Original article

Jianfeng Xu, Xiaoyan Li, Ling Long and Ru Liu*

Enhancement of the physical and mechanical properties of wood using a novel organo-montmorillonite/hyperbranched polyacrylate emulsion

<https://doi.org/10.1515/hf-2020-0042>

Received February 10, 2020; accepted September 4, 2020;

published online October 23, 2020

Abstract: In this work, a novel waterborne hyperbranched polyacrylate (HBPA) dispersed organo-montmorillonite (OMMT) emulsion was synthesized and used for the treatment of wood in a vacuum environment in order to enhance the physical and mechanical properties of the wood. The sapwood of Cathay poplar (*Populus cathayana* Rehd.) and Radiata pine (*Pinus radiata* D. Don) were used as the samples for experimentation. The results showed that the physical and mechanical properties of the wood improved significantly due to the successful penetration of the OMMT and HBPA into the wood cell wall. From it was also observed that OMET completely exfoliated from the HBPA matrix and formed a hydrophobic film covering on the inside walls of the cell lumen. Further, it was observed that the poplar sample displayed better mechanical properties than the pine sample because the pine has a more compact structure when compared to poplar and contains rosin. Furthermore, it was also observed that the mechanical properties of the modified wood sample gradually improved with an increase in the concentration of the emulsion. However, excessive concentration (>4 wt%) did not lead to further improvement.

Keywords: Cathay poplar (*Populus cathayana* Rehd.); emulsion; hyperbranched polyacrylate; organo-montmorillonite; Radiata pine (*Pinus radiata* D. Don); wood.

1 Introduction

As a sustainable and natural material, wood provides many special benefits, such as esthetic appeal, mechanical strength, thermal isolation, and humidity controllability (Jia et al. 2018; Liu et al. 2019). Therefore, it has a wide range of applications including decoration, architecture, and even railway construction (Dong et al. 2017; Montanari et al. 2019; Wang et al. 2014). However, wood is porous and hydrophilic, which easily absorbs water and results in shrinkage, deformation, decay, and strength drop. The chemical modification is an effective approach to solve this problem. Some studies reported that the mechanical properties of the wood can be improved by chemical immersing (Che et al. 2018; Daud and Shanks 2014; Furuno et al. 2004; Tanaka et al. 2016). However, most of the applied chemicals may result in environmental pollutions. For example, the phenol-formaldehyde resin-impregnated wood has the potential to release free phenol and formaldehyde, which is harmful to humans (Yu et al. 2018). Therefore, it is necessary to develop a kind of green chemical modifier.

Due to the development of nano-technology, the incorporation of nanoclay fillers as reinforcements has received great attention. Montmorillonite (MMT) which is a kind of nanoclay is naturally occurring and available abundantly. It is a layered silicate material with a high aspect ratio and specific surface area (Fini et al. 2017). The addition of MMT can significantly improve the physical and mechanical properties of the polymer even when the content is lower than 5 wt% (Liu et al. 2018). Wood is a natural polymer composite composed of cellulose, hemicelluloses, lignin, and also a small amount of pectin and extractives (Xie et al. 2010). Moreover, the wood is full of pores such as cell lumen, pits, etc, which MMT can be deposited. Natural MMT contains cations of Na^+ and Ca^{2+} in its gallery and thus it is hydrophilic and easily agglomerates. Due to this property, the natural MMT imposes restrictions to disperse into wood cell walls

*Corresponding author: Ru Liu, Research Institute of Wood Industry, Chinese Academy of Forestry, Haidian, 100091, Beijing, China, E-mail: liuru@cwi.org.cn

Jianfeng Xu, Xiaoyan Li and Ling Long, Research Institute of Wood Industry, Chinese Academy of Forestry, Haidian, 100091, Beijing, China

and thus does not contribute significantly towards the improvement of the physical and mechanical properties except for the fire retardancy (Fu et al. 2017). Therefore, it should be first modified into organo-montmorillonite (OMMT) by cationic exchange reaction. However, OMMT cannot be directly dissolved in water. Therefore, the most essential way for the modification is to find a suitable carrier.

Waterborne hyperbranched polymers are a new kind of macromolecule with a unique tree-like structure. It is hard to crystallize and can be easily dissolved in water with a slight increase in the viscosity (Amin et al. 2010; Faris et al. 2016; Meyers et al. 2017). Besides, it possesses a smaller particle size when compared with the linear polymers of the same molecular weight (Lai et al. 2016), which makes it possible to enter into the cell wall of the wood. In addition, researchers have found that the hyperbranched polymers can effectively enter into the galleries of MMT to form exfoliated structures using individual 1 nm MMT sheets (Anandhan et al. 2011; Deka and Karak 2011; Maji et al. 2010; Wang et al. 2012). Thus, it is considered to be an excellent carrier for OMMT for wood impregnation. In order to further improve the properties of the modified wood, the hyperbranched polymers should be curable with a layer of the film after drying. For this process, the waterborne polyacrylate (PA) emulsion is a good selection. It forms a hydrophobic layer on the wood's inner surface of cell lumen when heated which leads to the bulking of the wood pores and thereby enhances the physical and mechanical properties of wood (Liu et al. 2016).

