Self-healing Coating to Reduce Isothiazolinone (MCI/MI) Leaching from Preservative-treated Bamboo

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A method was developed to reduce isothiazolinone (MCI/MI) leaching from treated bamboo, thereby extending the service life of bamboo. In this study, the self-healing coatings were prepared by incorporating 10 to 12 wt% microcapsules of urea-formaldehyde resin (UF)/tung oil into conventional polyurethane varnish and acrylate varnish. In the leaching test, the self-healing coatings outperformed the control coatings. Compared with the control coatings, the average leaching rates coated by the polyurethane and acrylate self-healing coatings were reduced by 6.22% and 6.29%, respectively. In impact damage and adhesion strength tests, the ability of the self-healing coatings to withstand damage was close to the control coatings. The results indicated that self-healing coating is a feasible method to reduce the leaching of MCI/MI from treated bamboo.

Keywords: Self-healing coating; Leaching; Isothiazolinone; Bamboo; Microcapsule

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INTRODUCTION

Bamboo is an abundant renewable natural resource and an important forest resource in China. Due to the advantages of high strength, strong toughness, high hardness, fast growth, low weight, and low purchasing costs, bamboo is a sustainable alternative to traditional structural materials (Archila *et al.* 2018). However, bamboo contains approximately 2 to 6% starch, 2% sugar, 1.5 to 6% protein, and 2 to 4% fat (Sun *et al.* 2011), and these nutrients are extremely susceptible to decay and mildew. Preservative treatment can protect bamboo from decay and mildew. With the increasingly serious environmental problems, organic preservatives have received more attention in China (Cao and Jiang 2014).

Isothiazolinones are a group of high efficiency, low toxicity, and broad spectrum organic preservatives used to control the growth of microorganisms such as bacteria, fungi, and yeast. They can control biofilm development and inhibit microbial growth and metabolism (Williams 2007). However, isothiazolinones leach from treated bamboo in a humid environment, posing a potential hazard to humans (Schwensen and Johansen 2012).

Coatings act as a physical barrier between bamboo and moisture to reduce preservative leaching. However, the long-term durability and reliability of conventional coatings are problematic due to microcracks induced by external factors such as UV light, temperature, and acid rain (Custódio and Eusébio 2006; Cogulet *et al.* 2018). Hence, new or optimized technologies are needed to improve coating quality. Self-healing coatings are an economic and facile way to identify and heal microcracks, which can restore the protective function of the coating to some extent (Blaiszik *et al.* 2010). Self-healing coatings can be classified broadly into three categories: capsule based, vascular, and intrinsic (Blaiszik *et al.* 2010). The self-healing coating embedded by microcapsules has attracted increasing attention due to the advantages of fast response to cracks, low cost, and simple synthesis (Blaiszik *et al.* 2010; Nesterova *et al.* 2011; Ye *et al.* 2016).

Although there are reports of self-healing coatings for metal corrosion and concrete protection (Kumar *et al.* 2006; Song *et al.* 2013; Thanawala *et al.* 2014; Chen *et al.* 2017), there has been no report on the effect of self-healing coatings on reducing preservative leaching from treated bamboo. The material properties of metal or concrete and bamboo are obviously different, so it is necessary to investigate the effect.

In the current work, the effect of self-healing coatings on reducing isothiazolinone leaching from preservative-treated moso bamboo (*Phyllostachys edulis*) was investigated for the first time. The self-healing coatings were prepared by incorporating 10 to 12 wt% microcapsules of urea-formaldehyde resin (UF)/tung oil into conventional polyurethane varnish and acrylate varnish. UF is a prevalent shell material for synthesis of microcapsules. Tung oil, a drying oil obtained from the nut of the tung tree (*Aleurites fordii*), was selected as a secondary-phase healing agent, the significance being its ability to form a hard, waterproof film automatically. Among a number of isothiazolinone products, the mixture of methylchloroisothiazolinone with methylisothiazolinone (MCI/MI) (also named Kathon™) is one of the most frequently used products (Schwensen and Johansen 2012). Polyurethane and acrylate are two commercial varnishes available in China. This study aims to provide a method of reducing MCI/MI leaching from preservative-treated bamboo, thus extending the service life of bamboo.

