

# Inserting Poly( $\epsilon$ -caprolactone) into Wood Cell Wall Structures for Dehydration and Consolidation of Waterlogged Scots Pine Wood

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Archaeological wooden artifacts are buried in wet environments, leading to water absorption and waterlogged wood. In order to conserve these wooden cultural heritage items, dehydration and consolidation are critical steps. This study used nontoxic  $\epsilon$ -caprolactone (CL) as the dehydration agent to replace the water in the simulated waterlogged wooden structures, inserting the poly( $\epsilon$ -caprolactone) (PCL) into the wood cell walls by oxalic acid catalysed CL ring-opening polymerization (ROP). The mechanical and chemical performance of the untreated and treated wood was evaluated. The weight gain percentage and dimensional stability of the treated wood were significantly improved. The polyester chains within the cell wall structures were analyzed by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA-DTA), and scanning electron microscopy (SEM). FT-IR showed that the intensity of hydroxyl (-OH) absorption peaks decreased, and carbonyl (C=O) peaks attributed to the PCL addition were observed. Thermal analysis revealed that the degradation of PCL polymers was faster than that of wood components. The morphology characterization demonstrated that the treated wood was bulked with the PCL polymers.

*Keywords:* Waterlogged wood; Dehydration; Consolidation; PCL; Ring-opening polymerization (ROP)

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## INTRODUCTION

Wood has been used as a renewable raw and engineering material for thousands of years. Most ancient ships were made of wood due to its desirable features, such as light weight, processability, good mechanical properties, sustainability, and aesthetic appearance. Wooden artifacts provide information on the skills and ingenuity of ancient cultures, and thus have important historical, archaeological, and scientific value (Tamburini *et al.* 2015).

Wooden ships in wet environments are saturated with water and is easily degraded by fungi, bacteria, and insects. However, archaeological wooden artifacts can survive better in wet environments, and the burial environments are usually in marine or in anoxic areas (Corfield 2015; Macchioni *et al.* 2016). These conditions promote the partial conservation of wooden items because of the low temperatures and low amounts of oxygen, which limit aerobic bacteria and fungi; this was the case with the waterlogged *Vasa* and *Mary Rose* shipwrecks (Hocker 2006; Sandström *et al.* 2005; Wetherall *et al.* 2008; Chadwick *et al.* 2016).

Wood is a natural complex porous material (Devi and Maji 2011; Salla *et al.* 2012; Miao *et al.* 2014). The cell wall is primarily comprised of cellulose, hemicellulose, and

lignin (Yin *et al.* 2017). Waterlogged cell wall components in all wood degrades due to a number of factors. In time, through hydrolysis, cellulose in the cell walls become disintegrated. The loss of the finer cellulose tissue does not cause much alteration in the gross volume of the wood, but the porosity is increased due to the degradation of bacterial action, and the wood absorbs water like a sponge (Babiński 2015; Cavallaro *et al.* 2015). If the wood is exposed to air, the excess water evaporates, and the resulting surface tension forces of the evaporating water cause the weakened cell walls to collapse, creating considerable shrinkage and distortion (Simão *et al.* 2017). Consequently, the dehydration and consolidation of waterlogged wood, the critical step during the conservation process, has been extensively studied (Pelé *et al.* 2015). The dehydration and consolidation of waterlogged wood is a complex process. The main difficulty is due to its sensitivity to the environment, and various challenges have to be considered, for example, the use of mild drying conditions to avoid damage in the wood components, or to eliminate harmful factors for human health during the treatment process.

The techniques and materials used over the years for the dehydration and consolidation of archaeological woods are numerous. While some methods use resin and co-solvents in acetone (Bugani *et al.* 2009), others employ polyethylene glycols (PEGs) with different molecular weights (Hayem *et al.* 2003). The optimum uptake of PEG enables high indices of dimensional stability of wood. However, PEGs have some drawbacks such as the high viscosity and hygroscopicity, which lead to a very long time for permeation and make the wood artifacts susceptible to the fungal attack (Christensen *et al.* 2012).

