall matrix (Rowell 1998).
- The second reason is that acids and acidic salts cause hydrolysis, whereas alkalis and alkaline salts dissolve lignin and hemicellulose. Deterioration is rapid in the presence of oxidants, especially with nitric acid and nitrate salts (Summitt and Sliker 1980). When the modification is catalyzed with conventional catalysts (Lewis acid or base) at high curing temperatures, the elevated temperature can lead to oxidative degradation or hydrolysis. Hydrolytic and oxidative degradation of hemicellulose and lignin are catalyzed (Xie *et al.* 2007).
- The third reason is that when heat treatment is applied alone in thermal wood processes, the elasticity and tensile strength may be considerably reduced (Militz 2002). Wood is primarily composed of cellulose, within which there are both crystalline and amorphous regions. Temperatures higher than the decomposition point will produce a breakup of the crystalline structure (Summitt and Sliker 1980). After thermal modification, the major causes of strength losses are hydrolytic and oxidative degradation of hemicellulose and lignin, whereas cellulose degradation has a minor contribution (Tjeerdsma *et al.* 1998).

It was found that a temperature of at least 100 ˚C is necessary for effective curing of resin (Militz 1993). In fact, the temperature of 120˚C is usually found as a treating temperature in DMDHEU modification of wood (Videlov *et al.*1989; Yusuf *et al.*1994, 1995; Xie *et al.* 2005, 2007; Verma and Mai 2010). However, the treatment negatively affects the strength (Xie *et al.* 2007). The effects of DMDHEU and of the single constituents of the reaction system (catalyst and reactant) on the tensile strength of wood during the modification were studied by Xie *et al.* (2007), who suggested that new catalytic systems are needed and that water should be removed by gentle pre-drying at low temperature prior to final curing.

Few studies concerning mechanical properties of DMDHEU-treated wood have been reported. However, for wood utilization, the strength of wood is a significant factor that needs to be carefully considered. The aims of this study were: (a) to try a relative low curing temperature (60˚C or 90˚C) for DMDHEU curing in the wood; (b) to explore the influence of temperatures and catalysts on strength of wood treated with DMDHEU; and (c) to explore the relationship between strength and pore-size distribution of the treated wood for further understanding of the change of mechanical strength of DMDHEU-treated wood.

EXPERIMENTAL

Wood Samples

Wood samples measuring 150 mm × 50 mm × 3 mm were prepared from the sapwood of *Populus ussuriensis* Kom, according to the European Standard EN 310 (1999) "Wood-based panels. Determination of modulus of elasticity in bending and of bending strength." These samples were used for bending strength test of DMDHEU-modified wood. They were oven-dried (approx 60˚C) and then weighed.

Treatment of Wood

DMDHEU, in concentration of 30% (w/w) of the stock solution, was used together with different kinds of catalyst or without catalyst. Catalysts were 1.5% or 3% (w/w) of citric acid, or 1.5% (w/w) of $MgCl_2•6H_2O$.

To determine the evaporation of DMDHEU, 50 g of 30% (w/w) of the stock solution in a beaker of 50 mL was heated in oven under 60˚C, 90˚C, 120˚C, or 150˚C for 90 min, respectively. And the beaker was weighed every 15 min.

All wood samples were vacuum-impregnated in solutions completely (2 h at -0.8 bar; 2 h at 3 bar). After treatment, excess treatment solution was blotted off the samples with filter paper. After conditioning (20˚C, 65% RH) for 24 h, all samples were dried for 4 h under 60˚C, 90˚C, 120˚C, or 150˚C and then weighed. Twenty replicates were used for each DMDHEU treatment. In addition, samples treated with distilled water were chosen as controls.

After the treatment, 10 samples of each DMDHEU treatment were rinsed with running tap water for 24 h to test the anti-leaching of DMDHEU in wood.

Strength Determination

The samples (treated and untreated), measuring 150 mm × 50 mm × 3 mm, were used to determine the modulus of rupture (MOR) and modulus of elasticity (MOE) of samples (100 mm distance between the centres of the supports), according to the European Standard EN 310 (1993) standard, which were determined using a static test machine at an elongation rate of 7 mm min^{-1}. For each treatment, 10 samples were used.

