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Mechanical and Thermal Properties of Waterborne Polyurethane Coating Modified through One-Step Cellulose Nanocrystals/Graphene Materials Sols Method

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Abstract: Developing multifunctional coatings with excellent mechanical and thermal properties is highly desirable for wood-based composite application. The recent development of waterborne coatings for wood products suggests that a promising thermosetting material needs to also have properties like low volatile organic contents (VOCs), hardness, and fast curing. The cellulose nanocrystals/graphene materials (CNC/GM) sols were prepared through the one-step method as the thermally conductive and reinforced modifier for preparing waterborne polyurethane (WPU) coatings. The influence of this modifier on the thermal and mechanical properties such as thermal conductivity, abrasion resistance, and adhesion of WPU coatings was investigated. The results indicated that adding CNC/GM sols increased the hardness, abrasion resistance, and thermal conductivity of the WPU coatings, and meanwhile maintained the coating adhesion at the highest grade (level 1). The highest abrasion resistance value of 0.023 g/100 r was obtained for the modified WPU coating when the addition of GM was 3%.

Keywords: waterborne polyurethane coating; cellulose nanocrystals; graphene materials; property

1. Introduction

Waterborne coatings recently have been increasingly used in the worldwide wood industry because of low health and environmental impact [1,2]. These environmentally friendly coatings have low or no emissions of volatile organic contents (VOCs) and good mechanical properties and durability [3,4]. Currently inorganic nano-additives (fillers) such as Al_2O_3 [5,6], SiO_2 [7,8], TiO_2 [9], ZnO [10,11], CaCO_3 [12], Cr_2O_3 [13,14], etc. are used to improve the durability and functionality of waterborne coatings. However, these inorganic nano-fillers encounter the dispersion issues in waterborne coatings of organic polymer matrixes, like incomplete dispersion of nanoparticles in the polymer matrix and poor adhesion between cured coatings and wood substrates [7,8]. Directly incorporating organic nanoparticle materials into aqueous media is one of the most promising strategies [15]. Cellulose nanocrystals (CNCs) have received tremendous attention in sustainable biomaterial-based society [16–18] because of their remarkable physical and chemical properties.



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CNCs, a new renewable nontoxic nanoscale materials isolated from native cellulose sources like wood [19,20], bamboo [21–24], cotton [25,26], hemp [27], bacteria [28], green algae [29], tobacco stalk [30], etc. have excellent properties such as a high specific surface area of 300 m²/g, a Young's modulus of 150 GPa, and a tensile strength of 10 GPa [31]. CNCs are proven to be an excellent mechanical reinforcement filler when mixed with aqueous polymer matrixes. Pei et al. [32] prepared a nanocomposite film of poly(L-lactide) (PLLA) reinforced with CNCs or silylated cellulose nanocrystals (SCNC) using the solution casting method. Rao et al. [33] investigated the rheological behavior of composite polymer-CNC gels in dimethylformamide because the behavior of CNC-polymer gels in organic solvents can affect the processable ability of the polymer mixture. Kargarzadeh et al. [34] reviewed the studies related to CNC- and cellulose nanofibril (CNF)-reinforced rubbers or thermoset polymers, including preparation methods, morphology, mechanical behavior, thermal properties, and barrier action.