In addition to the research on improving waterlogged wood properties, the development of dehydration and consolidation material is driven by ecological concerns. Poly( $\epsilon$ -caprolactone) (PCL) is a semi-crystalline hydrophobic polyester that can be polymerized by ring opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) monomers; it is a novel nontoxic and low viscosity liquid agent. PCL has gathered remarkable popularity in different applications such as drug delivery, food packing, and tissue engineering (Jiang *et al.* 2016; Simão *et al.* 2017). Using the CL in the wood conservation field is uncommon. Ermeydan *et al.* (2014) made a successful wood modification through grafting solid wood with poly(caprolactone) by the ROP of caprolactone monomer, in order to improve the wood dimensional stability and water absorption. However their experimental conditions were harsh and complicated.

In the present research  $\epsilon$ -caprolactone monomer is considered for the first time as an interesting candidate reagent for waterlogged wood dehydration. For that purpose, CL was used to penetrate the waterlogged wood to replace the original water. The ROP of CL monomers was induced by -OH groups from the existing water, and then PCL polyesters were locked into the wood structures to consolidate the frail wood cell wall components. The experimental conditions are mild and easy to handle.

Soluble salts usually remain in the waterlogged wood. Upon their evaporation, salts in the wood will slowly crystallize, resulting in possible distortion and exfoliation of the artifact (Smith *et al.* 2003). Soluble salts must be removed before the dehydration and consolidation treatment. So the dehydration step is mainly replacing the water in the wood structures. The most waterlogged wood has been degraded seriously, and the wood cell walls will collapse without the consolidation step, but the dehydration and consolidation process is based on the condition that wood structures remain saturated with water.

In this study, the fast-growing tree Scots pine wood was cooked in hot water (95 °C) for one week, and the water content reached approximately 250%. Under this condition the wood cell walls and cell lumens were filled with water and the spaces between the cells

and molecules had increased due to hot water swelling effect, making this wood material suitable as a model samples in order to simulate the water-saturated condition of waterlogged wood. The ROP reaction of CL in the wood cell walls was studied. At the same time, the mechanical and chemical performance of the reference and treated wood was evaluated, including the dimensional stability, group reactivity, thermal stability, and micro-structures. The weight gain percentage and dimensional stability of the treated waterlogged wood were significantly improved, as well as the water resistance, which showed that the PCL can potentially be used as conservation material for waterlogged wood.

## EXPERIMENTAL

### Materials

Fast-growing planted Scots Pine (*Pinus sylvestris* var. *mongolica*) wood was collected in northern China.  $\epsilon$ -Caprolactone (CL) was obtained from Alfa Aesar (Shanghai, China), and oxalic acid was obtained from Beijing Chemical Works (Beijing, China). All the chemicals were of analytical grade and used directly.

### Waterlogged Wood Samples Preparation

Healthy Scots pine samples of 20 mm  $\times$  20 mm  $\times$  20 mm (tangential  $\times$  radial  $\times$  longitudinal, respectively) were cut along the grain and oven-dried at 50 °C for two days to reach a nearly dry wood. The dry wood samples were placed in distilled hot water at 95 °C for one week, and the distilled water was changed every 1 to 2 d. The healthy wood samples were saturated with water when the moisture content reached approximately 250%. The waterlogged wood samples were divided into two sets of twelve cubes: one set as untreated wood, the other set as treated wood for dehydration and consolidation. After the treatment, eight samples from each set were used for physical characterization (*i.e.*, weight percentage gain (WPG), volume increase, equilibrium moisture content (EMC), shrinking efficiency), and the remaining samples were used for structural and chemical analysis.

### Dehydration and Consolidation

#### *Step one: Pre-treatment with impregnating catalyst*

The experimental group samples were put into the 0.5% (w/v) oxalic acid aqueous solution for one day to ensure that the catalyst was entirely dispersed into waterlogged wood structures.

#### *Step two: Dehydration process*

The untreated wood samples were placed in distilled water as a control group, and the experimental group wood samples were placed in the  $\epsilon$ -caprolactone (CL) monomer solution. Both group samples were impregnated for two days at room temperature.