Pore size Distribution Determination

Samples were prepared with a knife-mill to a particle size of approximately 3 mm. The weight of samples was 7 mg to 20 mg and they were rewetted with distilled water and placed into aluminum pans of 5 mm in diameter. The pans were hermetically sealed and analyzed in a scanning calorimeter (Netzsch5 DSC 204). Samples were frozen at a cooling rate of -5˚C min^{-1} to -40˚C and held for 5 min, then thawed to 30˚C at a 5˚C $min.^{-1}$ heating rate. The influence of the heating rate was kept constant during experiments (Simpson and Barton 1991; Park *et al.* 2006). At least 5 replicates were tested for each DMDHEU treatment.

The melting temperature of the water in voids (T_m) was determined for at least 5 samples for each treatment. The average diameter of pores in sample by Gibbs-Thomson equation (Park *et al.* 2006):

$$D = \frac{-4T_0\gamma_{1s}\cos\theta}{(T_0 - T_m)\rho H_f} \tag{1}$$

where D is average pore diameter (m), T_0 is the melting temperature of pure water (K), T_m is the melting temperature of water contained in voids of porous materials (K), θ is the contact angle between ice and the pore wall, γ_{1s} is the surface energy at the ice-water interface (J m^{-2}), ρ is the density of water (g m^{-3}), and H_f is the specific heat of fusion (J g^{-1}) (Park *et al.* 2006). In the study the following values for these variables were used:

$T_0 = 273.5$ K (Park *et al.* 2006);
$\theta = 180^\circ$ (Park *et al.* 2006);
$\gamma_{1s} = 12.1$ J m^{-2} (Park *et al.* 2006);
$\rho = 1\times10^6$ g m^{-3} (Park *et al.* 2006); and
$H_f = 333.6$ J g^{-1} (Simpson and Barton 1991; Repellin and Guyonnet 2005; Park *et al.* 2006).

Fourier-Transform Infrared Spectrometry

Fourier-transform infrared (FT-IR) spectra of wood powder (100 to 120 mesh) untreated and treated with DMDHEU and 1.5% or 3% citric acid, or 1.5% (w/w) of $MgCl_2•6H_2O$ were obtained using a Magna-IR 560 (Thermo Nicolet) at room temperature operating on 40 scans and at 4 cm^{-1} resolution.

Scanning Electron Microscopy (SEM) - Energy Dispersive Analysis of X-rays (EDAX)

The cross sections of wood samples treated with DMDHEU and 1.5% citric acid under 90˚C and 120˚C were scanned for macroscopic inspection, respectively. The samples were then sputter-coated with a layer of gold and examined using a scanning electron microscope (FEI QuanTa200 SEM, Holland) operating at an accelerating voltage of 12.5 kV. Besides, the substance on the cell wall of DMDHEU-treated wood was analyzed through EDAX.

RESULTS AND DISCUSSION

Weight Percentage Gain (WPG)

With curing temperature increasing and with time going, the evaporation of DMDHEU increased (Fig. 1a). The weight percentage gain of treated wood decreased with curing temperature increasing (Fig. 1b). The probable reason is that with the treating temperature increasing, the evaporation of DMDHEU solution from the wet treated-samples increased when they were heated in oven so that the weight percentage gain of DMDHEU-treated wood decreased with curing temperature increasing. In addition, the effect of the catalyst used on WPG was not obvious. After leaching, the trend of weight percentage gain reversed. The weight percentage gain of treated samples after leaching increased with curing temperature increasing (Fig. 1c). During impregnation of small molecular-size resin, monomers penetrate into the cell wall and later are polymerized to prevent leaching (Bodig and Jayne 1982). The influence of catalysts on the weight percentage gain of treated wood samples after leaching was significant, especially at the relative low curing temperature (60˚C and 90˚C), which implied that the presence of catalyst enhanced the chemical cross-linking between DMDHEU and wood constituents.