The waterborne hyperbranched polyacrylate can be used as a dispersant of OMMT. Further, it is a promising modifier for wood modification, which can be easily dissolved in water during modification without using any of the poisonous organic solvents such as benzene or toluene. Therefore, in this study, a novel waterborne HBPA emulsion containing OMMT was synthesized by a free radical seeded emulsion polymerization process. The OMMT/HBPA emulsion was used to treat wood through vacuum treatment with various concentrations. The sapwoods of Cathy poplar (*Populus cathayana* Rehd.) and Radiata pine

(*Pinus radiata* D. Don) were selected and the results were compared. Some of the physical and mechanical properties of the modified woods were tested. Moreover, the emulsion and the modified woods were further characterized for a better understanding of the results.

2 Materials and methods

2.1 Materials

Cathay poplar (*Populus cathayana* Rehd.) was harvested from a forest in Luohe, Henan province, China. Radiata pine (*Pinus radiata* D. Don) was obtained from Linyi Fuhe Wood Co., Ltd., Shandong, China. The woods were bucked into lumbers and air-dried in order to eliminate the excessive water. Further, the sapwood was chosen without any visible defects of knots, decay, etc. The basic parameters of the two

Table 2: Parameters of the reagents.

Reagents	Type	Abbreviation	Manufacturer
Methyl methacrylate	Monomer	MMA	1
Butyl acrylate	Monomer	BA	1
Acrylate acid	Monomer	AA	1
Glycidyl methacrylate	Monomer	GMA	2
Diethanolamine	Monomer	DEA	1
Methanol	Solvent	–	1
<i>N,N</i> -Dimethylethanolamine	Catalyser	DMEA	1
Ammonium persulfate	Initiator	APS	1
Sodium dodecyl sulfate	Emulsifier	SDS	3
Disodium laureth sulfosuccinate	Emulsifier	DLS	4
Polyoxyethyken	Emulsifier	OP-10	3
Polyvinyl alcohol 1788	Retarder	PVA1788	3
Sodium bicarbonate	pH regulator	–	3

1 Xilong Chemical Co. Ltd. (Guangzhou, China).

2 Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China).

3 Tianjin Jinke Fine Chemical Institute (Tianjin, China).

4 Guangzhou Nanjia Chem-Engineering Technology Co. Ltd. (Guangzhou, China).

Table 1: Parameters of the two kinds of wood.

Woods	Scientific name	Density (kg/m ³) ^a	Chemical components (%)			
			Extractives ^b	Holocelluloses ^c	α -Cellulose ^d	Lignin ^e
Cathy poplar	<i>Populus cathayana</i> Rehd.	490–520	2.7	62.3	44.1	23.6
Radiata pine	<i>Pinus radiata</i> D. Don	520–550	9.0	63.4	43.4	27.5

^aThe values found at 12% MC.

^bBenzene-ethanol soluble extractives.

^cThe values found by chlorite method.

^dThe values found according to TAPPI 203 CM-09.

^eThe values found according to TAPPI 222 om-11.

kinds of woods are listed in Table 1. The woods were cut into samples with required dimensions. OMMT (I.31PS; Nanocor Inc. Chicago, USA) was purchased from East West Company, Beijing, China. It is a hydrophobic clay powder that was modified using octadecyl ammonium salt with an organic chain of $(\text{CH}_3[\text{CH}_2]_{17})_2\text{N}(\text{CH}_3)_2^+$ in its lamellar state. The interlayer distance of OMMT was 2.32 nm. The reagents of the HBPA are listed in Table 2.

2.2 Synthesis of waterborne OMMT/HBPA emulsion

The first step of the experiment was to prepare OMMT/hyperbranched basal polymer (HBBP). The parameters that are necessary for the synthesis were determined based on the literature (Kuang et al. 2010; Liu et al. 2016; Omara et al. 2015) and a large number of prior experiments were conducted in order to ensure the process. The DEA was dissolved in methanol. Thereafter, it was mixed with MMA with a mole ratio of 1:1.2 and OMMT with a mass ratio of 6:1. The mixture was kept under continuous stirring at a speed of 240 rpm at room temperature for 2 h. The temperature was kept at 60 °C for 2 h, 100 °C for the next 2 h, and finally at 150 °C for 4 h using an oil bath. After the completion of the reaction, a brown sticky liquid was obtained.

The second step of the experiment was to graft vinyl groups onto the end groups of the OMMT/HBBP. During this step, the HBBP was mixed with GMA and DMEA with a mass ratio of 1:0.5:0.1 and further oil-bathed at a temperature of 80 °C for 2 h under continuous stirring at a speed of 240 rpm.

