Synthesis and Characterization of Loaded Nano/Zinc Oxide Composite Hydrogels Intended for Anti-Mold Coatings on Bamboo

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This study investigated the antibacterial activity of nano-zinc oxide (ZnO) composite hydrogels on the types of mold organism that commonly affect bamboo. The nano-ZnO was produced via the in situ method in poly(Nisopropylacrylamide-co-acrylic acid) (P(NIPAm-co-AAc)) hydrogel. The structures and properties were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), differential scanning calorimeter (DSC), equilibrium swelling ratio (ESR), deswelling and swelling tests, and antimicrobial activity. The nano-ZnO particles were monodispersed in the P(NIPAm-co-AAc) hydrogel. The concentration of the nano-ZnO was higher in the ZnO/P(NIPAm-co-AAc) hydrogel than in the ZnO/PNIPAm hydrogel. The swelling properties in the ZnO/P(NIPAm-co-AAc) hydrogel were more favorable than those of the ZnO/PNIPAm hydrogel, while the deswelling properties were more favorable in the ZnO/PNIPAm hydrogel. The hydrogels that contained more ZnO nanoparticles demonstrated greater antimicrobial properties against Trichoderma viride and Penicillium citrinum of bamboo, while the all of the hydrogels had much less antimicrobial activity against Aspergillus niger.

Keywords: Composite hydrogel; Nano-ZnO; Swelling; Antibacterial; Mold; Bamboo

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INTRODUCTION

As the world's largest supplier of bamboo, China can harvest and utilize its nutrients, such as cellulose, hemicellulose, and starch, at very high yield rates (Jiang 2007; Zhang 2007; Yu *et al.* 2016). However, these nutrients are susceptible to mildew, which can affect the value and usefulness of bamboo. To combat this issue, the anti-fungal properties of nano-silver (Ag) composite hydrogels on bamboo were investigated (Wei *et al.* 2016; Yu *et al.* 2016). However, the color of nano-Ag particles is easily changed, which can affect the color of the bamboo itself. Additionally, the Ag⁺ dissolved after a long time has harmful effects on the human body (Liu *et al.* 2017). Although Zn²⁺ could also be toxic for human cells when hydrogels are prepared with very high concentration of Zn²⁺ (Frígols *et al.* 2019), nano-ZnO composites are nontoxic, antimicrobial, and thermally stable (Ma *et al.* 2014). Therefore, nano-ZnO composites have promising applications in medicine, antimicrobial coatings, ceramics, and anti-mold coatings, among others.

Thermo-sensitive hydrogels are hydrogels that exhibit swelling or shrinking in response to slight changes in the local temperature (Asmarandei *et al.* 2013; Xia *et al.* 2013; Chen *et al.* 2017). Nanomaterials with antibacterial properties are loaded into the temperature-sensitive hydrogels, which control the release of the drug by using the unique

temperature response of the hydrogels (Huang et al. 2017). This application has been valued by many researchers in the fields of drug-controlled release, tissue engineering, and others (Jeong et al. 2012; Xu et al. 2014; ZareAkbari et al. 2016). In a previous study, carboxymethyl cellulose (CMC)/ZnO nanocomposite hydrogels were synthesized through the in situ formation of ZnO nanoparticles within swollen CMC hydrogels (Yadollahi et al. 2015). The nanocomposite hydrogels demonstrated antimicrobial effects against Escherichia coli and Staphylococcus aureus bacteria. Rakhshaei et al. (2017) prepared flexible nanocomposite hydrogel films by combining ZnO-impregnated mesoporous silica (ZnO-MCM-41) as a nano-drug carrier with CMC hydrogels. The drug delivery and antimicrobial properties of the nanocomposite hydrogel films were studied using tetracycline (TC) as a broad-spectrum antibiotic and showed a sustained TC release. However, it is difficult to find reports on the effects of ZnO/poly(N-isopropylacrylamide) (P(NIPAm)) composite hydrogels against the most common type of mold that forms on bamboo surfaces. Furthermore, the antibacterial ability of ZnO composite hydrogels is easily decreased by the agglomeration of nano-ZnO particles and slow reaction time. In this work, a quickly-reacted and monodispersed nano-ZnO/P(NIPAm-co-AAc) antimicrobial hydrogel was produced by an *in situ* method with N-isopropylacrylamide (NIPAm) and acrylic acid (AAc). In addition, the structure and characteristics of the hydrogel were analyzed.

