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Synergic flame-retardant effect of nano-cellulose crystalline and Magnesium hydroxide in polyurethane wood coating

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Abstract

In this paper, a wood coating based on waterborne polyurethane (WPU)/nano-cellulose crystalline (NCC)/Magnesium hydroxide (MH) was prepared. Efficient dispersion of MH in WPU in presence of 5wt% of NCCs was observed by biological microscope leading to a material with improved esthetic, thermal and fire retardancy properties. By thermogravimetric analysis (TG/DTG) and in comparison with WPU, the maximum weight loss rate (RTmax) of WPU/NCC/MH coating decreased dramatically from 13.2 to 6.63, and the residue increased sharply from 4.69% to 40.55%. The results of pyrolysis combustion flow calorimeter (PCFC) showed that the flame-retardant performance of the composite coating is also greatly improved,

and the peak of heat rate release (pHRR) being reduced from 350 w/g to 121 w/g. When applied to the wood panels, according to the Limiting oxygen index (LOI) experiment, for MH < 40 wt%, the combustibility grade is B2 level (combustible material), whereas for MH > 40wt% the grade is B1 level (flame retardant material).

Keywords: Nano cellulose crystalline, Waterborne polyurethane, Flame retardancy, Thermal stability

1.Introduction

Wood is a natural material with excellent properties. It has been widely used in many fields throughout history, including construction, consumer products, furniture, etc. (Frey et al., 2018; Zhu et al., 2016). However, wood material has important limitations such as biological degradation and flammability which limit its broad utilization (Harada, Matsunaga, Kataoka, Kiguchi, & Matsumura, 2009; Laura Anne Lowden, 2013; T. S. Wang et al., 2018). According to historical records, many ancient wooden buildings in China have been damaged by fires (Huang et al., 2009). Therefore, the use of flame retardant is important for the development of wood products. In general, wood must be treated before use and surface coating is the most common method for wood protection. (Bar, Alagirusamy, & Das, 2015; Holder, Smith, & Grunlan, 2017; Marney & Russell, 2007). Waterborne polyurethane (WPU) is a commonly used coating for wood protection and decoration and much work has been

done to improve its thermal, mechanical and self-healing properties (Chang et al., 2015). In order to improve the WPU flame-retardant properties, a variety of flame retardants have been used such as aluminium hydroxide $[\text{Al}(\text{OH})_3]$, magnesium hydroxide $[\text{Mg}(\text{OH})_2]$. In fact, adding inorganic materials to polymers is an effective method to improve thermal stability. These metal oxide have been widely studied because of their non-toxic, pollution-free and other characteristics (Khalili et al., 2019; Naguib, 2018). Besides, ammonium polyphosphate $[\text{NH}_4\text{PO}_3]$ boron salts, inorganic compounds like antimony, tin, zinc etc. are examples of inorganic flame retardants which are being significantly used for coating purpose (Khalili et al., 2019). Compared with other toxic materials, MH presents a lot of positive features such as environmental friendliness, low cost and thermal stability. (Naguib, 2018). It can effectively reduce the heat release, delay the ignition time, cool the combustion area, and be able to reduce the degree of loss caused by fire weightlessness. MH has been used in a variety of polymer matrices as flame retardants such as PE, PEt, PEtT, PP, epoxy and other composites (Holder et al., 2017; Luo, Yang, Lei, Zhao, & Tong, 2017; P.-J. Wang et al., 2019). In current commercial applications, in order to achieve a good flame-retardant effect, the proportion of MH added is usually relatively high. These conditions lead to an accumulation of MH, causing a non-uniform dispersion in the resin and ultimately affecting their properties.