EXPERIMENTAL

Materials

Moso bamboo (*Phyllostachys edulis*) of 4 years old and 8 to 12% moisture content was collected from Hangzhou, Zhejiang Province, China. Tung oil was obtained from Enshi, Hubei Province, China. Waterborne polyurethane varnish and waterborne acrylate varnish were supplied by Hebei Chenyang Industry and Trade Group Co., Ltd., Baoding, China.

MCI/MI (14.0 wt%: MCI 10.5 wt%; MI 3.5 wt%) was provided by Beijing Sunpu Biochemical Technology Co., Ltd., Beijing, China. Urea (AR) and ammonium chloride (NH_4Cl) (AR) were provided from Xilong Scientific Co., Ltd., Shantou, China. Resorcinol (AR, 99 wt%), poly (vinyl alcohol) (PVA) (alcoholysis degree: 92.0 to 94.0 mol% and viscosity: 23.0 to 30.0 mPa.s), sodium dodecyl sulfate (SDS) (GC, $\geq$ 99.0 wt%), and octanol (AR, 99.0 wt%) were purchased from Aladdin Industrial Corporation, Shanghai, China. Formaldehyde (37 wt%) was provided from Shandong Baiqian Chemical Co., Ltd., Jinan, China. All chemicals were used as received.

Methods

Synthesis and characterization of microcapsules

The microcapsules were prepared as described by Samadzadeh *et al.* (2011). Briefly, under 200 rpm agitation and 25 ± 2 °C water bath, 5 g of urea, 0.5 g of NH_4Cl, and 0.5 g of resorcinol were dissolved in 260 mL of deionized (DI) water with 10 mL of 4 wt% PVA and 1.0 wt% SDS solution. The pH was adjusted to 3.0 to 3.5 using 1 wt% HCl in DI water. One to two drops of octanol was added as an antifoaming agent. After 10 min of agitation, 50 mL of tung oil was added slowly to form an emulsion and allowed to stabilize for 30 min under agitation. After stabilization, 13.0 g of 37 wt% formaldehyde solution was added. The emulsion was slowly heated and maintained at 60 °C under stirring at 400 rpm. After 4 h, the agitation rate was decreased slowly, and the contents were cooled to ambient temperature. Microcapsules from the suspension were recovered by filtration under vacuum with coarse filter paper and were rinsed twice with deionized water and acetone. Microcapsules were air-dried for 48 h prior to storage. A scanning electron microscope (FEI XL-30 ESEM, Amsterdam, Netherlands) was used to determine the morphology and particle size of microcapsules.

Preparation and characterization of self-healing coatings

The self-healing coatings were prepared by dispersing the obtained microcapsules into polyurethane varnish and acrylate varnish under stirring at 200 rpm for a period of 5 min. The mass ratio of microcapsules and varnish in the coatings was 12:88 to 10:90.

The self-healing coatings were coated on one side of the glass slide. After 7 days of curing in the air, a straight-cut was made on the coatings with a razor blade, and the healing process was observed using an optical microscope (Leica DMLB2, Wetzlar, Germany) after 0 and 4 days. Control samples were prepared with polyurethane varnish or acrylate varnish without microcapsules.

Preparation and vacuum impregnation of bamboo

After removing bamboo green and bamboo yellow, 364 bamboo samples with dimensions of 40 mm (length) × 20 mm (width) × 5 mm (thickness) were prepared. Of these, 300 samples were used for leaching test and 64 samples were used for mechanical test.

The 14.0 wt% solution of MCI/MI was diluted with water to two concentrations of 0.3 wt% and 0.45 wt%. The impregnation procedure was as follows: 1) impregnate at a vacuum of -0.85 MPa for 5 min; 2) impregnate at atmospheric pressure for 5 min; 3) impregnate at a vacuum of -0.85 MPa for 10 min; and 4) impregnate at atmospheric pressure for 10 min.

A total of 100 bamboo samples were impregnated and weighed (accurate to 0.001 g) for each formulation. The retention of MCI/MI was calculated according to Eq. 1 (GB/T 29905 2013),

$$Ret = \frac{c \times m_G \times 1000}{V} \qquad (1)$$

where *Ret* is the preservative retention (kg/m^3), c is the mass fraction of preservative (%), m_G is the mass of preservative absorbed by bamboo (g), and V is the volume of bamboo (cm^3).