EXPERIMENTAL

Materials

N-isopropylacrylamide (NIPAm, analytical grade) was supplied from TCI Co., Ltd. (Shanghai, China). N,N'-methylenebisacrylamide (MBA), potassium persulfate ($K_2S_2O_8$, *i.e.*, KPS), N,N,N', N'-tetramethylethylenediamine (TEMED), and acrylic acid (AAc) were all analytical grade and purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China), and these chemical reagents were used as received without further purification. The 0.01 mol/L Zn(NO₃)₂ solution and 0.2 mol/L NaOH solution were formulated as needed. Deionized water was used throughout the experiment.

Methods

Preparation of P(NIPAm-co-AAc) hydrogel

A quantity of 0.8 g NIPAm monomer was combined with 8 mL of distilled water in a 50-mL beaker. 0.04 g of the MBA, 0.04 g of KPS, 50 μ L of AAc, and 100 μ L of TEMED were separately added into the mixture and stirred until entirely dissolved. The mixture then stood for 24 h after producing the hydrogel for future use. During the day, the distilled water was changed every hour to remove any unreacted monomers. Care was taken not to damage the hydrogel when removing the monomer with deionized water. Finally, the produced hydrogel was placed into an oven at 60 °C to dry P(NIPAm-co-AAc) hydrogel.

Preparation of ZnO/P(NIPAm-co-AAc) hydrogel

Dried P(NIPAm-co-AAc) hydrogel was immersed into 0.01 mol/L $Zn(NO_3)_2$ solution for 24 h, washed five times with distilled water, transferred into 0.2 mol/L NaOH solution, kept for 24 h, and then washed again five times. After being heated at 60 °C, the final product was created.

X-ray diffraction (XRD) analysis

The phase compositions of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels were $2\theta/\theta$ linked scanned at a rate of 2°/min *via* an XRD6000 X-ray diffractometer (Shimadzu, Kyoto, Japan) with Cu K α radiation in the range of 5 to 70° (2 θ) under 35 kV tube voltage and 30 mA tube current.

UV-vis absorption spectra analysis

Uv-vis absorption spectra of the hydrogels containing zinc oxide nanoparticles were recorded on an Agilent Cary 5000 UV-vis spectrophotometer. Wavelength range was from 300 to 550 nm.

Fourier transform infrared (FTIR) spectroscopy analysis

The molecular structure of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) was analyzed using a Nicolet 6700 FTIR spectrometer (Thermo Scientific, Waltham, USA) with the pellet mixed with dried ground hydrogel and KBr. The spectra were recorded in the 4000 to 400 cm⁻¹ wavenumber range and the resolution ratio was 4 cm⁻¹.

Scanning electron microscopy (SEM) analysis

The microstructure of the ZnO, ZnO/PNIPAm, and ZnO/P(NIPAm-co-AAc) composites were coated with gold for 60 s and recorded *via* SEM (MT-1000; Shimadzu, Kyoto, Japan). The accelerating voltage was 5.0 kV.

Energy-dispersive X-ray spectroscopy (EDS) analysis

A field emission SEM device (Sirion-100; FEI Company, Hillsboro, USA) equipped with EDS (Genesis 4000; AMETEK, Newark, NJ, USA) was used to perform the content analysis of Zn within the hydrogel with an accelerating voltage of 25 KV.

The equilibrium swelling ratio (ESR) test of hydrogels

Dried ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) gels of 0.2 g were immersed in distilled water at different temperatures (20, 24, 28, 32, 36, 40, and 44 °C) until they reached equilibrium. The swollen hydrogels were then weighed after wiping dry the water that was attached to the surface of the gels. The experiment was repeated three times under the same conditions to obtain the average. The ESR was calculated according to Eq. 1 (Serrano-Aroca *et al.* 2018),

$$ESR (\%) = \frac{m_{\rm s} - m_{\rm d}}{m_{\rm d}} \times 100 \tag{1}$$

where m_s is the weight (g) of the equilibrium hydrogels at a given temperature and m_d is the weight (g) of the dried gel.