Current waterborne coatings used in wood products started its application mainly in building industries [1,5]. The limitation of waterborne coatings in wood products is mainly because of their poor water resistance, hardness, wear resistance, and stability in some applications [35]. For fibrous wooden materials, conduction, convection, and radiation are the three main routes to processing heat transfer, among which the most significant way is conduction [12,24]. Therefore, their thermal conductivity needs to be improved if used in heating floor applications [2,8]. In the previous literature, various conductive materials, such as iron [35], steel, copper [36], and carbon materials [37,38], have been utilized to coat heating composite materials for making energy-saving wooden products. Among these modified materials, graphene (Gr) has emerged as a revolutionary functional material because of its superior thermal conductivity property (above 3000 W·m·K⁻¹) [33]. Tang et al. [39] observed that adding graphene materials into epoxy resin increased the resin thermal conductivity enhancement factor up to 1900% with a significantly improved stability at a high temperature. However, the large specific surface area of graphene-based carbon nanomaterials tends to agglomerate together when dispersed into other materials as property enhancement agents, thereby causing lower performance of these nanomaterials as property-enhancement agents. Carrasco et al. [40] reported that CNCs as stabilizer are very efficient for graphite exfoliation through tip sonication and stabilization, resulting in graphene flakes dispersed in aqueous media at a high concentration up to 1 mg/mL.

In our previous study, impregnating graphene materials/phenol-formaldehyde resin into wood floor products was successfully completed [41,42]. This work investigated the influence of CNC/GM sols as a modifier on the thermal and mechanical properties such as thermal conductivity, abrasion resistance, and adhesion of WPU coatings.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC) powder was provided by Shanghai Jinsui Biological Inc. (Changzhou, China). The multilayer graphene-based carbon nano-materials were provided by the Department of Sustainable Bioproducts, Mississippi State University (Starkville, MS, USA), which had an average particle size of 842 nm and an average dispersion degree of 0.451 [37]. Sulfuric acid (analytical reagent, mass fraction 98%) was provided by Nanjing Chemical Reagents Co. (Nanjing, China). Basswood (*Tilia*) pieces measured by 100 mm long × 100 mm wide × 10 mm thick were obtained from Dehua New Material Co., Ltd., Weifang, China. These wood samples had three groups in terms of their length directions, longitudinal, tangential, and radial. Two-component waterborne polyurethane coating (2K-WPU) was supplied by the Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry (CAF, Beijing, China). The ratio of hardener to resin of the 2K-WPU was 3.5:10 [43]. Deionized-distilled water (DDW) was used exclusively.

The three mixtures of microcrystalline cellulose (MCC) powder and graphene materials (GM) (Table 1) were hydrolyzed first by sulfuric acid (analytical reagent, mass fraction 64%) in water baths at 45 °C for 1 h. The supernatant, produced by centrifuging the acid-treated solution at 4000 r/min for 5 min, was replaced with distilled water. The mixed solution was then centrifuged again. The process was repeated until a white emulsion solution was obtained after 5–6 circulations. The white emulsion solution was dialyzed under flowing water for 3 days until pH 6 value was reached, and then the dialyzed solution was sonicated for 20 min; the black thick CNC/GM sols were finally obtained.

Table 1. Weight ratios of microcrystalline cellulose (MCC) and graphene materials (GM) for making cellulose nanocrystals (CNC)/GM sol mixtures through one-step method.

H_2SO_4 (g)	MCC (g)	GM (g)
98	10	0.1
98	10	0.2
98	10	0.3

2.3. Preparation of CNC/GM/2K-WPU Coating Samples

The modified 2K-WPU coating using CNC/GM sol, CNC/GM/2K-WPU, was prepared through magnetic stirring the mixture of 2K-WPU coating and CNC/GM sol at 25 °C for 20 min. The weight ratio of 2K-WPU coating to CNC/GM sol was 100:3. For conductive property test, the modified coatings were coated onto tin plates (120 mm long \times 50 mm wide \times 2 mm thick) using a paint film fabricator, followed by drying the coated tin plates under controlled conditions (25 °C and 50% of relative humidity) for one week according to GB/T1727-1992 [44]. The control samples without CNC/GM sols coated were also prepared. For adhesion, hardness, and abrasion resistance properties tests, the control and modified coatings were applied on the Basswood surface along the tangential direction. After coating, samples were put in an oven for 20 min at 60 °C and then air-dried in a fume hood for 7 days. The targeted coating thickness was 60 μ m.