#### *Step three: Consolidation and drying*

After dehydration, the excess solution on the surface of the samples was removed by a soft cloth, and the samples were oven-dried at 50 °C for 72 h until the weight remained constant. During the heat treatment, the ROP of the CL monomer was catalyzed by oxalic acid, and the wood structures were consolidated by the solid PCL. A detailed description of the experimental workflow is shown in Fig. 1.

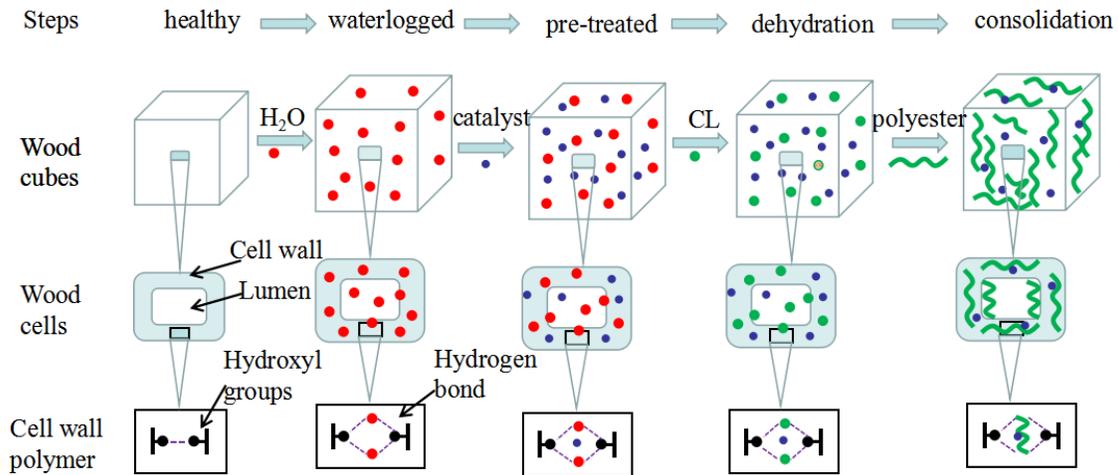


Fig. 1. Insertion of polycaprolactone into the cell wall structures

## Characterization

Dimensions and weights of the wood samples were measured before and after all treatments (healthy wood, waterlogged wood, dehydration, and consolidation) to determine the weight and volume changes caused by the treatment.

### The rate of cooking loss

The rate of weight loss ( $\omega$ ) was calculated by Eq. 1

$$\omega(\%) = \frac{W_{hu} - W_u}{W_u} \times 100 \quad (1)$$

where  $W_{hu}$  is the untreated wood samples oven dry weight at 50 °C before cooking (healthy wood samples), and  $W_u$  is the oven dry weight at 50 °C after cooking (untreated waterlogged wood samples).

The rate of volume loss ( $v$ ) was calculated by Eq. 2

$$v(\%) = \frac{V_{hu} - V_u}{V_u} \times 100 \quad (2)$$

where  $V_{hu}$  is the untreated wood samples oven dry weight at 50 °C before cooking (healthy wood samples), and  $V_u$  is the oven dry weight at 50 °C after cooking (untreated waterlogged wood samples).

### Weight percentage gain (WPG)

The weight percent gain (WPG) after consolidation step was an estimated value compared with the untreated wood and was calculated by Eq. 3

$$WPG(\%) = \frac{W_t - (W_{ht} - W_{ht} \times \omega)}{W_{ht} - W_{ht} \times \omega} \times 100 \quad (3)$$

where  $W_t$  is the oven dry weight of the wood samples after consolidation treatment, and  $W_{ht}$  is the oven dry weight (unit) of the healthy wood samples.

### Volume (%)

The percentage volume increase after inserted with PCL polymers was an estimated value compared with the untreated wood and was calculated by Eq. 4

$$\text{Volume}(\%) = \frac{V_t - (V_{ht} - V_{ht} \times v)}{V_{ht} - V_{ht} \times v} \times 100 \quad (4)$$

where  $V_t$  is the oven dry volume (unit) of the wood samples after consolidation treatment, and  $V_{ht}$  is the oven dry volume (unit) of the healthy wood samples.