NCCs, also known as nanowhiskers, exhibit elongated crystalline rod-like shapes, and have high rigidity (Thomas et al., 2018). Due to their excellent performance, NCCs have been attractively considered for a template of NCC-inorganic composite

materials (Zhao, Ding, Pan, & Zhai, 2018). Moreover, NCCs and NCC/inorganic compounds have been introduced to enhance waterborne coatings due to their unique reinforcement. El-Fattah et al.(2018) studied NCC/waterborne PU coating and pointed an optimum mechanical property for 1.5 wt % NCC. Arantzazu et al.(2016) reported that the thermal stability of WPU matrix was improved with the increase of CNC weight content in the bionanocomposites. However, NCC can not only improve the mechanical and thermal properties of polymers, but also act as a dispersant. Scholars had confirmed that NCC can also be effectively and evenly dispersed in WPU/nano-silver composites (Cheng, Ren, & Lu, 2020). In this paper, flame retardant composites based on WPU and MH have been produced, including the addition of NCC to improve the dispersion of MH. The final goal is to produce a simple, green and low-cost flame retardant coating for wood material.

2.Experimental

The larch panels were purchased on the market, Waterborne Polyurethane Transparent wood primer was supplied by CARPOLY Chemical Group Co., Ltd., nano-cellulose crystalline (2%) was acquired in Guilin Qihong Technology Co., Ltd., Magnesium Hydroxide ($Mg(OH)_2$)was afforded by Nanjing Chemical Reagent Co., Ltd., distilled water was homemade.

Characterization

The image of MH particles in WPU colloid with or without NCC was observed with biological microscope (E100, Nikon).

Thermogravimetric analysis

The thermal stability of the materials was evaluated using a Q500 thermogravimetric analyzer (TGA; TA Instruments, USA). Typically, 3 mg of the sample was taken in an alumina crucible and heated from room temperature to 700 °C at the rate of 20 °C/min under a continuous flow of N₂.

Pyrolysis combustion flow calorimetry (PCFC)

A pyrolysis combustion flow calorimeter (Fire Testing Technology) was used to investigate the fire behavior of samples at microscale (2–4 mg). Samples were pyrolyzed at 1°C/s under nitrogen flow from 90 to 750°C (anaerobic pyrolysis – method A according to the standard ASTM D7309). Pyrolysis gases were carried to a combustor in the presence of N₂/O₂ (80/20) flow. In such conditions, all gases are fully oxidized. Heat Rate Release (HRR) is calculated according to Huggett's relation (Hajj et al., 2018). According to this relation, 1 kg of consumed oxygen corresponds to 13.1 MJ of heat release. Each test was performed twice to ensure the reproducibility of our measurements. The peak of heat rate release (pHRR), the temperature at pHRR (TpHRR), the total heat release (THR), and the heat of combustion (Δh) were determined.

Limiting oxygen index (LOI) test

Limiting oxygen index (LOI) values were determined using a JF-3 oxygen index meter (Jiangning Analysis Instrument Factory, China) according to ISO 4589.

Preparation of flame retardant composite coatings

Preparation of WPU/ NCC/MH composites

NCC (1.0wt% of the solid content of WPU) was added to the distilled water (the mass of which was 20.0wt% of WPU), and the NCC colloid was obtained by using the high-speed shear mixer at the speed of 10000 rpm for 10 minutes. After that, this colloid was added to WPU, stirring the mixture with an electric agitator at a speed of 200rpm for 10 minutes. Then ultrasonic homogenization processor was under the condition of 100-200W, vibrating 4 seconds and interval for 4 seconds circularly, dispersed 20 minutes continuously, to get the WPU/NCC colloid. Afterwards, different mass percentages (percentage of mass of MH and WPU) of MH was added to the WPU/NCC colloid, which was 0.0wt%, 20.0wt%, 30.0wt%, 40.0wt%, 50.0wt%, 60.0wt% respectively. The WPU/NCC/MH composites was obtained at last by stirring with the electric mixer at the speed of 200rpm for 10 minutes.

Preparation of WPU/MH composites

MH (the mass of which was 40.0wt% of WPU) and distilled water (the mass of which was 20.0wt% of WPU) were added to the WPU without modification. The WPU/MH composites was obtained after stirring 10 minutes continuously at the speed of 200rpm. This composite was compared with the WPU/NCC/MH composites with 40.0wt% adding amount of MH.

