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IMPROVING SOY PROTEIN ADHESIVE WITH ORGANIC MONTMORILLONITE FOR POPLAR PLYWOOD

CUI JUQING,[*,**] HAN SHUGUANG,[*] WANG YAN,[*] ZHANG YANG,[*] DENG YUHE,[*]
ZHOU HANDONG,[*] ZHU SHANGWU[**] and LU XIAONING[*]

[*]*College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China*
[**]*Dare Technology Co., Ltd., Danyang 212300, China*
✉ *Corresponding author: Cui Juqing, cuijq@njfu.edu.cn*

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A new method to improve a soy protein adhesive by incorporating finely dispersed nanoscale silicate layers from organic montmorillonite was investigated. The results of Fourier transform infrared spectroscopy (FTIR) and small angle X-ray diffraction (XRD) indicated that benzyldimethyl dodecylammonium cations had exchanged with the hydrated ions in the galleries of montmorillonite. The shear strength of poplar plywood was enhanced by about 190% in the presence of 1 wt% organic montmorillonite in the soy protein adhesive. The water resistance of the plywood bonded with the soy protein adhesive also increased, along with the shear strength (above 0.7 MPa), after soaking. The reinforcement and physical barrier offered by the nanoscale silicate layers in the soy protein resin are the main reason for the high shear strength and water resistance of the plywood under study.

Keywords: soy protein adhesive, organic montmorillonite, poplar plywood, shear strength, water resistance

INTRODUCTION

Formaldehyde-based adhesives, such as urea-formaldehyde (UF), melamine-formaldehyde (MF), melamine-urea-formaldehyde (MUF) and phenol-formaldehyde (PF) resins, are widely used for production of plywood, medium density fiberboards, and particleboards.[1,2] Because of the emission of formaldehyde during the production and interior use of the panels,[3-5] formaldehyde-based adhesives have been labelled as environmentally unfriendly products. Environmental and health considerations have prompted the introduction of more severe standards to limit formaldehyde emission.[6-7] Besides, the high cost of synthetic resins was another reason that prompted the search for green adhesives derived from renewable resources, *i.e.* soy protein, tannin and lignin adhesives.[8-12] Soy protein has been used as wood adhesive for centuries due to its low cost, renewable and environmentally friendly nature. However, the relatively low mechanical strength and poor water resistance are the main disadvantages of soy protein adhesives.

Two different approaches have been used to improve soy protein adhesives for wood-based panels. The first approach is to add soy protein into formaldehyde-based adhesives to lower the emission of formaldehyde.[13] The second one is through the modification of soy protein with physical, chemical and enzymatic agents by altering the protein molecular structure or conformation at the secondary, tertiary, and quaternary levels.[14-20] At present, the use of soy protein adhesives is still limited to a laboratory level. The modification of soy protein adhesives is still a hot topic of research for achieving large scale application.

In recent years, a tremendous increase in the amount of research on nanocomposites to modify the properties of a polymer matrix has been reported. Polymer layered silicate (PLS) nanocomposites exhibit remarkably improved properties, when compared with conventional composites, due to the addition of just a small fraction of layered silicate.[21-24] The advantages include high mechanical properties, solvent and heat resistance. It is important to note that the dispersion of silicate layers at a nanoscale level in the polymer matrix is essential to this behavior. Thus, the combination of organic silicate in soy protein adhesives will be a promising way to improve the mechanical strength and water resistance of plywood bonded with such adhesives.

To the best of our knowledge, no reports have been published on the modification of soy protein adhesives with OMMT exchanged with benzyldimethyldodecylammonium cations. In this work, we investigated a new method to improve the shear strength and water resistance of soy protein adhesives with OMMT.

EXPERIMENTAL

Materials

Soy protein isolate (Pro-Cote 4610) was obtained from Dupont company, USA. Poplar veneer (400 x 400 x 2 mm) was provided by Xuzhou Zhongyuan Wood Industry Co., Ltd., China. The raw Ca-montmorillonite (MMT) used with a cation exchange capacity (CEC) value of 100 meq/100 g was purchased from Nanjing Feizhuan Montmorillonite Corporation, China. Benzyldimethyldodecylammonium bromide (BDDAB) (5 wt%) was received from Nanchang Baiyun Pharmaceutical Co., Ltd. China.