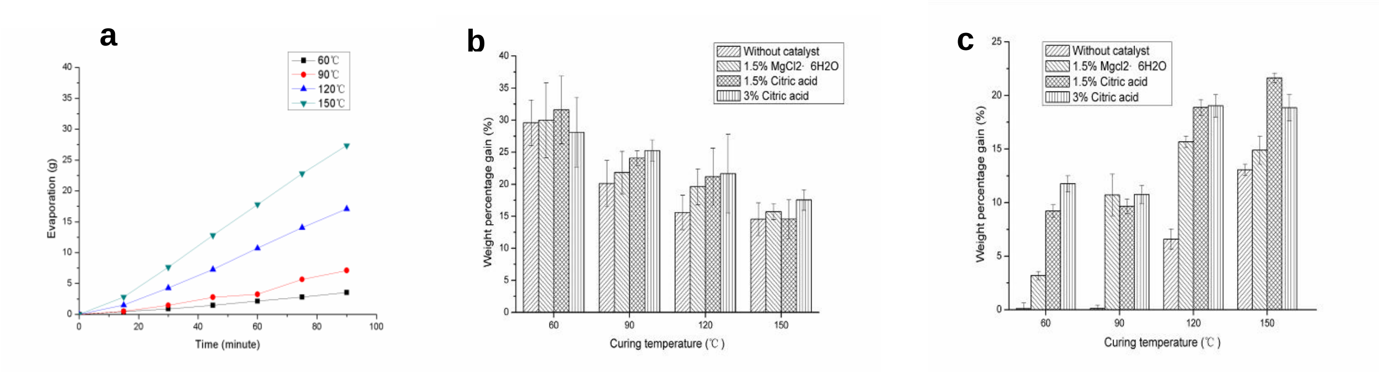

Fig. 1. (a) The evaporation of DMDHEU under different temperatures; (b) Weight percentage gain of treated samples; (c) Weight percentage gain of treated samples after leaching. Error bars show standard deviation.

MOE and MOR of Treated Wood

DMDHEU-modified wood was observed to provide some degree of increase or decrease of MOE and MOR relative to the control due to the different treatment conditions applied. The MOE of control samples declined with increasing curing temperature, which agreed with the results of Sano and of Youngs (Sano 1961; Youngs 1957). The MOE of all DMDHEU-modified samples cured at different temperatures was higher than that of the control samples (Fig. 2). This suggested that the cross-linking between wood and DMDHEU could have improved the elasticity of wood. The probable reason was that the cross-linking between the DMDHEU and wood body prevented the movement of wood fiber molecular chains. With curing temperature increasing, the MOE and MOR of all tested wood samples increased at first and then decreased (Fig. 2a and Fig. 3a). In comparison to the strength of control samples, the strength of modified wood did not decrease when the curing temperature was 90˚C or 120˚C (Fig. 3). On the contrary, the strength of the treated wood increased slightly. When wood was treated under 90˚C or 120˚C, the cross-linking between the DMDHEU monomers and between DMDHEU and wood constituents, may bring about some changes in the characteristics of wood that make the MOE and MOR of the treated wood increased. But when wood was modified under 150˚C, the MOE and MOR of the wood modified by DMDHEU alone was better than that of the wood modified by DMDHEU and catalysts. When the modification is catalyzed with conventional catalysts (Lewis acid or base) at high curing temperatures, the elevated temperature can lead to oxidative degradation or hydrolysis (Xie *et al.* 2007). The rate of hydrolysis increases with increasing proton concentration and reaction temperature (Pisarnitsky *et al.* 2004). When curing temperature was high (120˚C or 150˚C), the hydrolysis of catalysts may have accelerated the degradation of the polysaccharide cell wall components, which resulted in the decline of MOE and MOR.

Due to the different kinds of catalyst, the trends of MOE and MOR of treated samples were different (Figs. 2a and 3a). When the catalyst 1.5% (w/w) of $MgCl_2•6H_2O$ was used, the peak value of MOE appeared at 120˚C curing temperature and the peak value of MOR appeared at 90˚C curing temperature. When the catalyst 1.5% or 3% (w/w) of citric acid was used, the peak value of MOE and MOR appeared at 90˚C curing temperature. The presence of the catalyst significantly decreased the MOR under higher curing temperatures (Fig. 3). Hydrolytic degradation of polysaccharides occurs when wood is subjected to mineral acid such as HCl (Wangaard 1966). There is a large reduction in MOR following curing due to acid degradation of the polysaccharide components of the cell wall from HCl released by the aluminium chloride due to hydrolysis (Nicholas and Williams 1987).