Preparation of flame retardant panel

The larch specimens were machined into a dimension of 1000.0mmx100.0mmx4.0mm, and sanding the surface. According to the Chinese national standard of the general preparation method of lacquer film, the wood surface was sprayed with

the coating amount of 180g/m^2 . The weight of the unpainted larch specimen was weighed first, and then the weight of the WPU/NCC/MH composites sprayed evenly on the surface of the larch specimen was then recorded. The differential weight value between them must be controlled in a range from 17.90 grams to 18.10 grams. The specimen was then flattened into the drying oven for curing, which was removed after 96 hours. Three sets of specimens were prepared according to the above procedures, the adding amount of MH in each group was from 0.0wt% to 60.0wt%. Meanwhile, three sets of specimens coated with WPU/MH composites was prepared too.

3. Results and discussion

A preliminary study was performed to examine the dispersion of MH in WPU by biological microscopy. WPU films containing different MH contents (20%-60%) were prepared with or without NCC (5%w/w). In the presence of NCC (Fig. 1 a-e), it can be seen that MH is well dispersed in WPU (WPU in white and MH in black). Without NCC (Figure 1f), important aggregation phenomena are clearly observed. Based on literature date, this result can be explained by the interaction of MH with active hydrophilic hydroxyl groups on the surface of NCC leading to a physical adsorption them on the surface of nanoparticle (Zhang, Zhang, Wu, & Xiao, 2020).

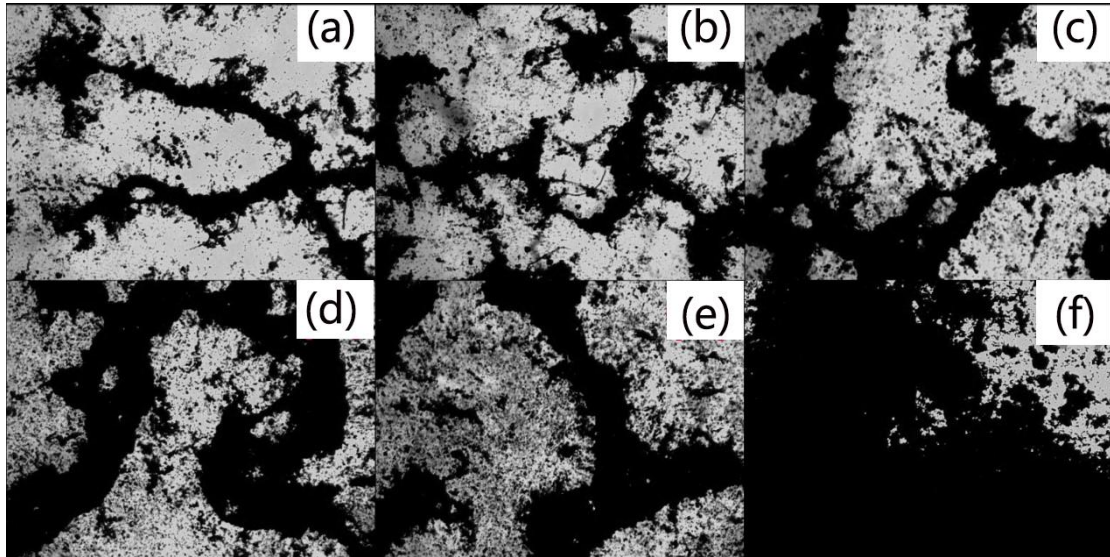


Figure.1. Biological microscope images(600X) of composites films with different MH contents(a)20.0wt%, (b)30.0wt%, (c) 40.0wt%, (d) 50.0wt%, (e) 60.0wt%, (f) 40.0wt% without NCC.