The final step was to synthesize the waterborne HBPA emulsion using seeded emulsion polymerization in a four-neck glass reactor. Before synthesis, the emulsifiers such as SDS, DLS, and OP-10 of the quantities of 5, 6, and 10 g respectively were dissolved in distilled water at 20 wt%. Similarly, 4 g APS was dissolved at 10 wt% and 2 g PVA1788 was dissolved at 8 wt%. Further, 20 g of GMA grafted OMMT/HBBP along with monomers such as MMA, BA, and taken in quantities of 65, 75, and 5 g respectively was blended with two-thirds of emulsifier solution, 150 g distilled water, PVA1788 solution, and 5 g NaHCO_3 at a temperature of 52 °C under a high-speed stirring of 800 rpm for 10 min in order to produce pre-emulsion. Thereafter, one-eighth of the produced pre-emulsion and 50 g distilled water were poured into the reactor. Further, when this mixture is heated up to 75 °C, one-third of the APS solution and the rest of the emulsifier solution were added into the reactor. The reaction was allowed to take place for 30 min until the liquid became blue, and then the seed emulsion was obtained. Then, the rest of the pre-emulsion and the initiator solution was dripped into the reactor within 2 h. After the drip addition was completed, the reaction was allowed to take place at 75 °C for another 2 h and heated up to 81 °C for 1.5 h. Thereafter, a light brown waterborne HBPA emulsion was obtained after cooling and filtration. The pH value was adjusted to 6.5 using NaHCO_3 . The solid content of the emulsion was 33%. The number average molecular weight was about 45000 g/mol with an average particle size of 100 nm and viscosity was 120 mPa·s.

2.3 Modification of wood

The wood samples were initially oven-dried at 103 °C before modification until a constant mass is achieved. Thereafter, the modification process was carried out in a vacuum-treating tank. In the vacuum-treating tank, the wood samples were exposed to a

vacuum at 0.01 MPa for 2 h. Further, the wood samples were submerged in the OMMT/HBPA emulsions with different concentrations of 2, 4, 6, and 8 wt% with respect to water and kept in a vacuum for another 8 h. Then, the wood samples were taken out of the tank and dried at 40 °C for 24 hours and then dried again at 103 °C in order to achieve a constant mass to avoid cracks. Finally, the weight percent gain (WPG) related to original wood was calculated.

2.4 Characterization of the emulsion and woods

The characterization of the emulsion and the wood samples were carried out as follows. The average particle size distribution of OMMT/HBPA emulsion was tested using a laser scattering particle distribution analyzer (Nano C, Beckman Coulter Inc., USA). In order to avoid curing before testing, the emulsion was freeze-dried in a vacuum freeze-drying machine (LGJ-10C, Sihuan Foring Instrument Co., Ltd., China).

The synthesized freeze-dried polymers, and the modified and unmodified wood samples were characterized for X-ray diffraction (XRD) using an XRD instrument (D8 Advance, Bruker, Germany). Further, the powders of the wood samples were made to pass through an 80-mesh sieve and oven-dried before the analyses. While performing characterization using the XRD instrument, Cu-K α with a wavelength of 0.154 nm ($\lambda = 0.154$ nm) was used for the radiation and was operated at 40 kV and 30 mA. The scanning rate was 2 °/s and the 2 θ was taken in the range from 2° to 40°.

Further, ^1H nuclear magnetic resonance (^1H NMR) measurement was carried out for the freeze-dried OMMT/HBPA using NMR spectrometer (Avance III 600MHz, Bruker, Germany) with DMSO- d_6 solvent at room temperature. Fourier transform infrared spectroscopy (FTIR) analyses (IS10, Nicolet, USA) were performed for the freeze-dried polymers, and the air-dried unmodified and modified wood samples using the KBr pellet technique. The KBr was used as a background for the characterization. The sample powder was mixed with KBr in a ratio of 1:100. All the measured spectra were displayed in wavenumbers ranging from 400 to 4000 cm^{-1} .

The tangential sections of the unmodified and the modified wood samples were observed using Gemini (Gemini 500, Carl Zeiss, Germany) field emission scanning electron microscope (FE-SEM) with an acceleration voltage of 15 kV. Further characterization was carried out using Transmission Electron Microscope (TEM) using a TEM instrument (TEM 1010, JEOL, Japan) in order to observe the structure and distribution of OMMT in the emulsions and the modified wood samples. In order to obtain TEM image acquisition, the emulsions were diluted with distilled water to 0.1 wt% and dropped onto a copper grid. Further, the wood samples were ground into fibers and embedded in an epoxy resin. Thereafter, they were cut into 50 nm thick slices using an ultra-microtome knife.

2.5 Physical and mechanical properties of woods

The testing of the wood samples to analyze their physical and mechanical properties was described briefly. The water uptake (WA) test was carried out according to the Chinese standard GB/T 1934.1–2009. In this test, the samples were completely immersed in water at 20 ± 2 °C. Further, the WA was calculated after the removal of the excess water that was present on the sample surface. The WA was calculated based

on the weight percent gains measured after various time periods such as 6 h, 1 day, 2, 4, 8, 15, 30, and 45 days of the immersion. The shrinkage test was carried out according to Chinese standard GB/T 1932–2009. The samples were completely immersed in water at 20 ± 2 °C till a constant dimension was achieved. Thereafter, the samples were dried in an oven at 60 °C for 6 h, and further dried at 103 °C until a constant dimension was achieved. Then, the shrinkage values for the volume change were obtained. The anti-swelling efficiency (ASE) was calculated according to Equation (1).

$$\text{ASE}(\%) = 100 \times (V_c - V_m)/V_c \quad (1)$$

In Equation (1), V_c and V_m refer to the volume of the control sample after water immersion and the volume of the modified sample after water immersion respectively. Thereafter, the average values and the standard deviations were calculated for the WA and shrinkage tests, based on 12 replicates with the dimensions $20 \times 20 \times 20$ mm.