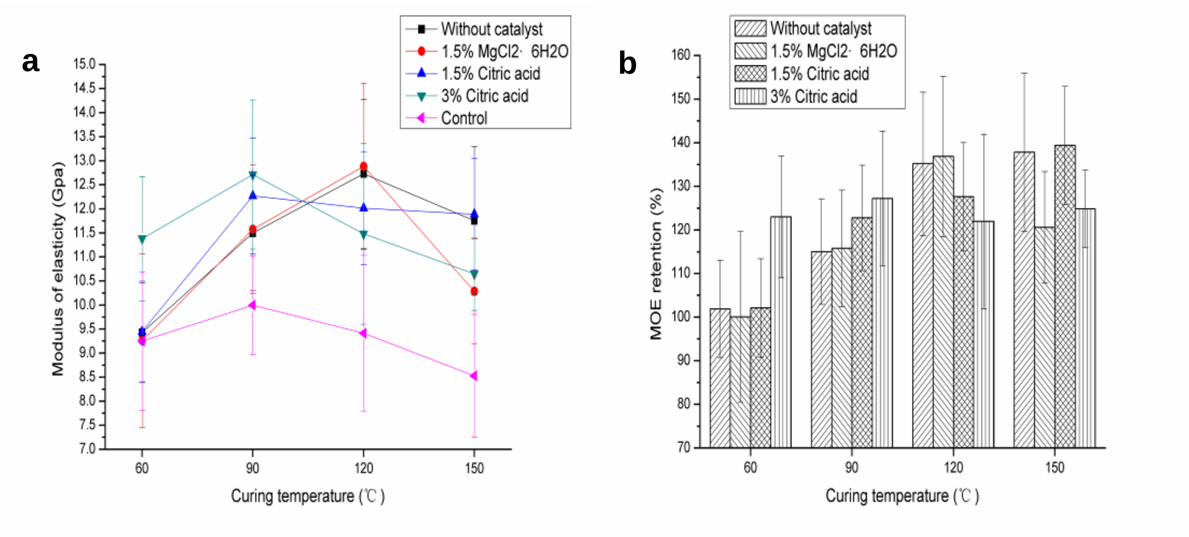

Fig. 2. (a) The MOE change of wood treated with DMDHEU and different catalysts under different temperatures; (b) The MOE retention of wood treated with DMDHEU and different catalysts under different temperatures. Error bars show standard deviation.

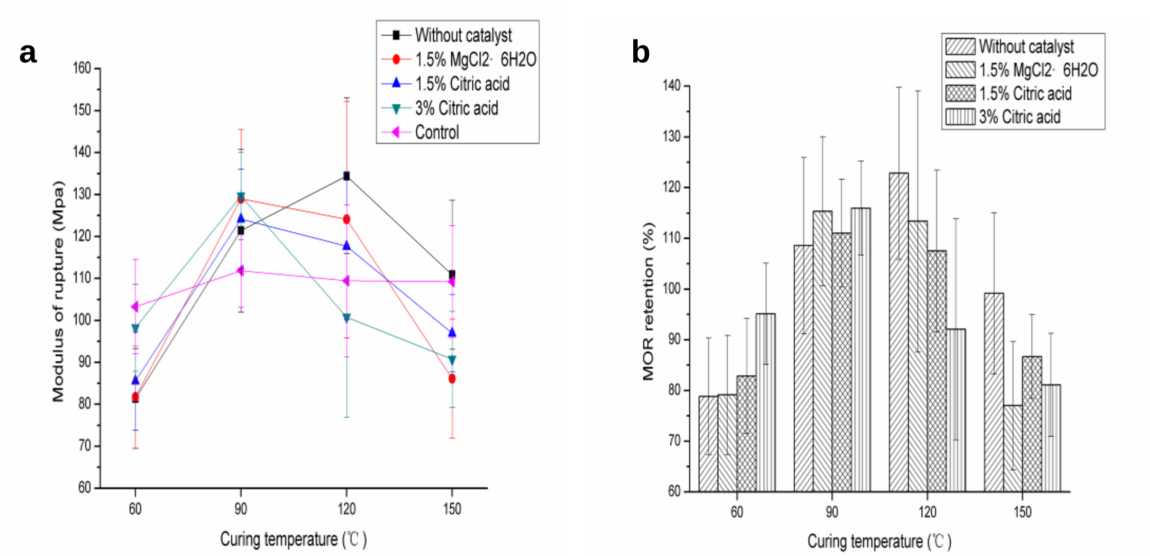

Fig. 3. (a) The MOR change of wood treated with DMDHEU and different catalysts under different temperatures; (b) The MOR retention of wood treated with DMDHEU and different catalysts under different temperatures. Error bars show standard deviation.