Montmorillonite (MMT) modified with BDDAB and testing

50 g of montmorillonite was dispersed in 932 ml of distilled water and 68 ml of BDDAB solution. The dispersion was acidified by an appropriate amount of hydrochloric acid to a pH below 5. Then, the resultant suspension was vigorously stirred for 6 h at 80 °C. The BDDAB treated montmorillonites were repeatedly washed by distilled water until no AgBr precipitate occurred at room temperature when the filtrates were titrated with 0.1 N $AgNO_3$. The filtered cakes were then dried at 80 °C for 12 h. The dried cakes were ground to obtain organic montmorillonites (OMMT). FTIR analysis of the pristine MMT and OMMT was conducted on a VECTOR 22 IR analyzer. X-ray diffraction (XRD) analysis was performed on the powder samples with a Scintag X-ray diffractometer operating in the theta-theta geometry, using Cu Kα radiation ($\lambda = 1.5406$ Å). The 2 theta diffraction diagrams were determined between 2 and 10 degrees.

Three-layer poplar plywood preparation and testing

100 grams of SPI was suspended in 300 mL deionized water and stirred for uniform dispersion. The suspension was then adjusted to a pH of 10.0 using 30 wt% NaOH, and different contents of OMMT were added for 6 hours at room temperature. Poplar veneer was dried in an oven at 105 °C for 1 hour. The spread rate of the adhesive was of about 125 g/m^2 for each surface of the three-layer plywood. The adhesive-coated veneer was stacked with the grain directions of two adjacent veneers perpendicular to each other. The stacked veneers were put on a table at ambient environment for 5 min, and hot-pressed at pressure, temperature and time of 1.0 MPa, 120 °C and 1.25 mm/min, respectively.

Shear strengths were determined by using a Shenzhen SANS versatile materials test machine operated at a crosshead speed of 2.4 cm/min. The force required to break the glued wood specimen was recorded. All the adhesive strength data reported are means of three replications.

The water resistance of the adhesive layer was tested as follows: the glued-wood plywood samples were placed in a container and soaked in tap water for 2 h at 30 °C, and then were dried at 63 °C for 1 h in a fume hood. Three samples were used for each treatment. After soaking and drying, the dried-wood specimens were examined for delamination and shear strength.

RESULTS AND DISCUSSION

FTIR of MMT and OMMT

In the present work, BDDAB was applied to treat montmorillonite because it is not only an alkylammonium cationic surfactant with long chain, but also a mild disinfectant, most effective against bacteria in migrule form and lipophilic virus. To demonstrate the effect of BDDAB in the modification of MMT, the FTIR spectra of MMT and OMMT are shown in Figure 1. In the spectra, the peaks at 2927 cm^{-1} and 2855 cm^{-1} could be attributed to the absorbance of methylene asymmetric and symmetric stretching vibrations, the absorbance at 1474 cm^{-1} belongs to methylene bending vibration, which means that BDDAB was successfully tethered to montmorillonite.

X-ray diffraction (XRD) pattern of MMT and OMMT

For detecting the interlayer heights before and after the treatment, the small angle XRD spectra of the pristine MMT and OMMT are depicted in Figure 2. The *d*-spacings of the MMT before and after the treatment were calculated using Bragg's relation from the (001) peak. $2d\sin\theta = \lambda$, where λ is the wavelength of the X-ray radiation used in the diffraction experiment, d is the spacing between diffractional lattice planes, and θ is the measured half diffraction angle or glancing angle. It indicated that the d_{001} increased from the value of 1.39 nm for pristine MMT to 1.54 nm for OMMT. It means that the exchange of hydrated ions with organic quaternary ammonium cations, which expands the interlayer space, has happened.