A three-point flexural test was carried out on a wood sample of a length of 250 mm, a radius of 20 mm, and a thickness of 20 mm, as per the Chinese standard GB/T 1936.1–2009 with a crosshead speed of 10 mm/min and a span of 200 mm. During the test, the load was applied to the tangential direction and the flexural strength and the modulus were obtained. Further, the compression test was carried out on a wood sample of a length 30 mm, a radius of 20 mm, and a thickness of 20 mm as per the Chinese standard GB/T 1935–2009 with a crosshead speed of 5 mm/min and the results were obtained. Thereafter, the average values and the standard deviations were calculated based on 20 replicates for the flexural and compression test.

3 Results and discussion

3.1 Characterization of OMMT/HBPA emulsion

The XRD patterns of OMMT and the freeze-dried OMMT/HBPA emulsion are shown in Figure 1a. From Figure 1a, it was observed that OMMT possessed a diffraction peak at $2\theta = 3.80^\circ$, corresponding to the interlayer distance of 2.32 nm. However, there were no obvious diffraction peaks found for OMMT/HBPA at $2\theta = 2\text{--}10^\circ$. From literature, it was observed that if the MMT was completely exfoliated into individual and collapsed silicate layers, the regular crystalline structure cannot be found from the XRD patterns (Ji et al. 2017; Osman et al. 2017; Xu et al. 2019a). From Figure 1a, it was observed that there were some small peaks at 25° , 32° , and 34° . These peaks may be due to the presence of sodium bicarbonate pH regulator and impurities in reagents (Kontoyannis and Vagenas 2000). The TEM images of the morphologies of OMMT/HBPA emulsion that were obtained during characterization are shown in Figure 1b, c. From Figure 1b, it was observed that the OMMT had completely exfoliated with an individual silicate layer by absorbing the emulsion particle. From Figure 1c, it observed that the thickness and length values were very

similar to the dimensions of the ideal single layer of MMT. The thickness and length observed were 1 and 100 nm, respectively. Further, the results of the particle size distribution of OMMT/HBPA emulsion as shown in Figure 1d confirmed that the average particle size was 94 nm. Therefore, the monomers were initially entered into the galleries of OMMT before performing the synthesis process. Furthermore, it was observed that during polymerization, the hyperbranched structure enlarged the interlayer distance of OMMT and finally broke the interlaminar force, resulting in an exfoliated structure.

The FTIR spectra of the freeze-dried OMMT/HBPA emulsion are shown in Figure 1e. From Figure 1e, it was observed that the spectra did not show a peak at 1640 cm^{-1} (C=C bond). This indicated that the monomers were successfully polymerized. Furthermore, the following characteristic peaks of HBPA were observed in Figure 1e. These included 3363 cm^{-1} (–OH groups stretching vibration), $2995\text{--}2823\text{ cm}^{-1}$ (C–H stretching vibration in alkyl groups), 1730 cm^{-1} (C=O stretching vibration in ester groups), 1587 cm^{-1} (N–H bending vibration), 1451 and 1385 cm^{-1} (C–H bending in methyl and methylene groups), 1238 cm^{-1} (O–C=O stretching vibration in ester groups), 1137 cm^{-1} (C–O–C stretching vibration in ester groups), and 618 cm^{-1} (O–C=O bending vibration in carboxylic acids) (Kuang et al. 2010; Xu et al. 2019b). The peak observed at 1061 cm^{-1} related to Si–O–Si proved the existence of silicate layers of OMMT. Figure 1f shows the ^1H NMR results of the freeze-dried OMMT/HBPA emulsion. From Figure 1f, it was observed that the obtained results were consistent with the results obtained in the literature (Hong and Pan 2001; Lligadas and Percec 2007; Omara et al. 2015) and the characteristics of HBPA existed. It was further observed that the signals of the protons of the main chains HBPA ($\text{CH}_3\text{--CH}_2\text{--}$) were present in the regions of 1.30–2.70 ppm. Furthermore, a functional linear group of $\text{N--CH}_2\text{--CH}_2\text{--O--}$ was found at 2.80 ppm. This was due to the combination of the N element. It was also observed that the dendritic groups of $\text{N--CH}_2\text{--}$ and $\text{CH}_2\text{--O--CO--}$ were fitted at 3.40 and 4.05 ppm, respectively. Further, the grafted groups of $\text{--CH}_2\text{--OH}$ of GMA had a signal at 4.80 ppm. Therefore, the hyperbranched structure of HBPA was confirmed, and the layer of OMMT may be absorbed by the HBPA particles.