The decrease of MOR of treated wood might be caused by the hydrolyzing effect of the catalyst, which accelerated the degradation of wood. In addition, this effect was different for which type of catalyst was used, so the MOE and MOR of wood modified with DMDHEU and different catalysts were different. Also, the hydrolysis effect of catalyst was influenced by its concentration. Higher concentration of catalyst accelerated the degradation of wood. So the MOE and MOR of the wood treated with 1.5% (w/w) of citric acid were better than that of the wood treated with 3% (w/w) of citric acid when the treating temperature was 120˚C or 150˚C.

Pore Size Distribution Determination

The micro-pores diameters were calculated (Table 1) in accordance to the Gibbs-Thomas equation (Eq. (1)). It was found that the modified wood had smaller pore size distribution than the unmodified wood. The average pore diameter in the cell wall (*D*) was arranged in 3 classes: (1) < 50 nm; (2) 50 - 100 nm; and (3) >100 nm. The frequency of the micro-pores < 100 nm in the modified wood was higher than that of the unmodified wood (Fig. 4).

The main reason for the higher frequency of smaller pores in DMDHEU-modified wood might be that the DMDHEU fills some of the larger pores. And the void content of DMDHEU-treated wood decreased. The strength of materials with voids decreases with the void content increasing (Liu *et al.* 2005a, Liu *et al.* 2005b).

When the curing temperature was 90˚C or 120˚C, the MOR of modified wood increased. It can be hypothesized that the DMDHEU filled the micro-pores, causing the voids content to decrease and giving a support for the pore wall to resist external force. But when the curing temperature was 150˚C, the MOR could not be improved because of the chemical degradation increasing of the modified wood resulted from the hydrolysis of catalyst. The filling of cured DMDHEU could not compensate the strength loss caused by the wood degradation by the catalyst. So the MOR decreased abruptly.

Table 1. Pore Diameter Calculated with the Gibbs-Thomas Equation for Wood Modified with DMDHEU under Different Temperatures

DMDHEU treatment	WPG (%)	MC (%)	T_m (℃)	*D* (nm)
Untreatment		84.57%	-0.4	99.07
		107.58%	-0.4	99.07
		111.31%	-0.2	198.15
		115.21%	-0.5	79.26
		142.69%	-0.2	198.15
Treatment under 90˚C	4.08%	50.54%	-1.1	36.03
	10.75%	123.91%	-0.7	56.61
	21.98%	124.51%	-1.1	36.03
	26.39%	130.83%	-0.7	56.61
	11.46%	146.96%	-1.6	24.77
Treatment under 120˚C	13.92%	49.19%	-2.3	17.23
	6.25%	82.86%	-0.5	79.26
	5.77%	88.65%	-1	39.63
	26.03%	144.66%	-0.7	56.61
	29.89%	158.61%	-0.6	66.05

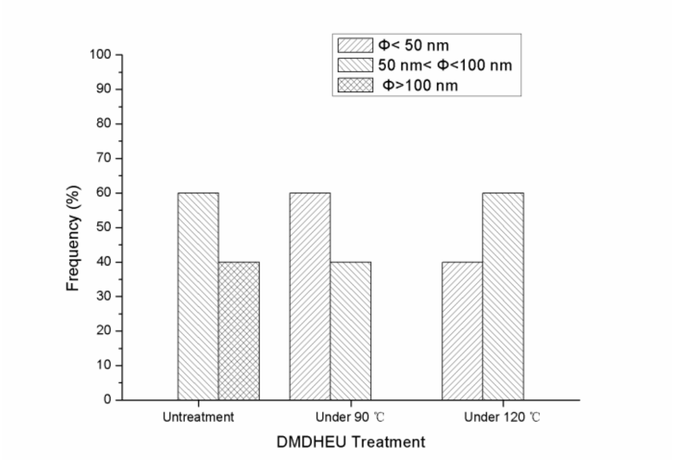

Fig. 4. Frequency of pore diameter distribution in wood modified with DMDHEU

FTIR Analysis

Compared to unmodified wood powder, DMDHEU-treated powder showed additional absorbance maxima at about 1475 cm^{-1} and 1236 cm^{-1} (Fig. 5). These were attributed to CH_2-deformation (1475 cm^{-1}) and C-O-stretch vibration (1236 cm^{-1}), respectively, in the N-methylol group of DMDHEU (Xie *et al.* 2005).