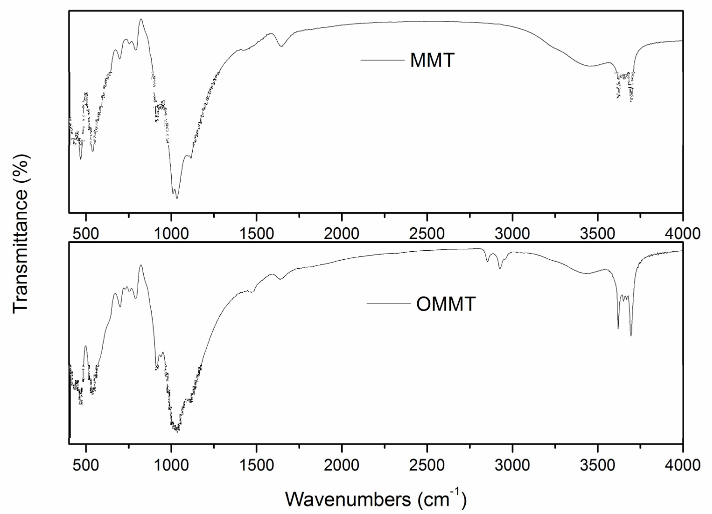

Figure 1: FTIR of MMT and OMMT modified with BDDAB

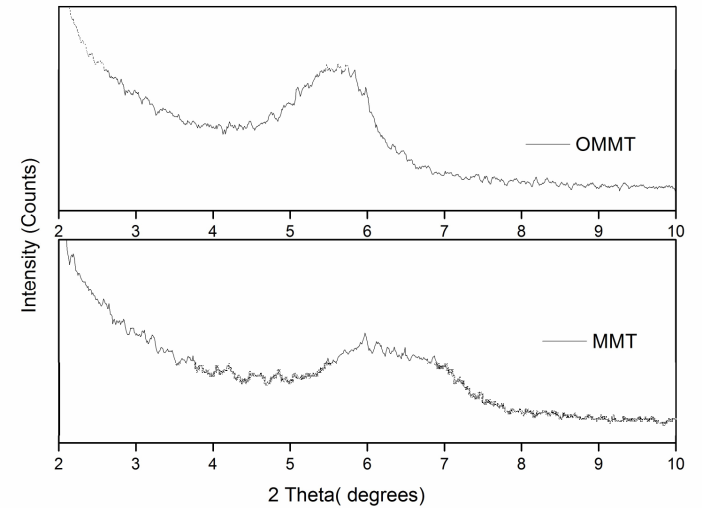

Figure 2: X-ray diffraction pattern of MMT and OMMT modified with BDDAB

Shear strength of poplar plywood bonded with soy protein adhesives

Soy protein polymers have recently been considered as alternatives to petroleum polymers to ease environmental pollution. The use of soy proteins as adhesives for plywood has been limited because of their low mechanical strength. The shear strengths of poplar plywood bonded with soy protein adhesive in the presence of OMMT are shown in Figure 3. Compared with the control, the soy protein adhesive modified with OMMT for poplar plywood showed higher shear strength. The adhesive strengths of soy protein progressively increased from 0.61 to 0.75 and 1.17 MPa with the addition of OMMT below 1%. The highest shear strength was higher by nearly 190% than that of the control. However, more OMMT (above 3 wt% and 5 wt%) in soy protein adhesives did not result in significantly higher strengths. The possible reason may result from the aggregation of a nanoscale silicate layer in the matrix. Therefore, the optimum content of OMMT in the soy protein adhesive is 1 wt%.

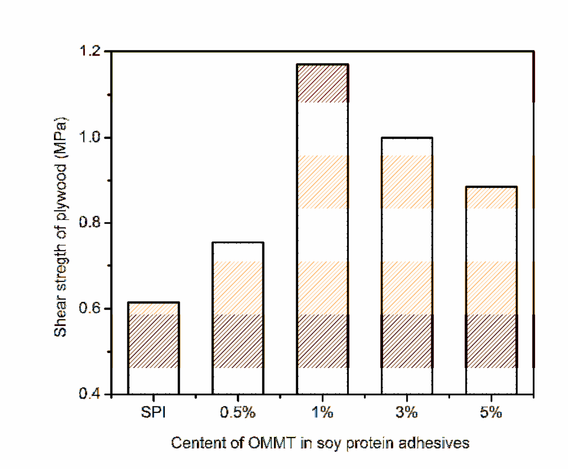

Figure 3: Shear strength of poplar plywood bonded with soy protein adhesive in the absence and presence of OMMT