3.2 Characterization of OMMT/HBPA modified wood samples

The XRD patterns of unmodified and 8 wt% OMMT/HBPA modified poplar and pine are shown in Figure 2a. From Figure 2a, it was observed that the diffraction peak was not

Figure 1: Characterizations of OMMT/HBPA emulsion. (a) XRD patterns of OMMT and freeze-dried OMMT/HBPA emulsion; (b, c) TEM image of OMMT/HBPA emulsion; (d) particle size distribution of OMMT/HBPA emulsion; (e) FTIR and (f) ^1H NMR spectra of OMMT/HBPA emulsion. Note: (c) was 10-time magnification of (b).

seen at $2\theta = 2\text{--}10^\circ$ for all the wood samples. This may be associated with the complete exfoliated structure of the wood samples. The FTIR spectra of unmodified and 8 wt% OMMT/HBPA modified poplar and pine are shown in Figure 2b. From Figure 2b, it was observed that the obvious difference between the samples was found at $2995\text{--}2823\text{ cm}^{-1}$ and 1731 cm^{-1} in samples of OMMT/HBPA modified woods. These results corresponded to the asymmetrical and symmetrical stretching of C-H ($2995\text{--}2823\text{ cm}^{-1}$) and the C=O

stretching (1731 cm^{-1}), respectively. Furthermore, it suggested the impregnation of HBPA. Furthermore, it was observed that there were slightly enlarged bands at 1026 cm^{-1} and 1445 cm^{-1} . This may be due to the overlapping of C-O-C and C-H with the wood components. As no further differences were found, it can be concluded that the modification process did not cause much change to the pure wood.

The SEM images of the unmodified and 8 wt% OMMT/HBPA modified wood samples are shown in Figures 3a–3d.

From the figures, it was observed that the surfaces of unmodified wood samples in SEM images were very clean (Figure 3a and Figure 3c). It was further observed that even though the structures remained after the impregnation of the emulsions, thickened cell walls and blocked pits were observed due to the cured polymers on the cell walls (Figure 3b and d). During the first stage of drying at 40 °C, a large amount of water was lost, and a large part of the polymer was cured. In the next stage in which it was further dried at 103 °C, the bonded water which was hard to evaporate was removed, and the oven-dried sample was obtained. From the experimented samples, it was observed that the morphologies of the low concentration (2, 4, and 6 wt%) OMMT/HBPA modified wood samples were much similar to the 8 wt% modified sample except for slight thickening of the cell walls and blocked pits of cured HBPA. The SEM analysis suggested that the modification affected the original wood structures only marginally. Moreover, the viscosities of different concentrations of OMMT/HBPA emulsion modifiers which were tested by a rotational viscometer were found to be in the range from 6 to 20 mPa·s, which was not significant. Therefore, the influence of viscosity on emulsion impregnation can be ignored. From the results, the alternate pits of poplar and single pits of pine were clearly seen (Figure 3a and Figure 3c). Further, the results showed that the sizes of vessels of poplar were much larger than the sizes of the tracheid of pine (Figure 3a and Figure 3c). Therefore, it was concluded that the modifier had better permeability on poplar rather than on pine.

The TEM images of unmodified and 8 wt% OMMT/HBPA modified wood samples are shown in Figure 4a–d. In Figures 4a and 4c, it was observed that the samples had very clean cell walls. After modification, a layer of cured HBPA was found adhering to the poplar wood cell, which might be beneficial to the water repellence (Figure 4b).

Moreover, it was further observed that some of the HBPA had penetrated into the wood cell wall along with the exfoliated OMMT by using the wood pits as pathways. From Figure 4d, it was observed that much of the OMMT was located in the cell lumen instead of penetrating into the cell walls even though they remained as exfoliated structures. This may be due to the compact structure of the pine. Moreover, the OMMT partly entered into the cell walls together with the HBPA particles. In Figure 4c, some black dots were observed in the cell walls of pine. These black dots denoted the pine rosin which may be leached after impregnation during the immersion as shown in Figure 4d.

3.3 Physical and mechanical properties of OMMT/HBPA modified wood samples

The results of WA of the unmodified and different concentrations of the OMMT/HBPA modified wood samples are shown in Figure 5. From the results, it was observed that as the concentration of OMMT/HBPA increases, the WPG increased gradually for both poplar and pine samples. This result was expected because the impregnation condition of each group was the same, and the viscosity of different treating emulsions at different concentrations had very few variations. Further, from the results, it was observed that as the OMMT/HBPA concentration increased to 8 wt%, the equilibrium water uptake (EWA) value decreased from 145 to 120%. Furthermore, by comparing the results of pure pine and the modified pine, it was found that 8 wt% OMMT/HBPA modified group showed a 15.6% decrease. In order to eliminate the WPG effects on the WA results, the EWA value was calculated based on the weight ratio of absorbed water to sample before modification. From the results, it was found that 2 wt% OMMT/HBPA modified poplar showed the

Figure 2: XRD patterns (a) and FTIR spectra (b) of unmodified and 8 wt% OMMT/HBPA modified wood samples.

Figure 3: SEM images of unmodified (a, c) and 8 wt% OMMT/HBPA modified (b, d) wood samples. (a, b) poplar; (c, d) pine.