After being air-dried for 21 days in a well-ventilated place, the samples were coated with self-healing and control coatings by manual brushing, and then air-dried for 7 days again. The coating thickness was adjusted by the number of brushings. Manual brushing was adopted because it was suspected in a previous test that mechanical brushing causes microcapsules to rupture during coating. A caliper was used to measure of the thicknesses of the coatings. And the difference in thickness was then evaluated by variance analysis.

Accelerated aging tests

The UV aging test was performed according to the BS EN ISO 16474-3 (2013) and ISO 11341 (2004) standards. The coated samples were exposed to UV light in an UV aging chamber (Pushen LUV) at 38 ± 3 °C for a period of 192 h. The UVB-313 lamp was used with an irradiance of 0.8 W/m^2 at 313 nm. The thermal aging test was conducted according to BS EN ISO 3248 (2016); the coated samples were heated in an oven at 125 ± 2 °C for 24 h. The acid aging test followed the BS EN ISO 15110 (2017) standard, where the pH of DI water in the leaching test was adjusted to 2.5 with 1 M HCl. To avoid damage to the chromatograph, HCl was used because it volatilizes as the collected leachates evaporate. In a comprehensive aging test, the UV aging test, thermal aging test, and acid aging test were sequentially performed. There were four bamboo samples for each aging condition at the same MCI/MI concentration and coating type.

Leaching test

According to the AWPA E11-12 (2012) standard, leaching tests were conducted using the above aged samples. Each set of four samples was placed into a 250-mL beaker and submerged in 60 mL of DI water. The beakers were subjected to mild agitation, and the leachates were replaced with an equal amount of DI water after 6 h, 24 h, 48 h, and thereafter every 48 h, for a total of 336 h (6, 24, 48, 96, 144, 192, 240, 288, and 336 h). The collected leachates were mixed and evaporated by a rotary evaporator, and the remains were extracted with methanol for high performance liquid chromatography (HPLC) analysis.

High performance liquid chromatography analysis

The chromatographic separation was performed on a HPLC (Elite P230, Dalian, China) device equipped with a diode array detector (DAD) (Elite UV230$^+$) and a C_{18} column (Elite Supersil ODS2, 5 µm, 200 mm × 4.6 mm). The mobile phase ratio and flow rate were MeOH:H_2O = 15:85$_{V:V}$ and 1 mL/min, respectively. The UV-detected wavelength was 276 nm, the injection volume was 20 µL, and the column temperature was 30 ± 2 °C. The chromatographic data of MCI and MI were collected by a chromatography data workstation (Elite EC2000).

According to the external standard method, the peak area of the standard solution at different concentration was detected by HPLC. The standard curves of MCI and MI drawn according to the test results are shown in Fig. 1.

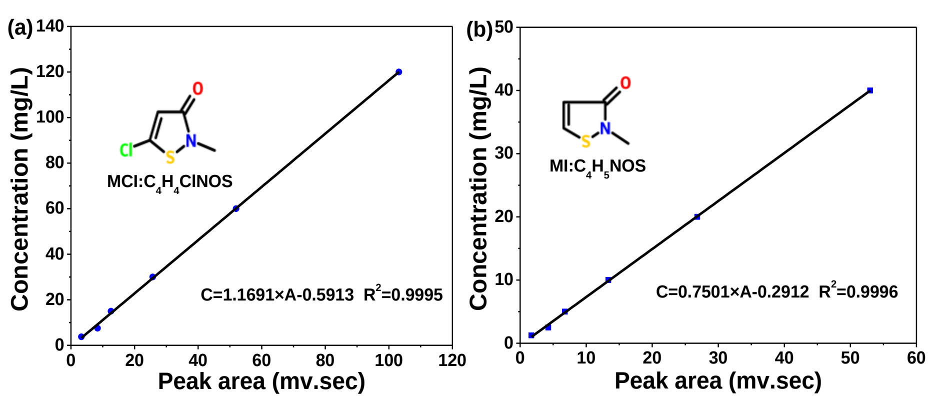

Fig. 1. Standard curves of (a) MCI and (b) MI; C is the concentration (mg/L); A is the peak area (mv.sec)

Impact damage test

Based on the method reported by Chen *et al.* (2017), an impact damage test was conducted to determine the effect of the microcapsule embedment on the mechanical property of coatings. The coated samples were impacted with an impact tester (Instron Dynatup 9250HV, Norwood, MA, USA) with an energy of 2.9219 J. The bamboo cracked when the energy was greater than this value. Eight samples of each coating were tested, and photographs of the damaged area were analyzed to measure the damaged areas.