#### *Equilibrium moisture content (EMC)*

The untreated and treated wood samples were equilibrated in a system with a relative humidity (RH) of 65% at 20 °C, and moisture was absorbed by the samples for two weeks. When the samples reached equilibrium (*i.e.*, constant weight), the weight was calculated to determine the final moisture content. Equation 5 shows the EMC calculation,

$$\text{EMC}(\%) = \frac{W_e - W_d}{W_d} \times 100 \quad (5)$$

where  $W_d$  and  $W_e$  are the weights of the untreated and treated wood before and after moisture absorption, respectively.

#### *Shrinking efficiency (% Shrinking)*

After dehydration, the wood samples were oven-dried at 50 °C for 72 h until the consolidation step was completed. The shrinking during drying was considered as a change in radial direction, tangential direction, and volume decrease. The shrinking efficiency was calculated as follows,

$$\% \text{Shrinking} = \frac{L_{(T/R/V)_w} - L_{(T/R/V)_t}}{L_{(T/R/V)_w}} \times 100 \quad (6)$$

where  $L_{(T/R/V)_w}$  and  $L_{(T/R/V)_t}$  are the tangential direction, radial direction, and volume dimension of the waterlogged and treated samples, respectively.

### **Fourier Transform Infrared Spectroscopy (FT-IR) Analysis**

The untreated and treated wood samples were ground and used in the FT-IR spectroscopy measurement. The dried samples were embedded in potassium bromide (KBr) pellets and analyzed by using a VERTEX 70V (Bruker, Karlsruhe, Germany) spectrometer. The results were recorded in the absorption mode in the range of 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$  with an accumulation of 64 scans at a resolution of 4  $\text{cm}^{-1}$ .

### **Thermogravimetric (TGA-DTA) Analysis**

A modulated TGA-DTA (TGA Q5000 IR, NETZSCH, Selb, Germany) was used to characterize the decomposition and thermal stability of the untreated and treated wood. The sample pan was placed on the Pt basket in the furnace and then heated from room temperature to 600 °C. The heating rate was 10 °C  $\text{min}^{-1}$ , the nitrogen flows was 50  $\text{mL min}^{-1}$  and  $\alpha\text{-Al}_2\text{O}_3$  was taken as the reference material. During testing, the heating unit was flushed under a continuous nitrogen flow at a pressure of 8 kPa.

### **Morphological Analysis**

A JSM-7001F model scanning electron microscope (JEOL, Tokyo, Japan) was used to determine the morphological features of the untreated and treated wood. The microstructures of wood cross-section, radial section, and tangential section images were investigated. The samples were sputtered coated with gold before observation at a voltage of 5 to 15 kV, and the working distance is about 10 mm.

## RESULTS AND DISCUSSION

### Stability of Dehydration and Consolidation

The dehydration and consolidation process included three steps. First, the pretreatment with oxalic acid for one day dispersed the catalyst in the waterlogged wood structures. Next, the wood samples were immersed in the CL monomer liquid solutions for two days to ensure that the original water was completely replaced. The ring opening polymerization of caprolactone inside the wood structures was the third step. Wood impregnation with CL at atmospheric pressure was followed by drying at 50 °C to induce the ring opening polymerization for consolidating the waterlogged wood. This caused weight and volume changes. An effective way to evaluate the affinity of wood samples for water is to calculate the EMC; in this case, the samples were placed in a climate chamber with standard temperature (20 °C) and 65% RH to examine the water uptake exclusively at the cell wall level. Table 1 shows the weight and volume loss rate of untreated wood samples after cooking and the changes in WPG, volume, and EMC of the treated wood samples.

The WPG and volume change were determined after the drying process, when the caprolactone ROP was conducted. Both of the WPG and volume change provided the first indication of the success of the treatment. Compared with the untreated wood, the WPG of wood/PCL (treated wood) was noticeably increased. The weight loss represented the leaching of some cell wall components (mainly hot water extractives) during the cooking, which resulted in a re-organization of the cell wall polymers (especially in the amorphous lignin/hemicellulose matrix).