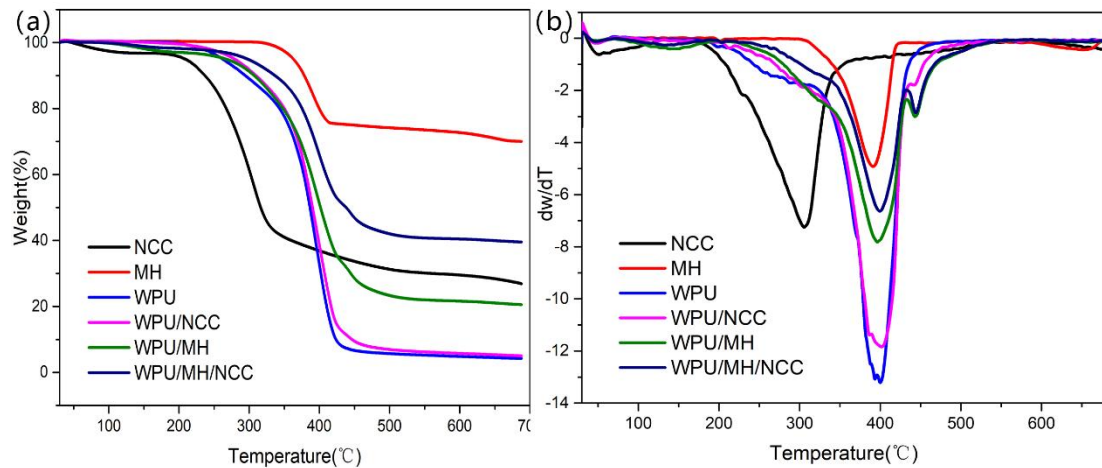


Figure 2 Thermogravimetric analysis: (a) mass (TG) and (b) mass loss rate (DTG) versus temperature curves of NCC, MH, WPU and their composites

The TGA thermograms and DTG curves of WPU, NCC, MH, WPU/NCC, WPU/MH and WPU/NCC/MH are shown in Figure 2. The TGA curves showed the weight loss pattern and DTG curves the maximum decomposition temperature for each thermal degradation step. The main data for each sample are gathered in Table 1.

The Fig 2 and table 1 show that the addition of NCC in PU led to a slight change of the TGA profile and a small increase of the residue at 600°C from 4.69% to 5.94%, which is consistent with the work of Santamaria-Echart et al. (2016). As expected, a higher residue % is observed for the WPU-MH (21.61 %). Interestingly, for WPU/MH/NCC, a significantly higher % of residue was observed (40.55 %) accompanied with a modified thermal degradation TGA profile. This synergic effect of both additives can be explained by (1) the better MH dispersion in WPU previously mentioned (2) some groups on the surface of NCC may have the effect of flame retardant and promoting char formation.

Table 1 The main information extracted from TG/DTG and PCFC test.

Sample code	TG/DTG			PCFC				
	T _{max} (°C)	R _{Tmax} (%/min)	Residue at 600°C (%)	pHRR (W/g)	TpHRR °C	THR (kJ/g)	Δh (kJ/g)	Residue at 750°C (%)
NCC	305.35	7.26	29.56					
MH	390.66	4.89	72.59					
WPU	400.57	13.20	4.69	333	397	25.1	22.7	0.5
WPU/NCC	401.12	11.84	5.94	353	393	25.9	27.1	5.1
WPU/MH	396.64	7.81	21.61					
WPU/MH/NCC	400.57	6.63	40.55	127	408	12.6	19.1	35.5