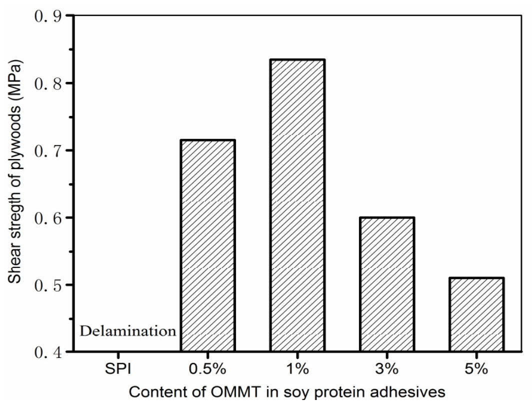

Figure 4: Shear strength of poplar plywood bonded with soy protein adhesive in the absence and presence of OMMT after water soaking tests

Water-resistance of poplar plywood bonded with soy protein adhesive

Water resistance is an important property for natural adhesives. Figure 4 illustrates the water resistance of poplar plywood bonded with soy protein adhesive in the absence and presence of OMMT. The overall shear strength was reduced significantly, but showed the same trend as that of the unsoaked samples. This indicates that, with the addition of OMMT, soy protein adhesives offer improved water resistance to plywood. No delamination was observed for the plywood bonded with OMMT soy protein adhesives after the water soaking tests. Compared to the control, the plywood bonded with OMMT soy protein adhesives also exhibited higher shear strengths after water soaking and drying. The shear strength of plywood was also above 0.7 MPa after water soaking in the presence of 1% OMMT in the soy protein adhesives. It is easy to relate the water resistance of the soy protein adhesive to the barrier property of the silicate layer in the matrix.

Mechanism of soy protein adhesive modified with organic montmorillonite

MMT belongs to the general family of 2:1 layered silicates. Their crystalline structure consists of layers of two silica tetrahedral sheets fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Stacking of the layers leads to a regular van der Waals gap or interlayer. Isomorphic substitution within the layers generates negative charges that are counter balanced by cations, usually Na^+ or Ca^{2+} ions, residing in the interlayers. Organophilic MMT facilitates the exfoliation of layered silicate in the polymer matrix. Because of their nanometer-size dispersion, polymer nanocomposites with layered silicate exhibit markedly improved properties, including high modulus and strength, low gas permeability, solvent and heat resistance, when compared with the pure polymers or conventional composites.

Hence, it is easy to understand the higher shear strength and water resistance of poplar plywood bonded with soy protein adhesives including OMMT. With the addition of a low amount of OMMT (0.5 wt% and 1 wt%), the reinforcement of the soy protein matrix increased with the content of OMMT. The decline of shear strength could be attributed to the aggregation of the silicate layer in the polymer matrix. For example, the dramatic lowering of permeability in the nanocomposites is due to the presence of dispersed large aspect ratio silicate layers in the polymer matrix, as reported for other polymer-layered silicate composites.[25-26] The variation of the water resistance of poplar plywood could also result from the presence of silicate layers, which prevent the interaction of the water molecule with the soy protein matrix. It forces water crossing the adhesion layer to follow a tortuous path through the soy protein matrix surrounding the silicate particles, thereby increasing the effective path length for water diffusion.

CONCLUSION

It is obvious that the shear strength and water resistance of plywood bonded with soy protein adhesives were largely improved with the addition of OMMT at a maximum loading of 1.0 wt%. The overall shear strength decreased after the water soaking test, but it demonstrated the same trend as that of the dry shear strength. The reinforcement and physical barrier offered by the nanoscale silicate layers in the soy protein resin are the main reasons for the high shear strength and water resistance of the plywood. Boiling water resistance will be considered for further research on adhesives including OMMT.

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