Differential scanning calorimeter (DSC) analysis

Swollen ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels of 10 mg were placed in an aluminum pan designed for liquids. The test was performed using a Q2000 DSC (TA Instruments, New Castle, USA). The temperature range was 20 to 50 °C to avoid water melting and crystallization (Aroca *et al.* 2015), the heating rate was 5 °C /min, and deionized water was used as a reference.

The deswelling kinetic test of hydrogels

Dried ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) gels of 0.2 g were immersed in distilled water at 20 °C until they reached equilibrium. The swollen hydrogels were weighed after wiping the deionized water with wet filter papers. The swollen hydrogels were then transferred into distilled water at 50 °C, where the hydrogels deswelled with shrinking and dehydration. The hydrogels were weighed every 5 min until the weight stabilized, while the temperature remained unchanged at 50 °C. The experiment was repeated three times under the same conditions to obtain average value. The water retention (WR) was calculated according to Eq. 2,

$$WR = \frac{m_{\rm t} - m_{\rm d}}{m_{\rm s} - m_{\rm d}} \tag{2}$$

where m_t is the weight (g) of swollen hydrogel at given time, m_s is the weight (g) of the equilibrium hydrogel at 20 °C, and m_d is the weight (g) of the dried gel.

The swelling kinetic test of hydrogel

Dried ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) gels of 0.2 g were immersed in distilled water at 20 °C. The hydrogels were weighed every 5 min, the change in the mass of the hydrogels was recorded over a 1-h period, and the temperature remained constant at 20 °C. The experiment was repeated three times under the same conditions to obtain average value. The swelling ratio (SR) was calculated according to Eq. 3,

$$SR = \frac{m_{\rm t} - m_{\rm d}}{m_{\rm d}} \tag{3}$$

where m_t and m_d have the same meaning as in Eq. 2.

Antimicrobial activity

The antimicrobial activity of the ZnO/P(NIPAm-co-AAc) nanocomposite hydrogels against common bamboo mold (*Penicillium citrinum*, *Trichoderma viride*, and *Aspergillus niger*) was tested according to the zone inhibition methods (Rakhshaei *et al.* 2017). The agar plates were inoculated spore suspensions of the mold. Swelled hydrogels were cut into disks 15 mm in diameter and placed on the agar plate. The antimicrobial-treated area of mold growth, in a constant temperature and humidity chamber at a temperature of 25 °C and a humidity of 85%, was observed for one week.

RESULTS AND DISCUDDION

Preparation of Nano-ZnO/P(NIPAm-co-AAc) Composite Hydrogel

The preparation procedures of nano-ZnO/P(NIPAm-co-AAc) composite hydrogels *via* the *in situ* formation of ZnO are shown in Fig. 1. The nano-ZnO was produced by the *in situ* method in the P(NIPAm-co-AAc) hydrogel. Initially, P(NIPAm-co-AAc) hydrogel was synthesized and sequentially immersed in 0.01 mol/L Zn(NO₃)₂ solution and 0.2 mol/L NaOH solution. Finally, the nano-ZnO composite hydrogel was prepared after being dried. Because the AAc was employed as a co-monomer in the synthesis, the carboxyl groups that were present would be able to bind any metal cations due to opposite signs of charge. In other words, the Zn²⁺ in Zn(NO₃)₂ was easily bounded by the P(NIPAm-co-AAc) hydrogel, producing a nano-ZnO structure with the reaction of Zn²⁺ and OH⁻ in the alkaline environment of the NaOH solution.



Fig. 1. Preparation of the ZnO/P(NIPAm-co-AAc) hydrogel

XRD and UV-vis Analysis

The XRD spectra of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) specimens are shown in Fig. 2.