Adhesion strength test

Using the ASTM D3359-17 (2017) standard, the effect of microcapsule embedment on the adhesion strength was investigated by tape test. The test involved applying and removing pressure sensitive tape over an X-cut made in the coatings, and assessing adhesion qualitatively on the 0 to 5 scale. Eight samples of each coating were tested.

RESULTS AND DISCUSSION

Microcapsule Morphology

The SEM micrographs and diameter distribution of the microcapsules are shown in Fig. 2. Slight variations in solution pH during synthesis can lead to variations in microcapsule diameter (Safaei *et al.* 2018), which may affect the waterproof performance of self-healing coatings. To ensure consistency throughout test, three batches of microcapsules were combined in this study. The diameter distribution of microcapsules was determined from three batches of the SEM micrographs. The size of microcapsule diameter ranged from 22 to 151 μm. The mean and standard deviation of microcapsule diameter were 92 μm and 23 μm, respectively.

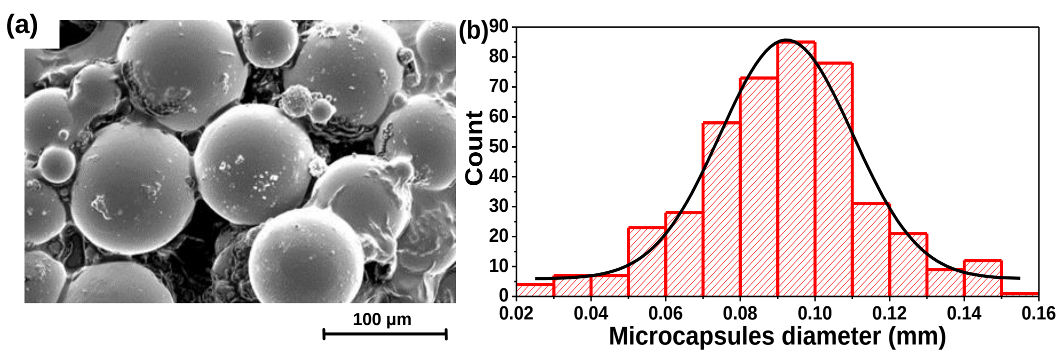

Fig. 2. (a) SEM micrograph of microcapsules; (b) diameter distribution of microcapsules

Self-healing Behaviour of Coating

As shown in Fig. 3, the self-healing coatings exhibited a light-colored band along the cut after 4 days. The result showed that the self-healing coatings had the ability of self-healing in the damaged zone. The self-healing behavior of the coatings is hypothesized as shown in Fig. 4. When the self-healing coatings were broken, the microcapsules released tung oil, which filled the damage site and oxidized to form a film, thus avoiding the preservative leaching. Chemically, the healing process could be that the C-H bond adjacent to one of the double bond within fatty acid of the tung oil automatically oxidizes to form an oxidized cross-linked film (Tatiya *et al.* 2016). In addition, it should be noted that the band did not completely spread along the cut, suggesting that self-healing coatings might not completely heal coating damage, depending on the size, orientation, and location of the damage site.