The treated wood showed a permanent volume change after PCL polyester inserting in the cell wall structures. The positive dimensional changes of wood/PCL samples were related to the presence of polymers within the wood cell wall. Table 1 shows that the volume of untreated wood was reduced by 2.24%, mainly due to the loss of hot water extractives. The untreated and treated wood samples were equilibrated in a wet system with a relative humidity of 65% until the samples reached equilibrium. The untreated wood had an EMC of 10.33%, and the wood/PCL samples adsorbed less moisture with 7.93%. This result indicated that the humidity adsorption of the treated wood was reduced, and the treated wood exhibited water resistance.

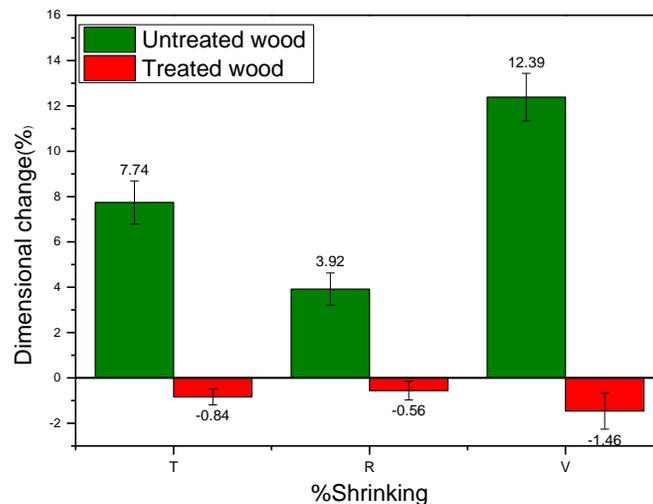
**Table 1.** Weight and Volume Change of Reference and Treated Wood Samples

Parameter	Reference Wood	Treated Wood
$\omega(\%)$	-7.10±0.19	-
$u(\%)$	-2.24±1.01	-
WPG (%)	0	121.83 ±0.84
Volume (%)	0	15.00±0.38
EMC(%)	10.33±0.08	7.93 ±0.16

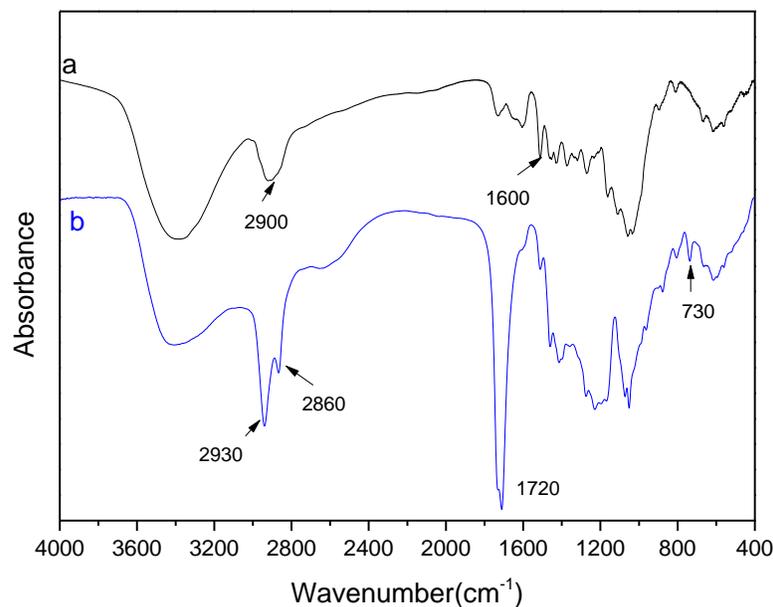
### Dimensional Stability

To evaluate the improvement of dimensional stability of the dehydrated and consolidated wood, the tangential direction, radial direction, and volumetric changes of the wood cubes were determined. The wood dimensional changes upon drying was a result of shrinking of the wood cell walls, and lower shrinking values indicate the better dimensional stability.

The shrinking efficiency of the wood samples are shown in Fig. 2. The tangential, radial, and volumetric shrinkage of the untreated and treated wood samples after drying were evaluated. The shrinking efficiency of the untreated samples was much higher than that of the treated wood, as the waterlogged wood lost a large amount of water during drying, which caused dramatic dimensional changes. Compared with the untreated samples, the treated wood exhibited better dimensional stability and the shrinkage of tangential, radial, and volumetric were -0.84%, -0.56% and -1.46%, respectively, which means the dimensional did not change, a slight swelling could be explained by changes in the humidity and temperature of the surrounding atmosphere.



