Hybrid Cellulose-Copper Nanoparticles Embedded in Polyvinyl Alcohol Films for Antimicrobial Applications

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ABSTRACT

The long-term goal of this research is to develop a cellulose based composite with antimicrobial properties for active food packaging applications.

The incorporation of the hybrid cellulosic materials and copper nanoparticles in thermoplastic resins (used in the packaging field) represents a promising way to control undesirable growth of microorganisms on the surface of food.

In our current research hybrid cellulose-copper nanoparticles were embedded into thermoplastic resins polyvinyl alcohol (PVA). The resulting composites were investigated in terms of antimicrobial, mechanical, thermal and copper ion release properties.

EXPERIMENTAL

- Copper nanoparticles were synthesized *in situ* on TEMPO nanofibrillated cellulose (TNFC) and carboxymethyl cellulose (CMC).
- The resulting hybrid cellulose-copper nanoparticles embedded in PVA was fabricated using solvent casting method.
- The prepared PVA composite films were coded as PVA/TNFC-Cu0.6 and PVA/CMC-Cu0.6 according to cellulose template (i.e., TNFC and CMC) and the weight ratio of copper in the composites (i.e., 0.6 wt.%).
- Morphology of copper nanoparticles on the cellulose templates was observed under transmission electron microscopy (TEM).
- Antimicrobial activities against *E.coli* DH 5α were tested.
- Copper ion release from the films was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).
- Crystalline structure of copper nanoparticles within the films was analyzed by X-ray diffraction (XRD).
- Thermal property was analyzed using thermogravimetric analysis (TGA).
- Mechanical property was determined using dynamic mechanical analysis (DMA).

RESULTS AND DISCUSSION

1. Morphology of copper nanoparticles on cellulosic templates

Fig.1: Copper nanoparticles on (a) TNFC and (b) CMC

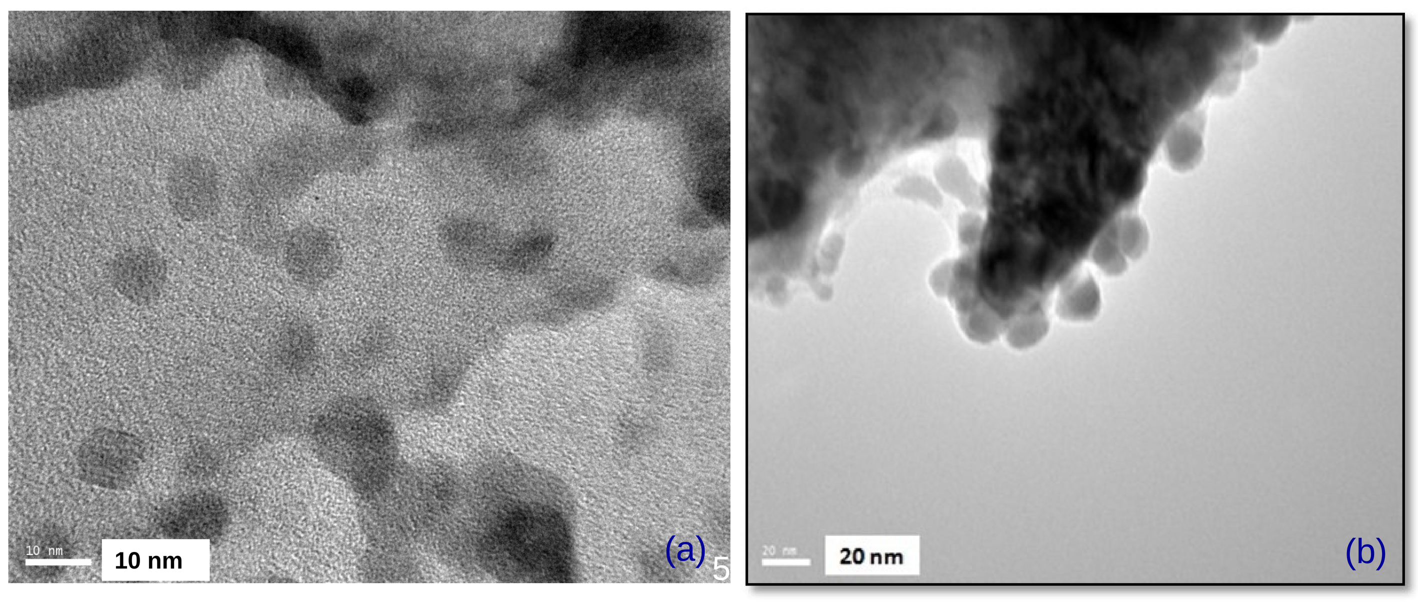


Figure 1 displays TEM images of copper nanoparticles on TNFC (a) and CMC (b) templates with diameters of **9$\pm$2.0 nm** and **12.5$\pm$2.8** nm, respectively.