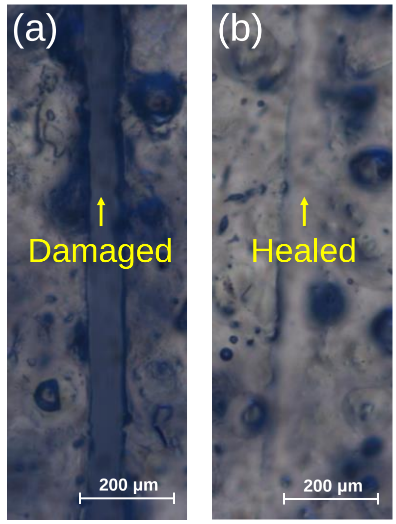

Fig. 3. Optical microscope images of damaged self-healing coatings after (a) 0 and (b) 4days

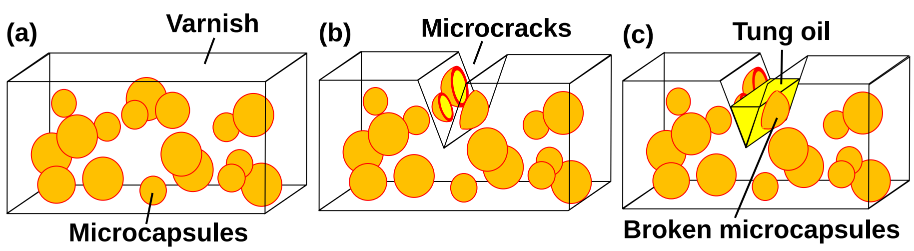

Fig. 4. Schematic diagram of self-healing behavior; (a) Not damaged; (b) Damaged; (c) Self-healing

Accelerated Aging and Leaching Test

As shown in Fig. 5, the leaching rates of MCI and MI were decreased after coating, and the self-healing coatings outperformed the control coatings. Compared with the control coatings, the average leaching rates coated by the polyurethane and acrylate self-healing coatings were reduced by 6.22% and 6.29%, respectively. The result indicated that the self-healing coatings reduce MCI/MI leaching.

In addition, Fig. 5 shows that the leaching rates of the aged samples were lower than those of the unaged samples. Isothiazolinone degradation was suspected as the reason for this result. However, previous studies indicated that although isothiazolinones were degradable when kept at sufficiently high temperature, they were relatively stable in UV and acid conditions (Barman and Preston 1992; Park and Kwon 2016). Therefore, degradation might only have a partial effect for the leaching of MCI/MI. At the same time, after thermal aging, the leaching rates of the coated samples were significantly lower than those of the uncoated samples. This result might be affected by two factors: thermal degradation and thermal aging. Some of MCI and MI might be degraded during thermal aging, resulting in a reduction in the leaching rate, and the current thermal aging condition might not cause sufficient damage to the coatings. Future studies will focus on the effect of aging conditions on coatings.