Fig. 2. (a)The XRD spectra of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels; (b) The Absorption spectra of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels

According to Fig. 2(a), the broad peak of 2θ at 20° in ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels are the characteristic peaks of its crosslinked network structure. This signified that the original three-dimensional (3D) structure of PNIPAm did not change via the polymerization of ZnO and PNIPAm. As such, the thermal-sensitive characteristics were not affected. In Fig. 2(a), the diffraction peaks of 31, 34, 37, 47, 56, 62, 64, and 68° correspond to the characteristic crystal planes (100), (002), (101), (102), (110), (103), (200), and (112), respectively, of the hexagonal wurtzite structure of ZnO, which corresponds to the ZnO diffraction peak of JCPDS No. 36-1451 (Li et al. 2010; Wang et al. 2016). It was concluded that the ZnO was synthesized in the P(NIPAm-co-AAc) hydrogel. Remarkably, the characteristic diffraction peaks of ZnO were weak. This was attributed to the fact that free Zn^{2+} was easy to move without being bound, which resulted in poor crystallinity of the ZnO. However, the characteristic peaks of ZnO/P(NIPAm-co-AAc) hydrogel were clear, indicating that the crystallinity of nano-ZnO particles was better. The Zn^{2+} with a positive charge was bounded by the connection of COO⁻ in AAc with a negative charge *via* electrostatic force. The weak peaks appearing around 28, 37, and 44° indicated that the hydrogel contained nano-Zn(OH)₂ particles. Compared with the PNIPAm hydrogel, the structure of ZnO/PNIPAm and ZnO/P(NIPAmco-AAc) hydrogels did not change except for the characteristic peaks of ZnO, so the incorporated nanoparticles did not affect the original structure of hydrogel. According to Fig. 2(b), ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels had UV absorption at 370 nm, indicating the formation of nano-ZnO in the hydrogel matrix (Sween et al. 2010). And in the PNIPAm and P(NIPAm-co-AAc) hydrogels matrix, the optical properties of nano-ZnO did not change.

FTIR Analysis

The FTIR spectra of the ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels are shown in Fig. 3.



Fig. 3. The FTIR spectra of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels

According to Fig. 3, the FTIR spectra of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) were almost the same. The peaks of 3428 cm⁻¹ and 3300 cm⁻¹ are the asymmetric and symmetric stretching vibrations, respectively, of N-H. The peak of 3360 cm⁻¹ is the stretching vibration. The peak at approximately 3077 cm⁻¹ represents the overtone band of the stretching vibration of the N-H secondary amide band. The peaks of 2974 cm⁻¹, 2933 cm⁻¹, and 2876 cm⁻¹ are the vibrations of C-H of methyl and methylene. The peak of 1650 cm⁻¹ is ascribed to the characteristic peak of the C=O stretching vibration at the amide I band. The peak at 1548 cm⁻¹ is attributed to the C-N stretching vibration at the amide II band. The peak at 1460 cm⁻¹ corresponds to the asymmetrical stretching of C-H in the methyl groups. The peaks at 1386 cm⁻¹ and 1368 cm⁻¹ arose from the coupling split of the symmetrical bending vibrations originating from the two methyl groups of $-CH(CH_3)_2$. The absorbance band at 1173 cm⁻¹ is attributed to the C-C stretching vibration of -CH(CH₃)₂. Furthermore, the peaks at 928 cm⁻¹ and 882 cm⁻¹ were related to the end-vinyl group. As a result, the hydrophilic -CONH- and the hydrophobic -CH(CH₃)₂ were the main functional groups of the hydrogel. On the FTIR of the monomer NIPAm, there was a -C=Cabsorption peak at 1662 cm⁻¹. However, the peak of 1662 cm⁻¹ disappeared on the FTIR spectra of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc), which indicated the successful polymerization of the ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) polymers.

SEM Analysis

The SEM images of the ZnO, ZnO/PNIPAm, and ZnO/P(NIPAm-co-AAc) hydrogels are shown in Fig. 4.



