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Modification of Poplar Wood via Polyethylene Glycol Impregnation Coupled with Compression

Yuhan Liu 1 ©, Jiangtao Shi 1,2 ©, Weiqi Leng 1,2 and Qiongtao Huang 3

1 College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China; liuyh@njfu.edu.cn (Y.L.); wqleng@njfu.edu.cn (W.L.)
2 Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing 210037, China
3 Yihua Life Technology Co., Ltd., Shantou 515000, China; qthuagn@yihua.cn
* Correspondence: shijt@njfu.edu.cn; Tel.: +86-25-85426907

Abstract: Wood permeability and compressibility are affected by cell wall structure and chemical composition. These properties can be improved by appropriate wood pretreatments. Low-density poplar wood was converted to a more dense structure by the following steps: First, lignin and hemicellulose were removed using a mixture of NaOH and Na2SO3. Second, they were impregnated with polyethylene glycol (PEG, mean molecular weight of 1200), nano-SiO2, and a silane coupling agent at atmospheric temperature and pressure. Finally, impregnated wood was compressed at 150 °C. Results showed that the tracheid lumens on the transverse section of the compressed wood almost vanished. Specifically, the lumens in the wood cells, especially those that were compressed, were almost completely filled with PEG. In FTIR, the asymmetric absorption peaks of Si–O–Si at 1078–1076 cm−1 were clearly observed, which confirms the existence of bonding between nano-SiO2 and wood. The highest melting enthalpy and crystallization enthalpy showed a heat storage capacity of modified wood, which were 20.7 and 9.8 J/g, respectively. Such phase change capabilities may have potential applications in regulating the rate of change of room temperature. In summary, the modified wood could be utilized as material for construction to conserve energy.

Keywords: fast-growing poplar wood; wood modification; densified wood; PEG-treated wood

1. Introduction

Wood is a renewable, environmentally friendly, and sustainable material, which is widely used in furniture manufacturing, building construction, decoration materials, and other fields [1,2]. On the other hand, the qualities of wood products are also limited by the inherent properties of wood. As a material, the hydrophilic character of wood leads to decay, dimensional instability, and discoloration [3–5]. Many works have employed physical, chemical, and biological modification methods to improve these inherent defects in wood [6,7]. Some of them have been commercially productized in the past years, for instance, melamine–urea–formaldehyde (MUF) resin impregnation [8], thermal treatment [9], acetylation [10], and furfuryl alcohol modification [11]. However, these modification strategies are limited by energy consumption, special equipment, and high costs. Therefore, for the purpose of efficiency and environmental friendliness, accelerating the discovery of modification and functionalization approaches has attracted much attention.

Wood densification is a reliable method to increase the density and hardness of low-density wood. In order to obtain the best of densification wood, some pretreatment methods are employed during wood densification processing, such as saturated steam pretreatment [12], hydrothermal pretreatment [13], and microwave-assisted heat treatment [14,15]. One of the most worrying effects of wood densification is the swelling of the thickness along the compression direction in a humid atmosphere. It is mainly affected by the hygroscopicity of the wood cell walls. In recent years, the compaction method...
of temperate chemical pretreatment combined with densification has been adopted by many researchers. Song et al. [16] used a sodium hydroxide/sodium sulfite system to pretreat the wood, and then compressed it to reach a compression ratio of 80%, becoming a modified wood with a 422.2 ± 36.3 MPa cm³ g⁻¹ specific tensile strength. Using the same chemical pretreatment, Shi et al. [17] obtained densified fir wood with 228.5 MPa (MOR) and 33.55 GPa (MOE). Chemical pretreatment can remove part of hemicellulose and lignin, which can obtain the maximum compression ratio during the next hot pressing, and effectively improve the dimensional stability of the densified wood. After chemical pretreatment, direct compression brings the discrete state between wood fibers, resulting in a large change in the dimension of the wood’s cross-grain direction. Therefore, considering the use of an appropriate impregnation treatment method, it can not only make up for the pore structure due to the removal of hemicellulose and lignin, but also help to improve the dimensional stability between the fibers.