2.4. Characterizations

2.4.1. CNC/GM Sols

The absorbance values of CNC/GM sol mixture were measured on a Lambda 950 ultraviolet spectrophotometer (PE Co., Melville, NY, USA). The wavelength scanning range of absorbance was 200–800 nm. The FT-IR spectra were recorded on a VERTEX 80V spectrometer (Bruker, Berlin, Germany) over the scan range of 400–4000 cm⁻¹. The dried CNC/GM sol mixtures (1 part in weight) were mixed to potassium bromide (KBr) (100 parts in weight). The transmission mode was selected. The Raman spectra were collected from 50 to 3300 cm⁻¹ using an NRS 300 laser Raman spectrometer (Themor DXR532, Waltham, MA, USA) with an excitation wavelength of 532 and 780 nm at room temperature. The X-ray diffraction (XRD) was performed using Cu k α radiation source (step size 0.02°, scanning speed 5°/min, voltage 40 kV, current 100 mA) in an Ultima IV XRD instrument (Rigaku, Tokyo, Japan). The morphology and structure of the CNC/GM sol mixtures were characterized by transmission electron microscopes (TEM, Hitachi JEM-140, Tokyo, Japan).

2.4.2. CNC/GM/2K-WPU Coating

The hardness of the coated wood samples was determined with the pencil hardness according to the GB/T 6739-2006 standard [45], and abrasion resistance and adhesion tests were measured in accordance with the GB/T1768-2006 and GB/T4893.4-1985 standards [46,47], respectively. The thermostability was determined with a TG209F3 thermogravimetric analyzer (Netzsch, Germany) with the heat ramping temperature set from 25 to 800 °C at 40 mL/min under nitrogen atmosphere.

A heat conduction coefficient tester (ISOMET 2104, Shanghai, China) was employed to record heating temperatures according to GB/T 11048-2018 standard [48]. An improved test method is used here. A standard sample and a test sample are placed in the middle of two heating plates with a constant temperature gradient to measure and obtain the thermal conductivity of the target material [49]. The thermal conductivity (λ) was calculated by using the following formula; the measurement accuracy to 0.001.

$$\lambda = mc \frac{\Delta T}{\Delta t} \Big|_{T=T_2} \cdot \frac{h}{T_1 - T_2} \cdot \frac{1}{\pi R^2}$$
(1)

where λ is the thermal coefficient (W/m·k), *m* is the quality of copper cooling plate (kg), *c* is the specific heat capacity of copper cooling plate, 385 J/(kg·K), $\frac{\Delta T}{\Delta t}|_{T=T_2}$ is the heat dissipation rate of copper cooling plate at T_2 (mV/s), *h* is the thickness of tested sample (m), $T_1 - T_2$ is the temperature difference between upper and lower sample surfaces (K), and πR^2 is the area of copper cooling plate (m²).

3. Results and Discussion

3.1. Properties of CNC/GM Sols

3.1.1. Absorbance Analysis

According to Lambert Beer's law, the absorbance at 660 nm of CNC/GM sols was taken for comparison and analysis. Figure 1 indicates that increasing the amount of GM from 1% to 2% can increase the absorbance value of GM dispersion, but continuing the increase of GM to 3% could decrease the absorbance value. These indicate that the dispersion of GM had its optimum dispersion when 2% GM was added. Adding 1% of GM can weaken its dispersion stability.



Figure 1. Absorbance of CNC/GM sol mixture at 660 nm.

3.1.2. FT-IR Spectra Analysis

The infrared spectrum of CNC/GM sol mixtures (Figure 2) indicates that there was a broad and strong absorption peak near 3432 cm⁻¹, which belongs to the stretching vibration peak of –OH [50]. There was an obvious C–O stretching vibration peak at 1720 cm⁻¹ and an obvious C–OH stretching vibration peak at 1380 cm⁻¹. There was a C–H tensile vibration peak near 2903 cm⁻¹. The C–O stretching vibration peak at 1052 cm⁻¹ was also relatively strong, indicating the presence of GM in the dispersion [51,52]. However, the FT-IR spectra alone will not be able to tell whether or not the GM could be successfully grafted to the surface of CNC to form chemical bonds.