**Fig. 2.** Shrinking efficiency of the untreated and treated wood



**Fig. 3.** FT-IR curves of different samples a: untreated wood; b: treated wood

### Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

Figure 3 shows the FT-IR spectra of the untreated and treated wood. The band at  $3380\text{ cm}^{-1}$  was due to -OH stretching vibration, and the intensity of the treated wood hydroxyl groups was decreased. The bands at  $2930\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$  were attributed to  $\text{CH}_2$  stretching for PCL, which were highly apparent in treated wood. This was evidence that the PCL polymers had been inserted in the wood structures. The characteristic C=O absorption band attributed to PCL appeared at  $1710\text{ cm}^{-1}$  and represented PCL polyesters loaded inside the wood; this band covered the  $1600\text{ cm}^{-1}$  peak, which was from the untreated wood lignin component. The new peaks at  $730\text{ cm}^{-1}$  were observed along with the PCL long chain vibration. The FT-IR analysis verified the successful ring-opening polymerization of CL in the treated wood.

### Thermogravimetric Analysis

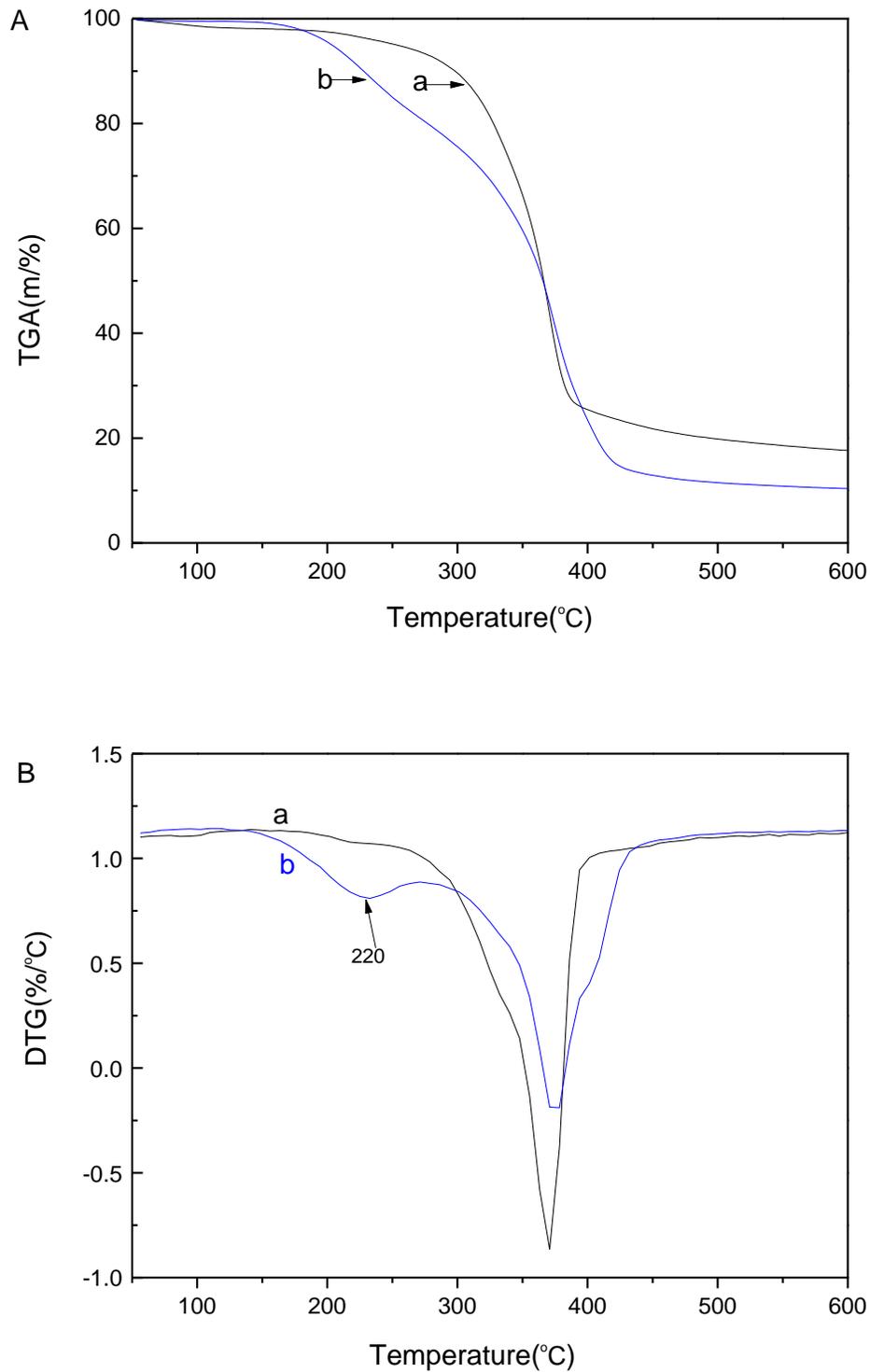
Table 2 shows the degradation temperature at different mass loss and the residual weights (RW) of untreated and treated wood. In Fig. 4, the TGA, DTG, and DTA curves of the untreated and treated wood are compared. From these curves, the weight change up to  $100\text{ }^\circ\text{C}$  was assigned to the evaporation of water. The initial decomposition temperature ( $T_i$ ) of the treated and untreated wood was different that the treated wood sample was at  $170\text{ }^\circ\text{C}$  and  $260\text{ }^\circ\text{C}$  for the untreated wood. The maximum degradation of PCL peak was shown in the DTG curve at  $220\text{ }^\circ\text{C}$ . The DTG and DTA curves illustrated the maximum pyrolysis temperature ( $T_m$ ) of the untreated and treated wood at  $370\text{ }^\circ\text{C}$ , which corresponded to the degradation of cellulose and lignin. After the  $450\text{ }^\circ\text{C}$  decomposition stage, the degradation was completed. TGA showed that the PCL acted as a barrier and hindered the diffusion of volatile decomposition products. PCL protected the wood structures and consolidated the wood cell wall. The lower thermal stability of wood/PCL was caused by the PCL polymer decomposition temperature, which was lower than that of the wood polymers.