Figure 4: TEM images of unmodified (a, c) and 8 wt% OMMT/HBPA modified (b, d) wood samples. (a, b) poplar; (c, d) pine. Note: The images in the circles were 10 times magnified compared to the original.

value at 142%, while the value of 4 wt% groups reached 133%. Further, the values of 6 and 8 wt% groups rose up to 137 and 141%. Similar results were observed for pine samples also. Therefore, it was concluded that a higher concentration of OMMT/HBPA did not contribute towards the

lowering of the WA. Moreover, the OMMT/HBPA modified wood had lower WA values at each interval because highly exfoliated OMMT could result in a tortuous path for water moving. Therefore, within the same immersion time, the WA value was reduced. However, as time increased, the real

final WA might be the same. Moreover, the cured hydrophobic HBPA took up the position of wood cell pores and reduced the accessible volume for water. Furthermore, the coverage reduced the number of accessible hydroxyls on wood cells and thereby contributed to the lower value of WA. Similar trend was observed for both poplar and pine with increasing OMMT/HBPA concentration and the modification effects were weakened. It was observed that the 4 wt% modified one showed an 11% decrease than 2 wt% OMMT/HBPA modified group, while the 6 wt% modified group only had a 3% decrease when compared to that of the 4 wt% modified one. It was further observed that the concentration of 4 wt% OMMT/HBPA was the key point after which a plateau was achieved.

The shrinkage test and ASE were carried out for dimensional stability. The results of the shrinkage test and ASE are listed in Table 3. From Table 3, it was observed that the shrinkage trends of each group were similar to that of

the WA results. Moreover, the modification had remarkably improved the dimensional stability of the woods. This was due to the bulk of cells and the seal of channels that were for water transport. The ASE results also confirmed the better performance of the OMMT/HBPA modified groups. It was observed that at 2 wt% concentration, the ASE was 17%, whereas, beyond 4 wt%, the ASE increased to 23%. This was because the cured hydrophobic HBPA film covering the inner space of wood cell walls prevented the wood cell from absorbing water during immersion. Further, the bulking effect of OMMT/HBPA inside wood cell walls propped up the cell during dehydration and also locked the OH groups in wood, resulting in minimum variation in the dimensions. When the results of the pine were compared with that of the poplar, it was observed that the poplar groups performed better after modification with OMMT/HBPA. It was further observed that beyond 4 wt% OMMT/HBPA, the modification reached an equilibrium

Figure 5: Water uptake of unmodified and different concentration OMMT/HBPA modified wood samples. (a) Poplar; (b) pine. Note: Bars stand for standard deviations.

Table 3: Shrinkages, anti-swelling efficiency, flexural strength, flexural modulus, and compression strength of unmodified and different concentration OMMT/HBPA modified wood samples.

Wood	OMMT/HBPA concentration (wt%)	Shrinkag (%)	Anti-swelling efficiency (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Compression strength (MPa)
Poplar	0	12.8(1.0)	—	62.3(8.2)	2.05(0.21)	45.6(6.1)
	2	10.7(0.5)	18.0(2.7)	74.6(6.3)	2.44(0.12)	56.8(5.3)
	4	9.4(0.6)	22.7(3.3)	85.2(6.4)	2.74(0.19)	69.7(8.3)
	6	9.3(0.2)	23.3(4.2)	86.2(6.6)	2.77(0.12)	70.2(4.3)
	8	9.4(0.2)	24.0(3.5)	84.9(3.9)	2.88(0.33)	69.6(5.5)
Pine	0	13.5(1.6)	—	65.9(8.8)	1.88(0.19)	43.1(3.2)
	2	11.4(1.8)	17.1(2.2)	72.5(6.6)	2.20(0.32)	52.3(4.5)
	4	10.8(1.3)	23.8(4.1)	79.9(4.9)	2.48(0.39)	63.9(5.8)
	6	10.0(1.1)	23.2(5.1)	79.3(2.9)	2.44(0.28)	64.3(2.9)
	8	10.6(1.3)	24.2(5.4)	78.5(4.4)	2.46(0.31)	63.3(5.9)

Values in parentheses represent standard deviations.

where the values were almost unchanged. This was due to the saturation of the modifiers in cell walls.

The flexural strength, flexural modulus, and the compression strength of unmodified and different concentrations of OMMT/HBPA modified wood samples are listed in Table 3. From the results, it was observed that the flexural strength, flexural modulus, and the compression strength increased after modification. Moreover, it was also found that the poplar groups performed better after modification with OMMT/HBPA and 4 wt% concentration of modifier was suitable. The significant improvements were due to the synergistic effect of cured HBPA and highly exfoliated OMMT in wood cell walls (Utracki et al. 2007). Further, the cured HBPA can form a network structure to bulk the wood cell walls, which was beneficial to strengthen the wood cell components, and therefore the improved mechanical properties were achieved. Furthermore, it was observed that wood penetrated with HBPA also showed significant improvements. As the concentration of OMMT/HBPA increased, the mechanical properties reached a plateau with some fluctuations. Therefore, it can be concluded that 4 wt% concentration of OMMT/HBPA is acceptable. Beyond 4 wt%, lots of modifiers may be located in the wood cell lumen.