Phase-changeable energy storage materials are highly susceptible to loss during heat exchange, and renewable wood may be an ideal carrier for effective loss suppression due to its high porosity and high pore density [18]. Polyethylene glycol (PEG) impregnation is a highly effective strategy for wood modification. PEG molecules can penetrate into the wood cell lumen and wood cell wall, especially under high humidity conditions, to increase the dimensional stability of wood by means of compatibilization [19–22]. The synergy of compression and PEG impregnation may become an effective wood modification technology. In addition, PEG is a commonly used phase change energy storage material, and it has been explored to combine it with wood [23–25], to improve the loss of PEG in the phase change process. This work aims to develop a feasible method for densified poplar wood via the united technologies of chemical pretreatment, hot pressing, and PEG impregnation. Additionally, nano-SiO₂ and the silane coupling agent KH550 were added to form bonds with the wood in an attempt to improve the thermal stability of the modified wood. The microstructure, dimensional stability, and thermal stability of the modified wood were evaluated. For low-quality wood, this work would provide an insight into its potential utilization in energy-efficient building materials, where the PEG in the modified wood continuously stores and releases thermal energy as the temperature changes, reducing energy loss [26].

2. Materials and Methods
2.1. Materials

Poplar wood (Populus tremula Linn.) blocks with an initial moisture content of 8% ± 0.5% were cut into a size of 50 mm (longitudinal) × 25 mm (radial) × 20 mm (tangential). Sodium hydroxide (NaOH, 96%), anhydrous sodium sulfite (Na₂SO₃, 97%), acetone (CH₃COCH₃, 99.5%), polyethylene glycol (PEG) with a molecular weight of 1200, and deionized (DI) water were provided by Nanjing Chemical Reagent Co., Ltd., China. Nano-SiO₂ (average particle size of 20 nm) with a solid content of 40% was purchased from Hangzhou Zhitai Purification Technology Co., Ltd., China. KH550 (3-aminopropyltriethoxysilane, C₉H₂₃NO₃Si, 99%) was purchased from Aladdin Co., Ltd., China. All chemicals were used as received without any purification.

As shown in Table 1, the wood blocks were classified into eight groups and labeled as listed, with four replicates in each group.
Table 1. Labeling of various treatment groups.

<table>
<thead>
<tr>
<th>Labels</th>
<th>SiO$_2$ (%)</th>
<th>PEG (%)</th>
<th>KH550 (%)</th>
<th>Compressed</th>
<th>Delignification</th>
</tr>
</thead>
<tbody>
<tr>
<td>W $^a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>C $^b$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>DC $^c$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DC-P $^d$</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DC-SP-1 $^e$</td>
<td>0.1</td>
<td>50</td>
<td>0</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DC-SP-1K $^f$</td>
<td>0.1</td>
<td>50</td>
<td>0.1</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DC-SP-5 $^g$</td>
<td>0.5</td>
<td>50</td>
<td>0</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>DC-SP-5K $^h$</td>
<td>0.5</td>
<td>50</td>
<td>0.1</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

$^a$ Untreated wood; $^b$ Directly hot-pressing wood; $^c$ Delignified hot-pressing wood; $^d$ Delignified hot-pressing wood impregnated with polyethylene glycol solution; $^e$ Delignification impregnated silicon–polyethylene (the mass ratio was 0.1% nano-SiO$_2$ glycol mixed solution hot-pressing wood; $^f$ Delignification impregnated silicon–polyethylene (the mass fraction was 0.1% nano-SiO$_2$ and KH550); $^g$ Delignification impregnated silicon–polyethylene (the mass fraction was 0.5% nano-SiO$_2$ glycol mixed solution hot-pressing wood; $^h$ Delignification impregnated silicon–polyethylene (the mass fraction was 0.5% nano-SiO$_2$ and KH550) glycol mixed solution hot-pressing wood.

2.2. Delignification
The wood blocks were pretreated with a mixed solution of NaOH (2.5 mol/L) and Na$_2$SO$_3$ (0.4 mol/L), boiled at 75 °C for 4 h, and then rinsed with DI water three times to remove the residual of the chemicals, until the pH was tested to be 7–8. After rinsing, the wood samples were immersed into water and boiled for 4 h with stirring. The wood samples were re-washed when the yellowish-brown color disappeared. The delignified wood samples were obtained and reserved in water.