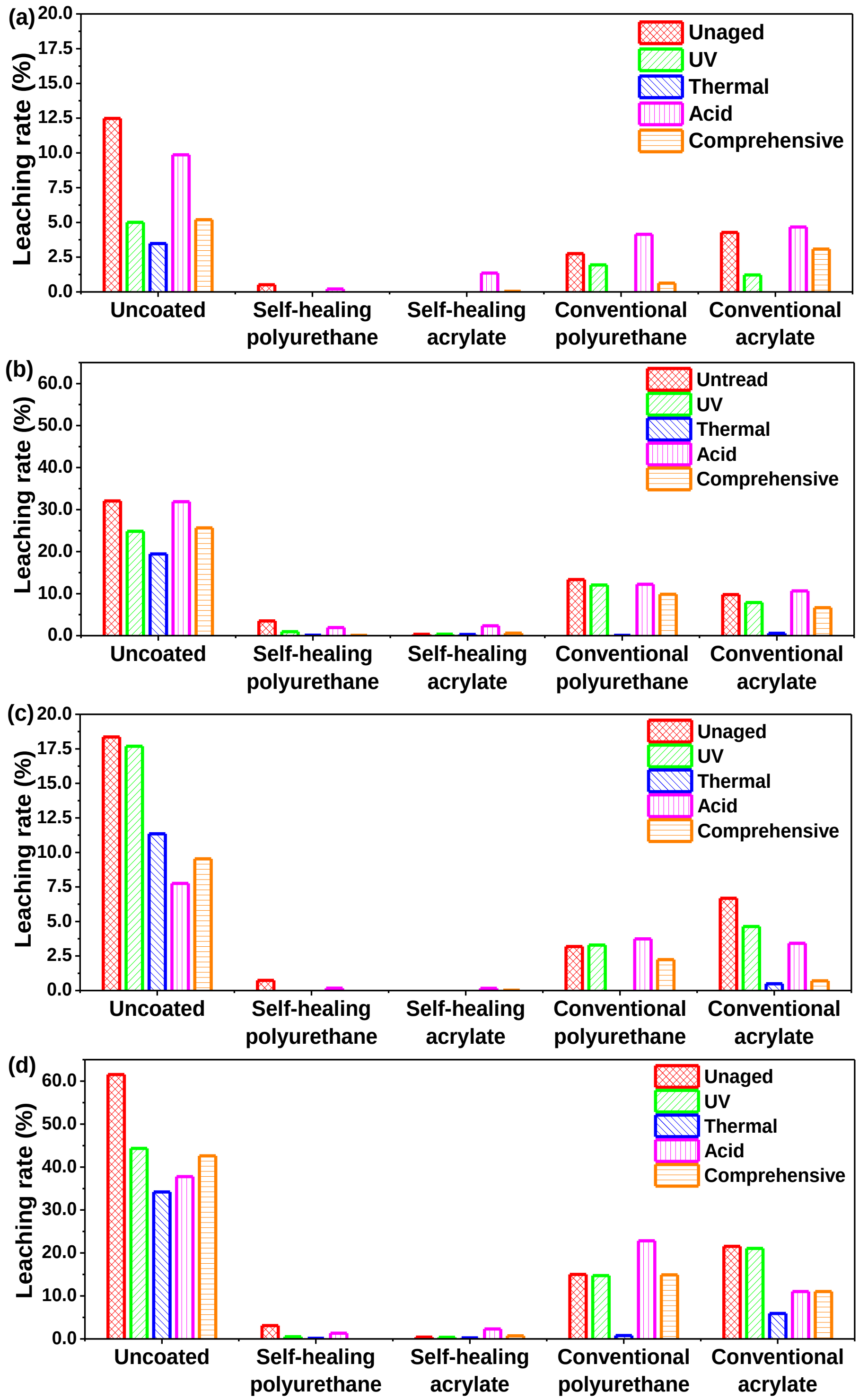

Fig. 5. Leaching rates of (a, c) MCI and (b, d) MI from bamboo treated with 0.3 wt% and 0.45 wt% isothiazolinone (MCI/MI) after accelerated aging

As shown in Table 1, the retention of MCI/MI increased with the increase of their concentration, and the increase ratio of both was consistent. In this study, the leaching rates of the high retention samples were generally higher than those of the low retention samples (Fig. 5). At the same time, the leaching rates under different aging conditions did not show strong regularity. This might be due to the anisotropy of bamboo (Dixon and Gibson 2014).

Table 1. Concentration and Retention of Isothiazolinone (MCI/MI) Formulations

No.	Active Ingredients	Concentration (%)	Retention (kg/m^3)		SD of Retention (kg/m^3)	
			MCI	MI	MCI	MI
A	MCI/MI	0.3	0.5422	0.1807	0.0227	0.0076
B	MCI/MI	0.45	0.8246	0.2749	0.0341	0.0114
CK	-	0	0	0	0	0

CK was water without the MCI/MI formulations.

Moreover, the thickness of coatings was considered as a potential variable for waterproof performance during leaching test. As shown in Fig. 6, the mean thicknesses of the four types of coatings were 372 μm, 420 μm, 297 μm, and 339 μm in turn. The difference in thickness between self-healing and control coatings was comparable with the diameter of microcapsules used in this study. Although the self-healing coatings had a greater average thickness, the difference was not statistically significant ($P > 0.05$).