**Table 2.** Degradation Temperature and Residual Weights of Untreated and Treated Wood

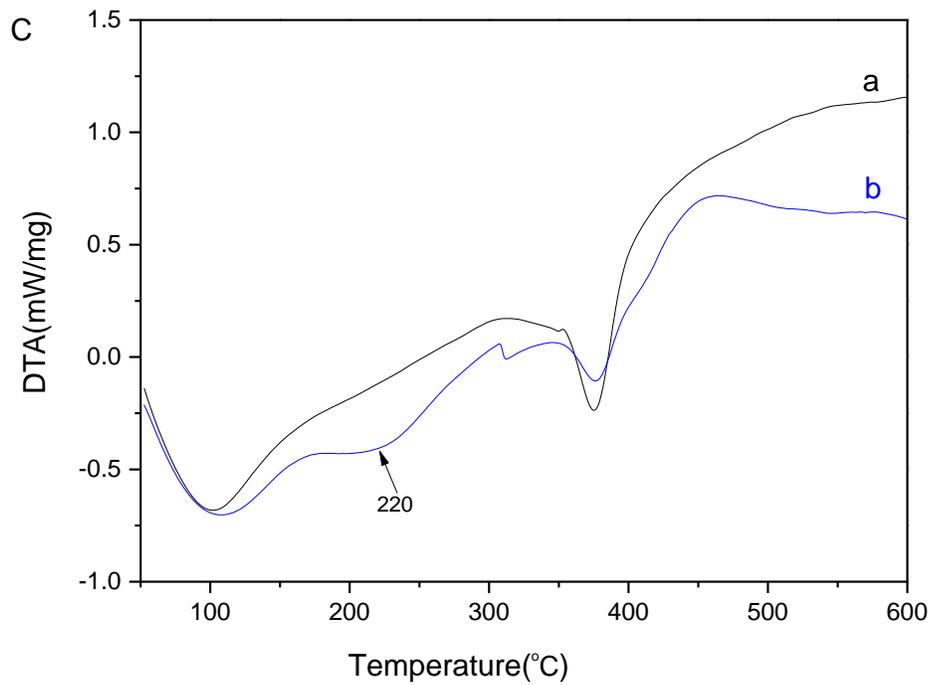
Samples	Temperature of decomposition in K at different mass loss(%)							RW/%	RW%
	5%	10%	20%	40%	50%	60%	80%	450 °C	600 °C
Untreated	252.70	297.94	327.36	357.58	365.99	373.18	493.78	21.76	17.64
Treated	203.09	227.79	276.71	349.20	365.38	376.16	406.87	12.88	10.37