2.3. Impregnation
PEG 1200 was heated at 70 °C until completely dissolved and then mixed with deionized water and acetone. As with our previous study [27], the basic system of mixed solution was 50% PEG + 25% deionized water + 25% acetone mass ratio. DC-P wood samples were immersed into the prepared mixed solution and heated at 70 °C for 2 days in a water bath. The other systems of mixed solution were a basic system + (0.1% SiO$_2$/0.5% SiO$_2$/0.1% SiO$_2$ + 0.1 KH550/0.5% SiO$_2$ + 0.1% KH550) mass ratio. DC-SP-1, DC-SP-5, DC-SP-1K, and DC-SP-5K wood samples were immersed into the mixed solutions and heated at 70 °C for 2 days in a water bath. Later, the wood samples were taken out from the bath and wiped off the residual liquid on the wood surface. The wood samples were kept at room temperature (~23 °C).

The weight percent gain (WPG) after impregnation was calculated from four replicates by Equation (1):

$$WPG (\%) = 100 \left( \frac{W_2 - W_1}{W_1} \right)$$

where $W_2$ is the weight of the wood after PEG immersion, and $W_1$ is the weight of the untreated wood. All wood samples were dried and then weighed.

2.4. Hot Pressing
Vulcanizing machine (Qingdao Xincheng, China) was employed to compress impregnated wood at 1.5 MPa and 150 °C for 4 h, followed by covering the wood (undried) surface with tinfoil, then interrupted heating and holding the pressure for 1 h. All the densified wood was set at room temperature for 8 h. The dimension and mass of each sample before and after densification were recorded, and the average value was calculated. The mass and dimension before and after immersion and hot pressing were compare to calculate the weight percent gain and compression ratio. A digital photograph of the actual compression
process is shown in Figure 1. The compression ratio (CR) after hot pressing and the density (\(\varrho\)) of the modified wood were calculated by Equations (2) and (3):

\[
\text{CR} (\%) = 100 \left( \frac{T_1 - T_2}{T_1} \right)
\]

\[
\varrho \ (g/cm^3) = \frac{m}{V}
\]

where \(T_2\) is the thickness of the untreated wood, and \(T_1\) is the thickness of the wood after hot pressing. All wood samples were dried and then tested.

2.5. Characterization

A Fourier-transform infrared spectrometer (Vertex 80v, Bruker) was used to check the status of the chemical bonds in the treated wood and whether nano-SiO\(_2\) and PEG were attached to the wood. Here, two sets of sampling points were taken from the surface and centroid of the modified wood. The FTIR spectrum was recorded between 400 and 4000 cm\(^{-1}\) with a resolution of 0.2 cm\(^{-1}\) (KBr pellet method). Scanning electron microscopy (SEM, Quanta 200, FEI, Hillsboro, OR, USA) was employed to observe the microstructure on the transverse section and tangential section of the densified wood. The wood samples were freeze-dried and gold-coated before observation. The thermal performance was recorded by a differential scanning calorimeter (Netzsch Photo-DSC 204 F1 Phoenix, Selb, Germany) from \(-20\) to \(100\ ^\circ\text{C}\) at \(5\ ^\circ\text{C}/\text{min}\) under nitrogen at a flow rate of \(20\ \text{mL}/\text{min}\). On a thermal analyzer (TG 209 F3 Tarsus, Netzsch, Selb, Germany) (0.1 mg, \(\pm 1\ ^\circ\text{C}\)), thermogravimetric analysis was performed at a temperature rise rate of \(10\ ^\circ\text{C}/\text{min}\) in a nitrogen atmosphere from \(10\) to \(600\ ^\circ\text{C}\).

3. Results and Discussion

3.1. WPG, CR, and Density of Modified Wood

From Table 2, DC-P showed the highest WPG under a 55.9% compression ratio, reaching 58.73%. The WPG of the other four groups was even lower than half of 58.73%. The reasons for this might be that low CR and PEG leaching led to a relatively large WPG, but the contribution to density growth was not as great as in the following high
CR groups. Previous studies have reported that the NaOH/Na$_2$SO$_3$ solution system can dissolve the extractives in wood and can also degrade hemicellulose and lignin in wood cell walls [28]. The degradation of hemicellulose and lignin was another reason for the PEG immersion improvement in the delignification wood. Nano-SiO$_2$ would have formed a weblike structure with the wood, and this could have affected the PEG penetration [29,30]. DC-SP-1 had the highest WPG of the four modified groups (22.94%), and DC-SP-1K had the highest CR and density of the four modified groups, but the WPG of DC-SP-1K was only 12.88%. We presumed that this needed to be attributed to the silane coupling agent KH550, which formed a more complete network of connections between nano-SiO$_2$ and the wood.