Fig. 4. SEM images of (a) ZnO, (b) ZnO/PNIPAm, and (c) ZnO/P(NIPAm-co-AAc)

According to Fig. 4a, the nano-ZnO particles are basically in agglomerated state. In Fig. 4b and 5c, it is easy to observe that the nano-ZnO particles dispersed evenly, indicating that the agglomeration of ZnO was brought about by combining nano-ZnO with hydrogel. The concentration of nano-ZnO in the P(NIPAm-co-AAc) hydrogel (Fig. 4c) was much higher than in the PNIPAm hydrogel (Fig. 4b), which was attributed to the AAc. In the ZnO/PNIPAm hydrogel, the concentration of ZnO in PNIPAm was low, which was because the free Zn²⁺ was not easily bound and the nano-ZnO was easy agglomerated. In ZnO/P(NIPAm-co-AAc) hydrogels, due to the addition of AAc, the negatively charged COO⁻ and the positively charged Zn²⁺ were electrostatically attracted to generate a binding force, which can bind the free Zn²⁺ to the hydrogel matrix. Accordingly, the quantity of nano-ZnO increased *via* the reaction of OH⁻ and Zn²⁺.

EDS Analysis

The EDS patterns of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels are shown in Fig. 5.



Fig. 5. The EDS patterns of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc)

According to Fig. 5, the feature peaks of C, O, and Zn appeared in the EDS patterns. The characteristic peak of C was mainly derived from the elements contained in the monomer NIPAm. The peaks of O and Zn, seen in the EDS of the hydrogel, indicated that the nano-ZnO was loaded into the hydrogel. The Zn content in the ZnO/PNIPAm hydrogel was 6.15 wt%, almost one-third as high as the content in the ZnO/P(NIPAm-co-AAc) hydrogel (19.33 wt%). This illustrated that the addition of AAc effectively increased the loading of nano-ZnO (Fig. 5 and Table 1).

Table 1. E	lemental Anal	ysis of Di	ifferent Hy	ydrogels
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Samples	C (wt%)	O (wt%)	Zn (wt%)
ZnO/PNIPAm	59.14	34.71	6.15
ZnO/P(NIPAm-co-AAc)	49.99	30.68	19.33

ESR Test of Hydrogel and DSC Analysis

The ESR and DSC curves of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) at different temperatures are shown in Fig. 6.



Fig. 6. a) The ESR of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) at different temperatures; b) the DSC kinetic curves of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels

According to Fig. 6a, the swelling properties of ZnO/PNIPAm and ZnO/P(NIPAmco-AAc) decreased, while the temperature properties were improved. It was concluded that both were heat-shrinkable hydrogels. The ESR value of the ZnO/P(NIPAm-co-AAc) hydrogel was much higher than that of the ZnO/PNIPAm hydrogel. This may have been caused by the hydrophilic group of -COOH in the AAc. More hydrophilic groups resulted in a greater swelling ability. In Fig. 6b, the ZnO/PNIPAm hydrogel had a temperature response at approximately 32 °C, which was consistent with the lower critical phase transition temperature (LCST) of PNIPAm. This indicated that the ZnO did not change the unique thermo-responsive property of PNIPAm. But the DSC curves of ZnO/P(NIPAmco-AAc) hydrogel had a inflection point at 35.2°C, which indicated it had a temperature response at 35.2°C. After the addition of AAc into the hydrogel, the PNIPAm molecular chain was hindered by the interaction of NIPAm and AAc in the hydrogel (Woodward *et* *al.* 2003). The free space was greatly reduced when the hydrogel began conformational transformation, so the phase transition was also bound to a considerable extent. Because AAc is a hydrophilic substance, its addition increases the hydrophilicity of the gel. To bring about the gel hydrophilic/hydrophobic transition, the temperature must be raised, and thus the LCST was increased.

Deswelling and Swelling Kinetic Test of Hydrogels

The deswelling and swelling kinetic test of ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels is shown in Fig. 7.