T_{max}: Maximum weight loss temperature R_{Tmax}: Maximum weight loss rate

pHRR: The peak of heat rate release

TpHRR: The temperature at pHRR

THR: The total heat release

Δh: The heat of combustion

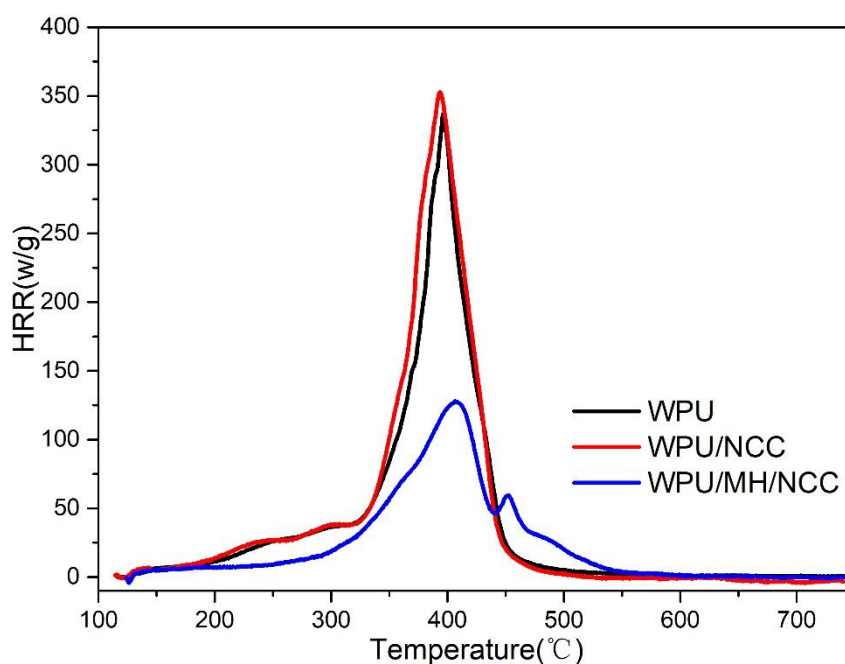


Figure 3. HRR curves for WPU, WPU/NCC, and WPU/MH/NCC in PCFC.

The thermal decomposition of WPU, WPU/NCC and WPU/MH/NCC at micro-scale was also carried out by PCFC (Figure 3). pHRR, HRR (area under the peak), TpHRR and ΔH (heat of complete combustion) are given in Table 1. It was confirmed that the addition of NCC alone in WPU did not significantly modified the thermal stability and pHRR. A slight increase of pHRR and ΔH is even observed. On the other hand, the simultaneous addition of NCC and MH dramatically changed the results of PCFC experiments: pHRR strongly decreased from 333 W/g to 127 W/g, THR decreased from 25.1 to 12.6 kJ/g, while the temperature of pHRR slightly increased from 397 to 408°C.

All these results demonstrated that the thermal stability of WPU-MH was

significantly improved by adding NCC.

Effect of modified WPU on the flame-retardant properties of wood panel

The photo of wood specimen with different coatings is given in Fig. 4. WPU/MH 0%/ NCC 5% sample has the color and pattern of the original wood. For WPU/MH40%/NCC0%, we observed a clear non-homogeneous surface with particles aggregates and agglomerates. In contrast, in the presence of 5% NCC, homogeneous specimen surfaces were observed regardless of the MH content (20-60%). The addition of NCC to the composite improves the aesthetic appearance of the material leading to a clear and smooth surface while keeping the wood grain visible. This result confirms the observations made above by microscopy concerning the better dispersion of particles in the presence of NCCs by physical absorption.

It can be seen from Fig. 4b that after combustion, the residual amount of char for the specimens were different as a function of the coating composition. For coating without NCC (NCC0%-MH40%), the sample burnt completely. In presence of 5% of NCC, it was observed that an increase in MH in the formulation led to an increase in the length of the coal residue. For 60.0% MH, the coating above the tick mark was not completely blackened, but a gradual transition from carbon black to brown and then to white was visible. This observation suggests that when the flame burned to the tick mark and went out, the coating above did not burn and decomposed rapidly.