Table 2. WPG, CR, and density data.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Weight Percent Gain (%)</th>
<th>Compression Ratio (%)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>/</td>
<td>/</td>
<td>0.41 ± 0.03</td>
</tr>
<tr>
<td>C</td>
<td>/</td>
<td>50.8</td>
<td>0.73 ± 0.05</td>
</tr>
<tr>
<td>DC</td>
<td>/</td>
<td>67.2</td>
<td>0.77 ± 0.04</td>
</tr>
<tr>
<td>DC-P</td>
<td>58.73</td>
<td>55.9</td>
<td>0.85 ± 0.03</td>
</tr>
<tr>
<td>DC-SP-1</td>
<td>22.94</td>
<td>72.2</td>
<td>1.13 ± 0.02</td>
</tr>
<tr>
<td>DC-SP-1K</td>
<td>12.88</td>
<td>74.7</td>
<td>1.22 ± 0.01</td>
</tr>
<tr>
<td>DC-SP-5</td>
<td>14.79</td>
<td>65.5</td>
<td>0.94 ± 0.01</td>
</tr>
<tr>
<td>DC-SP-5K</td>
<td>10.99</td>
<td>70.9</td>
<td>1.07 ± 0.01</td>
</tr>
</tbody>
</table>

With the addition of 0.1% SiO$_2$, the group exhibited the maximum density (1.22 ± 0.01 g/cm$^3$), an increase of 158% compared with DC, and about a threefold increase compared with the untreated wood. The results indicate that the addition content of SiO$_2$ should be 0.1% compared with 0.5% in improvement in wood density.

Direct hot-pressing wood (C) and delignified hot-pressing wood (DC) were further compared by compressed rate (CR). As shown in Table 2, the delignification wood reached 67.2% of that in pristine wood. In other words, delignification in this work was a pretreatment of degrading wood hemicellulose and partly lignin with NaOH/Na$_2$SO$_3$ solution, which made the wood easier to be compressed in the hot-pressing treatment [16,31]. However, the structural feature of the delignified wood itself was the lack of connectivity of the internal structure as a result of lignin deficiency [32] (after lignin removal, direct compression tends to be a discrete state between the fibers). In addition, PEG was a preferred conservation agent in preserving such wood with poor structural stability, which would crack easily even when only dried in air. PEG and SiO$_2$ were used to remove a number of hydroxyl groups in the delignified wood through hydrogen bonds in it, which could reduce the entry and loss of water [33]. Under the joint impregnation of PEG and delignification, the cellulose fibrils in the delignified wood were combined more tightly, ensuring that the hardness and toughness basically remained the same. Therefore, even if the CR was higher than that of the pristine wood directly compressed (C) after impregnating PEG, it will not produce large dimensional deformation or even collapse [34,35]. At the same time, the PEG contained in the modified wood had a plasticizing effect, keeping the wood internally swollen and maintaining dimensional stability [20,21].

3.2. Microstructures Analysis

Due to the difference in WPG caused by impregnation, the morphology observed on the transverse surfaces will be different. To verify the changes on the microstructure of wood cell walls, SEM was used to observe transverse surfaces of the wood samples before and after the densification. In Figure 2a, we can clearly see the porous structure of the untreated poplar wood. Figure 2b shows the compressed wood cells on the transverse surface of the delignified wood after hot pressing. After delignification, the softer structure
of the wood may facilitate compression, and high compression ratios can be achieved [16]. However, during the hot-pressing process, the water was evaporated from the delignified wood (hot-pressing temperature was 150 °C), which further increased the compressible space. As a result, the compression effect was more significant, which can be learned by comparing Figure 2b,c. Meanwhile, previous reports suggested that such hydrothermal conditions generated more microcracks on wood cell walls [36,37]. In Figure 2d–h, the modified woods were all impregnated with PEG on the basis of lignin removal, where the only difference between them was the SiO$_2$ and KH550 content. It can be seen that the microcracks after hot pressing were significantly reduced in Figure 2h, and the surface of the slice was smoother, which confirms the good bonding effect of PEG and wood cells. Due to the extrusion of hot pressing, small bulging pieces of PEG can be seen on the surface. In Figure 2g, the visible gaps in the densified wood DC-SP-5K (Figure 2h) were reduced, which can make us speculate that the coupling agent KH550 has a significant effect on improving the surface cracks. Silane coupling agents (such as KH550) were hydrolyzed to form bonds between organic (such as wood) and inorganic (such as nano-SiO$_2$) materials, and sometimes the nano-SiO$_2$ itself is involved in this bonding [38–40]. In conclusion, the immersion in PEG improved the cracks in DC-P compared with DC; after doping with silicon, the cracks could hardly be observed in the cross section of DC-SP-5K.