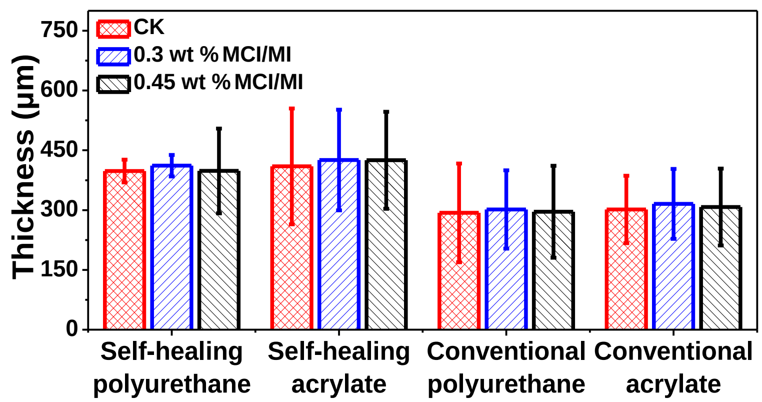

Fig. 6. Thickness of coatings; Error bars represent the standard deviation

Impact Damage and Adhesion Strength Test

The incorporation of microcapsules into the coating was suspected to decrease its mechanical properties. Therefore, the impact damage and adhesion strength test were performed, as impact and adhesion properties are related to mechanical properties of the coatings, such as the toughness, brittleness, hardness, *etc*.

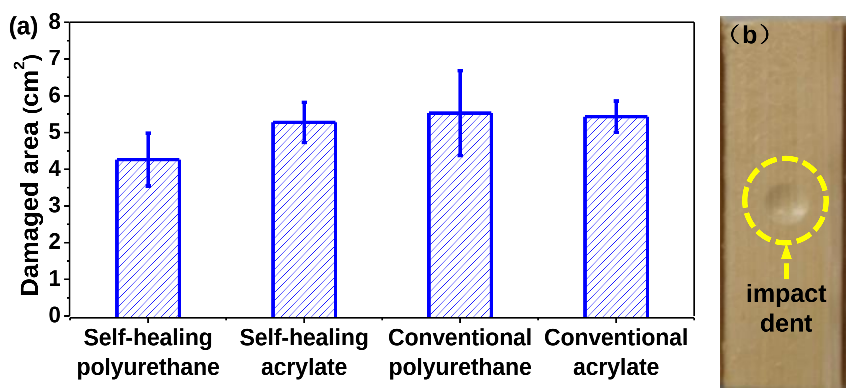

Fig. 7. (a) Damaged area of coatings; Error bars represent the standard deviation; (b) Impact dent of coatings

As shown in Fig. 7 (a), no significant difference in the impact damaged area was observed when comparing the self-healing coatings with the control coatings. No cracking, chipping, debonding, or delamination was observed on the self-healing and control coatings, while only an impact dent was shown (Fig. 7 (b)). The results showed that the impact resistance was not reduced by incorporation of microcapsules.

As shown in Table 2, there was no difference in the adhesion strength of the self-healing and control coatings. The adhesion strength of the self-healing coatings was not sacrificed by the addition of microcapsules.

Table 2. Adhesion Strength of Coatings

Coating	Adhesion Strength
Self-healing polyurethane	5A, 5A, 5A, 5A, 5A, 5A, 5A, 5A
Self-healing acrylate	5A, 5A, 5A, 5A, 5A, 5A, 5A, 5A
Conventional polyurethane	5A, 5A, 5A, 5A, 5A, 5A, 5A, 5A
Conventional acrylate	5A, 5A, 5A, 5A, 5A, 5A, 5A, 5A
Note: 5A No peeling or removal, 4A Trace peeling or removal along incisions or at their intersection, 3A Jagged removal along incisions up to 1.6 mm on either side, 2A Jagged removal along most of incisions up to 3.2 mm on either side, 1A Removal from most of the area of the X under the tape, and 0A Removal beyond the area of the X.	

CONCLUSIONS

1. The self-healing coatings exhibited a light-colored band along the cut after being damaged. The result showed that the self-healing coatings had the ability of self-healing in the damaged zones.
2. The self-healing coatings performed better than the control coatings during leaching tests. Compared with the control coatings, the average leaching rates coated by the polyurethane and acrylate self-healing coatings were reduced by 6.22% and 6.29%, respectively. The result indicated that self-healing coating is a feasible method to reduce the leaching of MCI/MI from treated bamboo.
3. The self-healing coatings showed no apparent differences in the ability to withstand impact and adhesion damage as compared with the control coatings.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the National Key R&D Program of China (Grant No. 2017YFD0600803).

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Article submitted: July 30, 2019; Peer review completed: January 23, 2020; Revised version received: January 25, 2020; Accepted: January 27, 2020; Published: January 29, 2020.

DOI: 10.15376/biores.15.1.1904-1914