Fig. 7. a) Kinetic curves of composite hydrogels water retention at 50 °C deionized water; b) kinetic curves of composite hydrogels swelling ratio at 20 °C deionized water within 1 h

According to Fig. 7a, the ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels shrank in deionized water at 50 °C. The water loss rate of the ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels was the most rapid in the period 0 to 5 min. Between 5 and 30 min, the hydrogels continued to lose water, while the dehydration rate slowed down. Past 30 min, the rates moved towards a constant and reached equilibrium. This was because most of the free water in the hydrogels moved to the 50 °C distilled water and equilibrium again. The water loss rate of the ZnO/PNIPAm hydrogel was 60.76% when the immersion time was 5 min, which was 7.96 times that of the ZnO/P(NIPAm-co-AAc) hydrogel. The deswelling performance of the ZnO/PNIPAm hydrogel was much better than that of the ZnO/P(NIPAm-co-AAc) hydrogel. This may have been caused by the polarity effects of AAc. The added AAc amplified the 3D network structure of the hydrogel and the NIPAm relative ratio decreased. The shrinkage degree of P(NIPAm-co-AAc) decreased

and the hydrophobic interaction was not notable. According to Fig. 7b, the ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) hydrogels both swelled in water within 1 h, and the water absorption rate was the fastest from 0 to 5 min. After 40 min, the swelling ratio of the ZnO/PNIPAm hydrogel was considerably lower than that of the ZnO/P(NIPAm-co-AAc) hydrogel. The swelling rate of the ZnO/P(NIPAm-co-AAc) hydrogel was higher than that of the ZnO/PNIPAm hydrogel, and the response rate was faster. This was due to the addition of AAc, which increased the hydrophilicity of the gel, thus the ZnO/P(NIPAm-co-AAc) hydrogel showed better swelling properties.

Antifungal Activity

The inhibition zones of the prepared nanocomposite hydrogel films against *Penicillium citrinum*, *Trichoderma viride*, and *Aspergillus niger* of bamboo for one week are shown Fig. 8 and Table 2.



Fig. 8. Photographs of the inhibition zone of the prepared nanocomposite hydrogels against *P. citrinum, T. viride,* and *A. niger* of bamboo for one week

Table 2.	Inhibition Zones	of the Prepared Nanocomposite Hydrogels	Against P.
citrinum,	T. viride, and A.	niger of Bamboo for One Week	

Samples/Inhibition Zones	P. citrinum (mm)	T. viride (mm)	A. niger (mm)
PNIPAm	0	0	0
ZnO/PNIPAm	20 ± 2	25 ± 2	0
ZnO/P(NIPAm-co-AAc)	33 ± 5	35 ± 5	10 ± 2

The in vitro antimicrobial properties of the PNIPAm, ZnO/PNIPAm, and ZnO/P(NIPAm-co-AAc) hydrogels were comparatively tested against P. citrinum, A. niger, and T. viride of bamboo via a disk diffusion test. Inhibition zones under and around the tested samples for mold growth were visually detected and are listed in Table 2. The results suggested that the pure hydrogels do not show toxicity, but the ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) nanocomposite hydrogels shows toxic effect on mold, which is confirmed by inhibition zone. The results in Table 2 show that the antimicrobial efficiency of the nanocomposite hydrogels was influenced by the concentration of the ZnO nanoparticles. The ZnO/PNIPAm nanocomposite hydrogel had no antimicrobial effect on A. niger of bamboo, likely because the activity of A. niger was too strong. The ZnO/P(NIPAm-co-AAc) nanocomposite hydrogel had a small antimicrobial effect on A. niger of bamboo, and strong antimicrobial properties against T. viride and P. citrinum of bamboo. This was attributed to the photocatalysis mechanism of nano-ZnO, which generates hydrogen peroxide and causes the degradation of the membrane structure of the cell (Sawai et al. 1998; Espitia et al. 2012; Ma et al. 2013). Overall, hydrogels with more ZnO nanoparticles demonstrated greater antimicrobial properties.

CONCLUSIONS

- 1. Monodispersed nano-ZnO P(NIPAm-co-AAc) hydrogel was produced *via* an *in situ* method.
- 2. The ZnO/P(NIPAm-co-AAc) hydrogel contained more nano-ZnO particles and had better swelling properties compared to the ZnO/PNIPAm hydrogel. The response temperature was 35 °C.
- 3. The ZnO/PNIPAm and ZnO/P(NIPAm-co-AAc) nanocomposite hydrogels were shown to have better antimicrobial properties on common bamboo mold than the pure hydrogels. The hydrogels that contained more ZnO nanoparticles demonstrated greater antimicrobial properties.

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