![Figure 2](image_url)

**Figure 2.** Comparison of microscopic characteristics: (a) untreated wood, (b) direct hot-pressing wood, (c) delignified hot-pressing wood, (d) DC-P, (e) DC-SP-1, (f) DC-SP-1K, (g) DC-SP-5, (h) DC-SP-5K.

### 3.3. FTIR Analysis

To further explore the impregnation effect of nano-SiO$_2$ in densified wood and uncover the changes of wood cell wall polymers during the densification process, the infrared spectra were collected and are shown in Figure 3. Comparing DC and DC-P in Figure 3a, it was found that DC-P has weak absorption peaks characteristic of PEG at 2886 and 1321 cm$^{-1}$ [41,42]. These absorption peaks were all C–H vibration absorption peaks and moved to the lower frequency band. However, according to a study by Xie et al. [43], there should also be a PEG characteristic absorption peak near 1460 cm$^{-1}$, but it was not observed in this experiment. It was speculated that the influence of delignification led to the loss of part of the C–H bonds. This peak weakened or even disappeared. In addition, the -OH stretching vibration absorption peak at 3411 cm$^{-1}$ was obviously broadened and shifted to the lower frequency band, indicating that the hydrogen bond was formed on the H atom of -OH in DC-P [44,45]. Additionally, the absorption peak of DC-P at 1103 cm$^{-1}$ was sharper than the absorption peak at 1070 cm$^{-1}$ in DC, and shifted to the higher frequency range. It shows that there was a difference at ~1103 cm$^{-1}$ between the C-O-C stretching vibration absorption peak of PEG and the C–O–C bonds of poplar wood, which was the result of the superposition of the antisymmetric stretching vibration absorption peak [42,46]. Figure 3a also shows that there was no obvious chemical reaction between PEG and wood after hot...
pressing, which was beneficial for giving full play to the phase change energy storage effect of PEG [43].

Figure 3. (a) FTIR spectral patterns of C, DC, and DC-P; (b) DC-SP-1, DC-SP-1K, DC-SP-1(C), and DC-SP-1K(C); (c) DC-SP-5, DC-SP-5K, DC-SP-5(C), and DC-SP-5K(C).

Comparing the four curves in Figure 3b, the -OH absorption peak in the range of 3400–3500 cm⁻¹ [47] gradually weakened with the addition of KH550 and the movement of the sampling point to the center of the wood, and also showed a tendency to move to the low frequency direction. The sharp absorption peak from large to small at 1078–1076 cm⁻¹ in Figure 3b was the asymmetric absorption peak of Si–O–Si [48,49], showing a similar trend of gradually weakening from the surface to the central of the wood. The probable reasons that affected the FTIR results were (1) the increasing diffusion resistance in the center of the sample, the less internal nano-SiO₂ content, and (2) the application of the coupling agent and the influence of the incompletely removed lignin of the delignification wood. The disappearance of Si–OH bonds in the densified wood was caused by the drying of wood powder before testing. Comparing Figure 3b with 3c, the -OH expansion and contraction of DC-SP-5 at 3419 and 1078 cm⁻¹ in DC-SP-1 and DC-SP-5 can be seen, and both the vibration peak and the Si–O–Si asymmetric stretching vibration peak were broader than those of DC-SP-1, which also confirmed that the silicon content in the sample was higher when the volume fraction of nano-SiO₂ was added at 0.5%. Comparing the four curves in Figure 3c, the silicon vibration peaks of DC-SP-5(C) and DC-SP-5K(C) in the four curves were sharper than those of both DC-SP-5 and DC-SP-5K, indicating that the optimization of impregnation systems were of great help in improving the impregnation effect of nano-SiO₂ in the wood so that the nano-SiO₂ can diffuse more to the center of the wood samples.
3.4. Thermal Properties