Figure 2. FT-IR spectra of CNC/GM sol mixtures containing 2 wt % of GM.

3.1.3. Raman Spectrum Analysis

The Raman spectrum of graphene is composed of many characteristic peaks, such as G peak, D peak, G' peak, etc. G peak appearing near 1580 cm⁻¹ is the main characteristic of graphene materials, which can effectively reflect the number of layers of graphene but be affected by stress [53]. D peak near 1350 cm⁻¹ is the disordered vibration peak of GM. G' peak near 2700 cm⁻¹, also known as 2D peak, is used to characterize the inter-layer stacking mode of carbon atoms in GM [54]. Figure 3 indicates that G, D, and G' peak signals observed in the CNC/GM sol mixtures were all stronger, indicating that the graphene flakes were evenly dispersed in CNC sols. The I_D/I_G ratios were 0.853 and 1.001 for GM and CNC/GM sol mixtures, respectively. The value of I_D/I_G ratios increased from 0.853 to 1.001, and the peak strength was significantly increased, and 2D peak occurred at 2700 cm⁻¹ in the Raman spectrum of the CNC/GM sol mixtures, which was caused by coupling between graphene sheets. These experimental results indicated that the graphene materials were deposited on the surface of cellulose nanocrystals, implying a good dispersion of graphene materials in the CNC sols.



Figure 3. Raman spectrum of graphene materials and CNC/GM sol mixtures containing 2 wt % of GM.

3.1.4. XRD Analysis

The XRD pattern of CNC/GM sol mixtures (Figure 4) indicates that a very sharp diffraction peak appears near 22° that is close to the diffraction peak of graphene materials, indicating the presence of graphene materials in CNC/GM sol mixtures [55]. There is also a wide diffraction peak near 15°, indicating that GM was successfully mixed with CNC sols and the CNC sol was evenly dispersed.



Figure 4. XRD of graphene materials and CNC/GM sol mixtures containing 2 wt % of GM.

3.1.5. TEM Analysis

The TEM images of CNC/GM sol mixtures (Figure 5) show that graphene materials could be evenly dispersed in CNC sols through depositing in the network of CNC structures.



Figure 5. TEM images of GM and CNC/GM sol mixtures containing 2 wt % of GM.

3.2. Mechanical Properties of CNC/GM/2K-WPU Coatings

3.2.1. Adhesion and Hardness

Adhesion and hardness were important properties of coatings, which were related to the durability and long-term performance [56]. In particular, it was required that the addition of CNC or GM did not worsen the adhesion characteristics of coatings for the actual using reason. Any particle or nanoparticle added to the coating would be expected to impact these properties and the system should behave as a true composite [57]. This experiment revealed that the adhesion strength of coatings with or without the addition of CNC/GM being practically at the same high level. Figure 6 indicates that the adhesion strengths of all coated samples being in the level 1, and the hardness of coatings with and without CNC/GM modifier added all meet the critical values outlined in standards, respectively. The higher GM loading yielded a harder coating (6H) than the control one (5H). This test revealed no significant difference of hardness between coatings with different GM additions, which was because GM was simply dispersed but not covalently bonded to or within the continuous phase, resulting in no increase of hardness [58].



Figure 6. Adhesion and hardness values of CNC/GM/ two-component waterborne polyurethane coatings (2K-WPU).