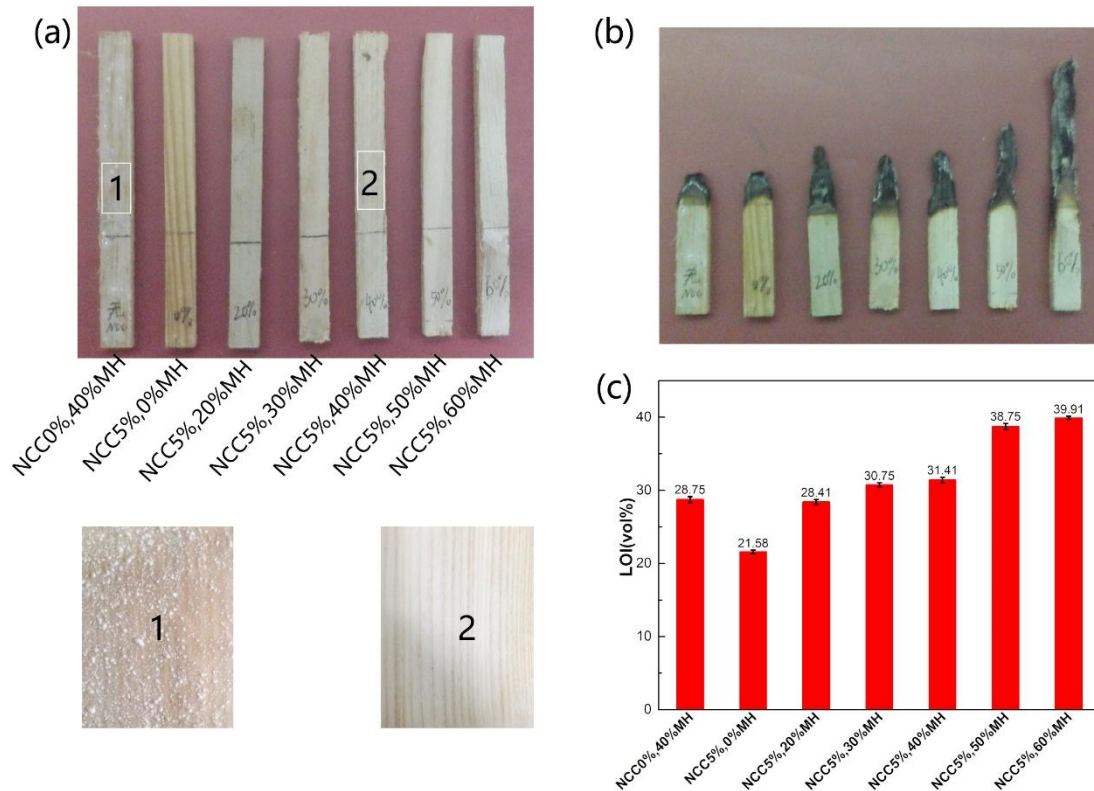


Figure 4. The specimen images of (a)before, (b)after oxygen index method and (c) LOI bar chart

As can be seen from Fig.4-c, with the increase of the amount of MH from 0wt% to 60wt%, the oxygen index value of the sample also increased from $\approx 22\text{vol}\%$ to $\approx 40\text{vol}\%$ respectively. A comparison of NCC0%-MH40% and NCC5%-MH40% showed that the addition of cellulose nanowhiskers in the formulation resulted in an increase in LOI value from 28.75vol% to 30.75vol% which can be explained by the better dispersion of the MH particles discussed above. According to GB/T 8624-1997 "Building Materials Combustion Performance Grading Method", for a MH content between 20.0wt% and 40.0wt%, the combustion performance of the material was B2 level combustible material. For MH >40wt%, the LOI values were very close, but greater than 32.0 vol%, corresponding to B1 level flame retardant material.

4. Conclusions

We have studied an innovative wood coating based on waterborne polyurethane (PU), inorganic metal oxide particles (MH) using cellulose nanowhiskers (NCCs) as additive. It has been shown that the presence of NCCs significantly improves the properties of the coating by promoting particle dispersion, improving the visual appearance of the material, its thermal stability and its flame-retardant performance. This approach could be regarded as a facile, efficient and eco-friendly modification to enhance the fire retardancy of wood panels.

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