The DSC curves of different samples are summarized in Figure 4, and some of the data related to them are recorded in Table 3. The endothermic and exothermic peaks were distinctly observed in pure PEG but lacking in pristine wood. This shows that poplar itself did not have phase change ability, and it was PEG that made the modified woods have endothermic and exothermic ability during the solid–liquid phase transition process. Compared with pure PEG, the melting enthalpies of DC-P, DC-SP-1, and DC-SP-5 were greatly reduced, only 62.0, 20.7, and 8.5 J/g, respectively. A study by Xu et al. [23] indicated that the restriction of the pore structure in wood and hydrogen bonds hindered the free movement of PEG molecular chains. This may be due to many reasons. First, the concentration of the PEG impregnation solution was only 50%, which was lower than that of pure PEG. Second, the loss of PEG during the hot-pressing process will also have an adverse effect on the last test results. Finally, due to the uneven dispersion of PEG in the sample powder during the DSC test, the PEG obtained during sampling will be less, resulting in a decrease in enthalpy. In addition, compared with DC-P, the melting enthalpy and crystallization enthalpy of DC-SP-1 and DC-SP-5 were both lower. The existence of a physical interaction of the PEG–SiO$_2$ network could not be cleared, such as hydrogen bonding, to limit the free movement of PEG, making accumulation difficult; it will also be affected by the low content of PEG in the test sample. Comparing DC-SP-1 and DC-SP-5, increasing the amount of nano-SiO$_2$ used will cause the melting peak and crystallization peak of PEG to be greatly weakened. Almost no crystallization peak was observed in DC-SP-5. We inferred that the high thermal stability of nano-SiO$_2$ inhibits PEG from showing strong heat absorption and exothermic ability in the low temperature range (≤100 °C), while in the high temperature range (≥300 °C), the endothermic and exothermic ability of PEG and the nano-SiO$_2$ network structure represented by nano-SiO$_2$ is not observed.

![Figure 4](image-url)

Figure 4. Comparison of DSC, TG, and DTG of samples. (a) DSC patterns of W, PEG, and DC-P; (b) DSC patterns of DC-SP-1 and DC-SP-5; (c) TG patterns of C, DC-P, and DC-SP-5K(C); (d) DTG patterns of C, DC-P, and DC-SP-5K(C).
Table 3. Thermal properties of PEG and modified wood.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta H_m) a (J/g)</td>
<td>(T_m) b (°C)</td>
</tr>
<tr>
<td>PEG</td>
<td>109.5</td>
<td>32.3</td>
</tr>
<tr>
<td>DC-P</td>
<td>62.0</td>
<td>51.5</td>
</tr>
<tr>
<td>DC-SP-1</td>
<td>20.7</td>
<td>50.0</td>
</tr>
<tr>
<td>DC-SP-5</td>
<td>8.5</td>
<td>44.6</td>
</tr>
</tbody>
</table>

a Melting enthalpy of each modified wood sample. b Peak temperature in the heating process. c Crystallization enthalpy of each modified wood sample. d Peak temperature in the cooling process.

Comparing the DSC curves and other performance characteristics of PEG with densified woods, it can be concluded that PEG has strong endothermic and exothermic capabilities. The increase in nano-SiO\(_2\) in the wood helped to grow the inhibitory effect of PEG impregnating, resulting in the endothermic and exothermic ability of PEG being difficult to show when the temperature was lower than 100 °C. Moreover, the highest melting enthalpy was 20.7 J/g, and the lowest was 0.9 J/g. At the same time, the crystallization peak can hardly be observed. During the phase change of PEG, wood, owing to its relatively stable properties, not only made little or no contribution to the enthalpy of the phase change, but also became an impurity phase of PEG, affecting the complete crystallization of PEG and thus reducing the enthalpy [43].