Liu et al. (2019) used 4 wt% OMMT suspension modified poplar wood and found a 17.8% decrease of water uptake compared with unmodified wood. In the group of 8 wt% OMMT/HBPA, the value was much the same as theirs, while the content of OMMT was much lower than Liu et al. (2019). Also, Wang et al. (2014) found that 4 wt% OMMT could result in a 26.7% increase of compression strength, while the group of 4 wt% OMMT/HBPA in this study possessed a 52.9% increase compared with the untreated one. As for the HBPA part, few studies reported the HBPA modified wood. However, for PA emulsions, Zhang (2014) prepared PA emulsion containing silica and used it for fir and pine wood modification. 13% improved compression strength was obtained when the WPG of wood was higher than 30%. However, the volume shrinkage was similar to the result of 4 wt% OMMT/HBPA treated poplar of 9.4%. Therefore, large PA particles might fail to enter into the cell wall. The improvements of Zhang (2014) were achieved because of high WPG.

4 Conclusion

In this work, the enhancement of the physical and mechanical properties of wood using a novel organo-montmorillonite/hyperbranched polyacrylate emulsion was studied. The study showed that the organo-montmorillonite (OMMT)

was highly exfoliated in the hyperbranched polyacrylate (HBPA) emulsion and the OMMT and HBPA can enter into the cell walls of the wood. By using the emulsion, improved water repellency and mechanical properties of the modified wood were obtained. From the results, it was observed that the modification progress was more suitable for poplar than pine owing to the fact that poplar had lower extractives contents than pine. The introduction of OMMT exhibited a synergistic effect for further improvements, which helped to bulk the wood cells, preventing water from free transport, and absorbing more stress. With the increasing concentration of the emulsion, the mechanical properties of modified wood were improved before the modifier concentration of 4 wt%. Further, the excessive concentration of modifier (>4 wt%) did not lead to further improvement because that large amount of the modifier beyond 4 wt% was located in wood cell lumen.

Acknowledgments: The authors would like to thank all the reviewers who participated in the review and MJEditor (www.mjeditor.com) for its linguistic assistance during the preparation of this manuscript.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This study was financially supported by the National Natural Science Foundation of China (no. 31800470).

Conflict of interest statement: The authors declare that they have no conflicts of interest.

References

- Amin, A., Taha, A.S., and El-Ghaffar, A.A. (2010). Aliphatic polyamidoamine hyperbranched polymers/layered silicate nanocomposites. *J. Appl. Polym. Sci.* 118: 525–537.
- Anandhan, S., Patil, H.G., and Babu, R.R. (2011). Characterization of poly (ethylene-co-vinyl acetate-co-carbon monoxide) layered silicate clay hybrids obtained by melt mixing. *J. Mater. Sci.* 46: 7423–7430.
- Che, W., Xiao, Z., Han, G., Zheng, Z., and Xie, Y. (2018). Radiata pine wood treatment with a dispersion of aqueous styrene/acrylic acid copolymer. *Holzforschung* 72: 387–396.
- Daud, N. and Shanks, R. (2014). Epoxy-silica composites replicating wood cell structure. *Compos. A-Appl. Sci.* 62: 11–15.
- Deka, H. and Karak, N. (2011). Bio-based hyperbranched polyurethane/clay nanocomposites: adhesive, mechanical, and thermal properties. *Polym. Adv. Technol.* 22: 973–980.
- Dong, X., Zhuo, X., Wei, J., Zhang, G., and Li, Y. (2017). Wood-based nanocomposite derived by *in-situ* formation of organic-inorganic hybrid polymer within wood via a sol-gel method. *ACS Appl. Mater. Interfaces* 9: 9070–9078.