### Morphological Analysis

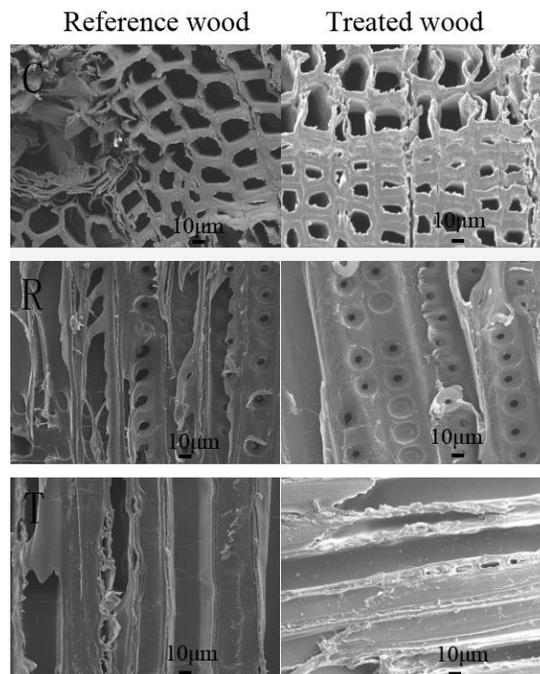
SEM micrographs of the wood samples are shown in Fig. 5. The cross-section, radial section, and tangential section of the untreated and treated wood were analyzed. For untreated wood, the cell wall and cell lumens were empty. In treated wood, the wood cell wall became thicker than the untreated wood. The treatment with CL resulted in a precipitation of PCL solid polymers, and the impregnated materials of PCL were located in the cell walls. The morphological analysis implied that the PCL polyesters were inserted in the cell walls to consolidate the wood structures and maintain the dimensional stability of the waterlogged wood during the dehydration and drying process.



**Fig. 4(A & B).** Thermogravimetric analysis curves of the untreated (a) and treated wood (b). A: TGA curves; B: DTG curves; C: DTA curves



**Fig. 4(C).** Thermogravimetric analysis curves of the untreated (a) and treated wood (b). A: TGA curves; B: DTG curves; C: DTA curves



**Fig. 5.** SEM analysis of the untreated and treated wood samples. (C) cross section, (R) radial section, (T) tangential section

## CONCLUSIONS

1. After the dehydration and consolidation treatment with CL monomers, the waterlogged wood samples weight gain percentage was greatly increased. The WPG of treated wood samples was 112.8% and the volume increased 15% due to insert the PCL into the waterlogged wood. The treated wood EMC was decreased, the treated wood was more hydrophobic due to the bulking with PCL.
2. The treated waterlogged wood exhibited better dimensional stability and the shrinkage of tangential, radial, and volumetric were -0.84%, -0.56%, and -1.46%, respectively.
3. The FT-IR analysis verified the successful ring-opening polymerization of CL in the treated wood. The PCL characteristic absorption peaks were obviously observed in the treated wood.
4. The thermal analysis illustrated that the treated wood thermal stability was decreased because the PCL polymers degradation was faster than that of wood components, the inserted PCL acted as a barrier and hindered the diffusion of volatile decomposition products
5. SEM demonstrated the treatment with CL resulted in a precipitation of PCL solid polymers, and the impregnated materials of PCL were located in the cell walls. The treated wood cell walls became thicker due to insert the PCL chains into the wood structures.

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