3.5. Thermal Stability

Thermal stability is a key parameter to evaluate the performance of high-efficiency thermal energy storage wood prepared by chemical pretreatment combined with hot pressing. The TG and DTG curves are shown in Figure 4c,d. As shown in Figure 4c, the DC-P curve has only one main peak, which is the weight loss peak starting at 220 °C. However, C and DC-SP-5K(C) both undergo an adsorption water evaporation process with a weight loss of about 5% between 25 and 100 °C. Therefore, wood sample C was not impregnated with PEG, and the concentration of DC-SP-5K(C) impregnated with PEG was only 50%, which will cause the wood to have a certain degree of obvious hygroscopicity. It can be basically confirmed that this peak is a weight loss of water evaporation. After that, the temperature range of wood components suffers pyrolysis, where the direct hot-pressing wood shows a narrower thermal decomposition temperature range between 200–430 °C in the DTG curve. In comparison, DC-SP-5K(C) inherited the excellent thermal energy storage characteristics of PEG, and the thermal decomposition temperature range was extended to 180–480 °C. In parallel, it was proved that PEG has a positive effect on improving thermal stability and antihygroscopicity [43].

Additionally, the differences of the weight loss ratio, the final residual mass, and the starting temperature of the weight loss peak of the three TG curves were further analyzed to evaluate the thermal stability of the modified woods. DC-P has the lowest onset temperature of the weight loss peak, which is presumably due to the high PEG content and the low temperature required for pyrolysis and melting of PEG. In this group of comparisons, a significant decrease in quality can be observed at the earliest. Comparatively speaking, the arrangement relationship of weightlessness speed is: C > DC-SP-5K(C) > DC-P. The probable reason is that the high heat resistance of nano-SiO\(_2\) plays a significant role in DC-SP-5K(C) and builds a stable network structure with PEG; the result is the residual mass of DC-SP-5K(C) taking the highest percentage. In addition, Guo and Wang [50] et al. found that the phase change enthalpy of PEG in composite materials is related to the pore size and shape of SiO\(_2\) and the thickness of the PEG layer. In this work, due to the different thickness of the PEG layer in the sample, the phase change enthalpy will also be different. The present research also shows that the presence of PEG can prevent the aggregation of nano-SiO\(_2\) particles, and the resulting decrease in SiO\(_2\) particle size
will further affect the phase transition enthalpy of PEG/SiO$_2$ composites [51]. The weight loss ratio of DC-SP-5K(C) was significantly slower than that of C. The effect of PEG/SiO$_2$ forming a stable network structure allowed the network structure even at temperatures above the phase transition temperature of PEG. PEG can maintain the original shape. This phase change hysteresis was conducive to the improvement of heat storage capacity [29].

The residual mass percentage of wood sample C was about 3% lower than the percentage tested by Xie et al. [43]. It was affected by delignification, and due to the long-time (4 h) compression under a high-temperature (150 °C) environment, such almost irreversible effect on the structure of the woods will lead to a slight decrease in the percentage of residual mass. Comparing DC-P with DC-SP-5K(C), because of the effect of delignification, the residual mass percentages of DC-P and DC-SP-5K(C) were both higher than that of wood sample C. Among them, the residual mass of DC-SP-5K(C) accounted for the largest proportion, which indicated that DC-SP-5K(C) has the best heat resistance among the three densified woods, and also confirmed the practicality of SiO$_2$-PEG system impregnation. Regarding the duration of the main peak weight loss process, the pyrolysis weight loss time of DC-P and DC-SP-5K(C) was significantly prolonged, which has a positive effect on the heat resistance time in practical applications.

4. Conclusions

In this work, a modified poplar wood was fabricated with joined compression and PEG impregnation after delignification treatment. After removing lignin and hemicelluloses and PEG–nano-SiO$_2$ impregnation, a modified wood with thermal energy storage was prepared by hot pressing for 4 h. The densified wood, WPG and CR, can reach 22.94% and 74.7%, respectively. The final composite wood has good heat storage capacity and thermal stability. The thermal storage capacity can be influenced by changing the content of PEG and nano-SiO$_2$ in the solvent system. The melting enthalpy and crystalization enthalpy of DC-P reached 62.0 and 50.0 J/g, respectively. The melting enthalpy and crystalization enthalpy of DC-SP-1 were 20.7 and 9.8 J/g, respectively. Such capabilities show the potential application on floor, wall, or roof insulation materials. For this modified wood, further research should focus on the improvement of the thermal properties.

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