3.2.2. Abrasion Resistances

The coatings can be cured to a hard finish and are known for their outstanding wear properties. It is important that an additive (modifier) does not worsen the wear characteristics of coating [59]. Figure 7 shows that CNC/GM modified coatings had significantly lower abrasion loss than the control one. Specifically, the addition of GM improved the mechanical resistance of coatings to 540%, 1180%, and 1500% if compared to the control one for GM loading 1%, 2%, and 3%, respectively. This improvement in abrasion resistance could be mainly because of the super-stiffness of graphene and CNC/GM higher dispersion state in modified coatings [58,60]. Adding CNC/GM and their proper dispersion within the coatings introduced the right hydrophobic/hydrophilic balance, creating suitable interfaces between the filler and matrix [54]. In addition, CNCs' intrinsic features, like high aspect ratio and Young's modulus, could also result in coating strengthening [61,62]. Furthermore, the geometrical characteristics of CNC and GM system might reinforce the binder matrix(coating) that is similar to the frameworks in the modern reinforced concrete-steel buildings at the nano-level [58].



Figure 7. Abrasion resistance of coatings as a function of GM loading.

3.3. Thermal Properties of CNC/GM/2K-WPU Coatings

3.3.1. Thermal Stability

The TG curves of the 2K-WPU and CNC/GM/2K-WPU coatings (Figure 8) indicate that the decomposition temperatures (T_d) of 2K-WPU coatings at 10%, 50%, and 80% mass losses were 51, 322, and 453 °C, respectively. The decomposition temperatures of CNC/GM/2K-WPU coatings at 10%, 50%, and 80% mass losses were 251, 322, and 681 °C, respectively. The results showed that the

CNC/GM/2K-WPU coatings had better thermal properties than 2K-WPU coatings, indicating that the addition of graphene materials could further improve the thermal resistance property of 2K-WPU coatings. This is because graphene materials have their initial decomposition temperature over 2800 °C under vacuum [63,64]. Meanwhile, the reaction between oxygen-containing functional groups such as hydroxyl in the composite system can improve thermal stability [60]. When the decomposition temperature increased from 300 to 430 °C, the mass losses values of CNC/GM/2K-WPU coatings were higher than the ones of 2K-WPU coatings, indicating that partial modifiers (CNCs) in coatings had begun to degrade. Particularly, the initial decomposition temperatures (T_d) of CNCs are about 360–600 °C [65].



Figure 8. Curves of 2K-WPU and CNC/GM/2K-WPU coatings containing 2 wt % of GM.

3.3.2. Thermal Conductivity

Figure 9 shows that the thermal conductivities of CNC/GM/2K-WPU coated samples ranged from 1.33 to 1.39 W/m·K, specifically, the maximum thermal conductivity of CNC/GM/2K-WPU coated samples was 4.5% higher than 2K-WPU coated ones, indicating better conductive behavior than 2K-WPU coated ones. The coated samples gained a thermal conductive functional ability because of the addition of GM in the coatings [66]. The statistical analysis indicated that there was no significant difference among GM loadings of coated wood samples. The lamellar structure of graphene materials can be maintained by van der Waals or restoration π - π stacking between adjacent Gr layers [67] if graphene materials were dispersed in CNC suspension uniformly. In addition, the addition of GM id not significantly improve the thermal conductivity, which may be due to the fact that GM is a multilayer material and the thermal conductivity improvement effect is limited compared with single-layer graphene [37,66].



Figure 9. Thermal conductivity of CNC/GM coated wood samples as a function of GM loading.

4. Conclusions

A one-step preparation process of CNC/GM sol mixtures as a modifier for the improvement of waterborne coating properties was proposed, performed, and evaluated. Experimental results showed that the thermal conductivity of the waterborne coating evaluated in this study can be improved up to its highest of 1.39 W/m·K when a 2% loading of graphene materials evaluated in this study was added. Moreover, the pencil hardness and abrasion resistance of CNC/GM sol modified waterborne coatings were also improved significantly. The abrasion resistance of modified coatings can reach 0.0213 g that was up to 59.2% if compared to unmodified ones. The pencil hardness was increased from 5H to 6H and adhesion did not change significantly. It is believed that the findings of this study can provide data support for the research and development of wooden heating products and promote their products with better energy-saving features.

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