- Faris, A.H., Ibrahim, M.N.M., and Rahim, A.A. (2016). Preparation and characterization of green adhesives using modified tannin and hyperbranched poly(amine-ester). *Int. J. Adhesion Adhes.* 71: 39–47.
- Fini, E.H., Høgsaa, B., Christiansen, J.C., Sanporean, C.G., Jensen, E.A., Mousavi, M., and Pahlavan, F. (2017). Multiscale investigation of a bioresidue as a novel intercalant for sodium montmorillonite. *J. Phys. Chem. C* 121: 1794–1802.
- Fu, Q., Medina, L., Li, Y., Carosio, F., Hajian, A., and Berglund, L.A. (2017). Nanostructured wood hybrids for fire-retardancy prepared by clay impregnation into the cell wall. *ACS Appl. Mater. Interfaces* 9: 36154–36163.
- Furuno, T., Imamura, Y., and Kajita, H. (2004). The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. *Wood Sci. Technol* 37: 349–361.
- Hong, C.Y. and Pan, C.Y. (2001). Synthesis and characterization of hyperbranched polyacrylates in the presence of a tetrafunctional initiator with higher reactivity than monomer by self-condensing vinyl polymerization. *Polymer* 42: 9385–9391.
- Ji, J., Ke, Y., Pei, Y., and Zhang, G. (2017). Effects of highly exfoliated montmorillonite layers on the properties of clay reinforced terpolymer nanocomposite plugging microspheres. *J. Appl. Polym. Sci.* 134: 44894.
- Jia, S., Chen, H., Luo, S., Qing, Y., Deng, S., Yan, N., and Wu, Y. (2018). One-step approach to prepare superhydrophobic wood with enhanced mechanical and chemical durability: driving of alkali. *Appl. Surf. Sci.* 455: 115–122.
- Kontoyannis, C.G. and Vagenas, N.V. (2000). Calcium carbonate phase analysis using XRD and FT-Raman spectroscopy. *Analyst* 125: 251–255.
- Kuang, X., Kuang, R., Zheng, X., and Wang, Z. (2010). Mechanical properties and size stability of wheat straw and recycled LDPE composites coupled by waterborne coupling agents. *Carbohydr. Polym.* 80: 927–933.
- Lai, N., Wu, T., Ye, Z., Zhou, N., Xu, Q., and Zeng, F. (2016). Preparation and properties of hyperbranched polymer containing functionalized nano-SiO₂ for low-moderate permeability reservoirs. *Russ. J. Appl. Chem.* 89: 1681–1693.
- Liu, R., Liu, M., Hu, S., Huang, A., and Ma, E. (2018). Comparison of six WPCs made of organo-montmorillonite modified fibers of four trees, moso bamboo and wheat straw and poly(lactic acid) (PLA). *Holzforchung* 72: 735–744.
- Liu, R., Luo, S., Cao, J., and Chen, Y. (2016). Mechanical properties of wood flour/poly (lactic acid) composites coupled with waterborne silane-polyacrylate copolymer emulsion. *Holzforchung* 70: 439–447.
- Liu, M., Yi, Q., Li, J., Ma, E., and Liu, R. (2019). Synergistic effect of montmorillonite/lignin on improvement of water resistance and dimensional stability of *Populus cathayana*. *Ind. Crop. Prod.* 141: 111747.
- Lligadas, G. and Percec, V. (2007). Synthesis of perfectly bifunctional polyacrylates by single-electron-transfer living radical polymerization. *J. Polym. Sci. A: Polym. Chem.* 45: 4684–4695.
- Maji, P.K., Das, N.K., and Bhowmick, A.K. (2010). Preparation and properties of polyurethane nanocomposites of novel architecture as advanced barrier materials. *Polymer* 51: 1100–1110.
- Meyers, K.P., Decker, J.J., Olson, B.G., Lin, J., Jamieson, A.M., and Nazarenko, S. (2017). Probing the confining effect of clay particles on an amorphous intercalated dendritic polyester. *Polymer* 112: 76–86.
- Montanari, C., Li, Y., Chen, H., Yan, M., and Berglund, L.A. (2019). Transparent wood for thermal energy storage and reversible optical transmittance. *ACS Appl. Mater. Interfaces* 11: 20465–20472.
- Omara, S.S., Rehim, M.H.A., Ghoneim, A., Madkour, S., Thünemann, A.F., Turkey, G., and Schönhals, A. (2015). Structure-property relationships of hyperbranched polymer/kaolinite nanocomposites. *Macromolecules* 48: 6562–6573.
- Osman, A.F., Fitria, T.F.M., Rakibuddin, M., Hashim, F., Johari, S.A.T.T.J., Ananthakrishnan, R., and Ramli, R. (2017). Pre-dispersed organo-montmorillonite (organo-MMT) nanofiller: morphology, cytocompatibility and impact on flexibility, toughness and biostability of biomedical ethyl vinyl acetate (EVA) copolymer. *Mater. Sci. Eng. C* 74: 194–206.
- Tanaka, S., Seki, M., Miki, T., Shigematsu, I., and Kanayama, K. (2016). Solute diffusion into cell walls in solution-impregnated wood under conditioning process II: effect of solution concentration on solute diffusion. *J. Wood Sci.* 62: 146–155.
- Utracki, L.A., Sepehr, M., and Boccaleri, E. (2007). Synthetic, layered nanoparticles for polymeric nanocomposites (PNCs). *Polym. Adv. Technol.* 18: 1–37.
- Wang, J., Zheng, X., Hao, W., Xu, N., and Pan, X. (2012). Synthesis of hyper-branched quaternary ammonium salt and its application into montmorillonite. *Powder Technol.* 221: 80–89.
- Wang, W., Zhu, Y., Cao, J., and Liu, R. (2014). Improvement of dimensional stability of wood by in situ synthesis of organo-montmorillonite: preparation and properties of modified Southern pine wood. *Holzforchung* 68: 29–36.
- Xie, Y., Hill, C.A.S., Xiao, Z., Militz, H., and Mai, C. (2010). Silane coupling agents used for natural fiber/polymer composites: a review. *Compos. Part A* 41: 806–819.
- Xu, J., Cheng, L., Zhang, Z., Zhang, L., Xiong, C., Huang, W., Xie, Y., and Yang, L. (2019a). Highly exfoliated montmorillonite clay reinforced thermoplastic polyurethane elastomer: *in situ* preparation and efficient strengthening. *RSC Adv.* 9: 8184–8196.
- Xu, J., Liu, R., Wu, H., Qiu, H., Yu, Y., Long, L., and Ni, Y. (2019b). A Comparison of the performance of two kinds of waterborne coatings on bamboo and bamboo scrimber. *Coatings* 9: 161.
- Yu, Y., Xu, P., Chen, C., Chang, J., and Li, L. (2018). Formaldehyde emission behavior of plywood with phenol-formaldehyde resin modified by bio-oil under radiant floor heating condition. *Build. Environ.* 144: 565–572.
- Zhang, Y. (2014). *Study on plantation modified by acrylate/silica emulsion and grain manifestation (in Chinese)*. Beijing, China: Chinese Academy of Forestry.