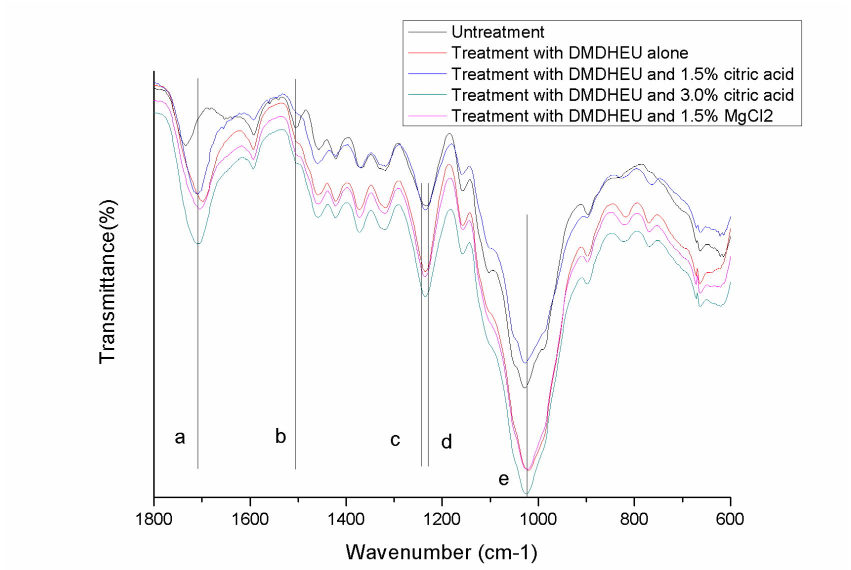

Fig. 5. FTIR spectra of DMDHEU-treated and untreated wood powder: (a) carbonyl stretching in wood and DMDHEU; (b) aromatic skeletal vibration in lignin; (c) C-O stretching in lignin and hemicellulose; (d) C-O stretching in lignin and acetyl and carbonyl vibration in hemicellulose, as well as C-O vibration at the N-methylol group of DMDHEU; and (e) C-O stretching in alcohol and ether groups of polysaccharides and lignin.

The highest absorption band was at approximately 1050 cm^{-1}. In native wood, a major part of absorption is assigned to the C-O stretching in alcohol and the ether group of polysaccharides (Higgins *et al.* 1961) and a minor part to lignin (Faix *et al.* 1992). In treated wood, the alcohol and the ether group of condensed DMDHEU also contribute to this absorption band (Xie *et al.* 2005). So the additional absorbance maxima at 1050 cm^{-1}

suggested that some reactions between cellulose and DMDHEU occurred. But the absorption bands assigned to cellulosic constituents at 1370 cm^{-1}, 1315 cm^{-1}, and 1160 cm^{-1} (Chang and Chang 2001) changed slightly.

Absorptions at 1260 cm^{-1} and 1224 cm^{-1} in untreated wood powder were caused by carboxylic vibrations in the xylans and other hemicelluloses (Evans *et al.* 1992; Faix *et al.* 1992). But in this study, both absorptions were not found in the DMDHEU-treated wood powder when compared to the untreated wood powder. The possible explanation for this observation is that hemicelluloses were degraded due to the curing temperature or the acidic condition of the catalysts, or the absorption at 1242 cm^{-1} was so strong that the both absorptions were overlaid.

A strong carbonyl band at 1712 cm^{-1} was present in DMDHEU-treated wood powder which overlaid the native carbonyl groups absorptions in wood (1737 cm^{-1}). This indicated that the carbonyl bands in DMDHEU were superimposed on those present in wood. Absorption bands attributable to lignin appeared at 1600 cm^{-1}, 1505 cm^{-1} (both aromatic stretch), and 1450 cm^{-1} (CH_2-deformation) (Faix *et al.* 1992). The aromatic stretching vibration (1505 cm^{-1}) was overlaid by the CH_2-deformation vibration (1467 cm^{-1}) in DMDHEU-treated wood. Meanwhile, in treated wood powder, the absorption at 1600 cm^{-1} became weaker compared to that of untreated wood. Therefore, it was inferred that some chemical cross-linking between DMDHEU and lignin might occur.

Through the FTIR analysis, the occurrence of chemical cross-linking between DMDHEU and wood constituents was proven. The reactions between the functional groups of wood and DMDHEU might alter the properties of wood. Regarding mechanical properties aspects, the chemical cross-linking between DMDHEU and wood could resist external forces and could change the MOE and MOR of the treated wood.

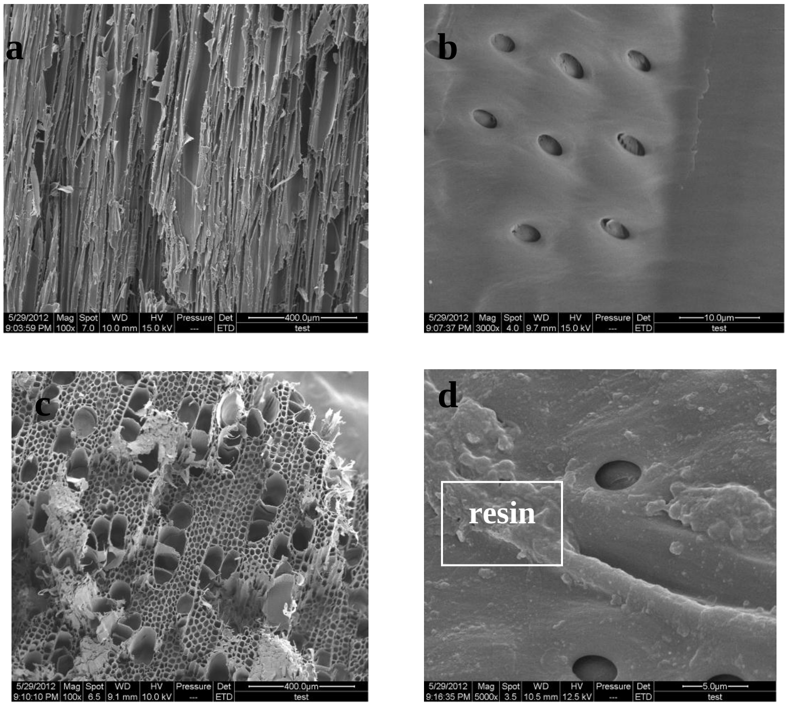

Fig. 6. SEM photomicrographs (a) typical failure of treated wood under 90˚C (b) nothing on the cell wall of treated wood under 90˚C (c) typical failure of treated wood under 120˚C (d) resin on the cell wall of treated wood under 120˚C.

SEM-EDAX Analysis

Due to different curing temperatures, the wood treated with DMDHEU showed different failure morphology. When the curing temperature was 90˚C, the typical failure of wood was as shown in Fig. 6a; the failure area was relatively large, and the angle between the broken plane and the fiber direction was much smaller than 90˚. It was not possible to find anything in the macro-pores of wood or on the cell-wall when the curing temperature was 90˚C (Fig. 6b).

When the curing temperature was 120˚C, the typical failure of wood was as shown in Fig. 6c, and the broken plane was nearly vertical to the fiber direction (Fig. 6c). It was possible to find some substance dispersed on the cell-wall when the curing temperature was 120˚C (Fig. 6d). Through the EDAX analysis, the nitrogen content of substance we found on the cell wall was higher than that of untreated wood, the nitrogen content of which was below about 0.05% (Xie *et al.* 2005) (Table 2). So the substance on the cell wall of DMDHEU-treated wood was concluded to be cured DMDHEU.

Table 2. EDAX Results for the Content of Different Elements in the Resin (Fig. 6d) in the Wood Cell Wall

Element	Wt%
C	13.39
N	39.43
O	44.34
Na	2.85
S	0

CONCLUSIONS

1. When wood was treated with DMDHEU, the WPG decreased with increasing temperature of treatment before leaching. However, the leaching decreased with increasing treatment temperature, suggesting that the cured degree and crosslink of DMDHEU in wood under low temperatures (60˚C or 90˚C) was lower than that under high temperatures (120˚C or 150˚C). With increasing temperature of treatment, the MOR and MOE of DMDHEU-treated wood first increased and then decreased. The mechanical strength of DMDHEU-treated wood under 90˚C or 120˚C was higher than that under 60˚C or 150˚C. Different catalysts were found to have different effects on the MOR and MOE of DMDHEU-treated wood. And when the treating temperature was higher than 120˚C, the MOR and MOE of DMDHEU-treated wood with lower concentration of catalyst were better than that with higher concentration of catalyst.
2. Through the DMDHEU modification, it was found that the pores of treated wood became smaller, suggesting partial filling of pores with DMDHEU. This filling effect of the cured DMDHEU in wood pores could provide additional mechanical support to the wood cell wall and compensate for the strength loss resulting from the degradation of wood.

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