2. Antimicrobial activity as function of copper nanoparticles contents within PVA composite films

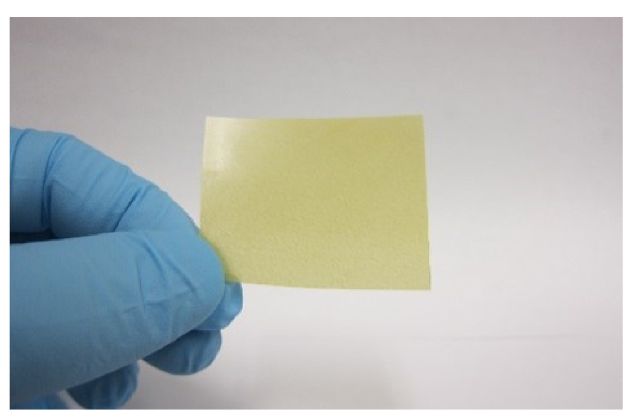


Fig.2: Photograph of a PVA/TNFC-copper nanoparticles film (copper loading: 0.6 wt.%).

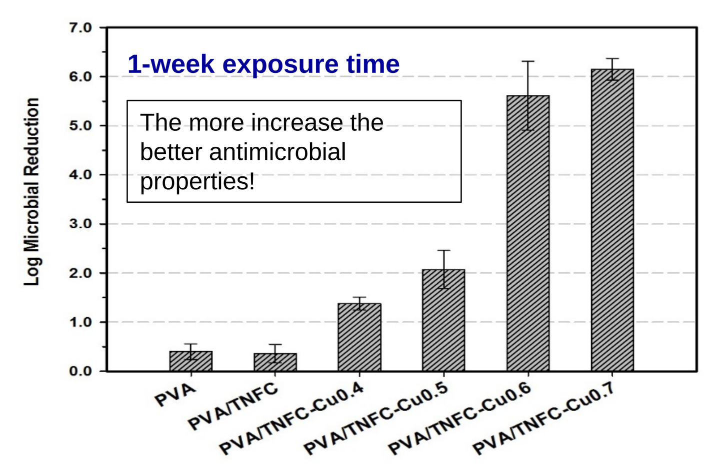


Fig.3: Microbial activity as a result of 1-week of exposure of *E.coli* to PVA/TNFC-copper nanoparticles with different copper contents.

Figure 3 displays that the antimicrobial performance is improved when more copper is added in those PVA films.

3. Antimicrobial activity and copper ion release as function of exposure time

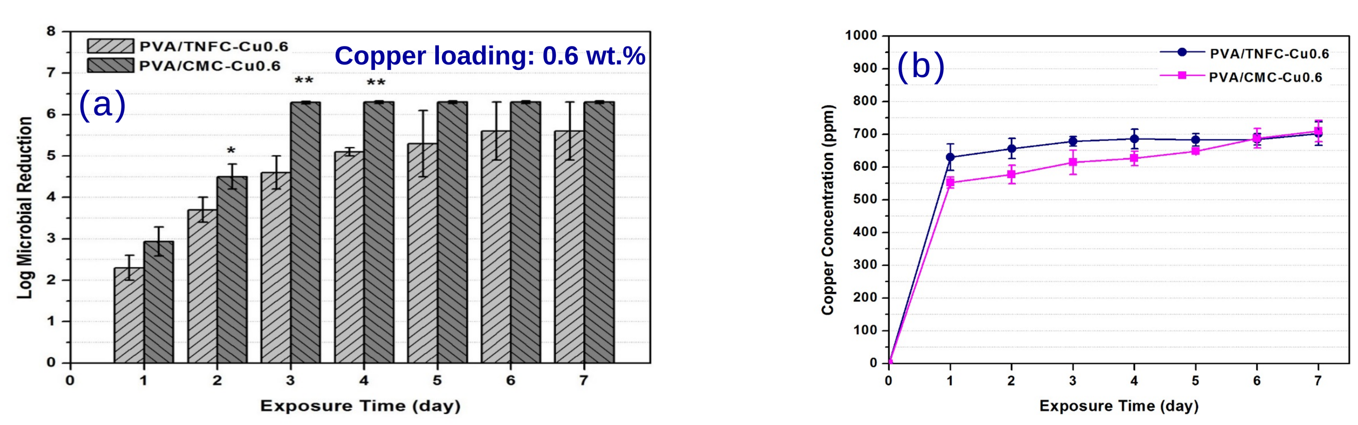


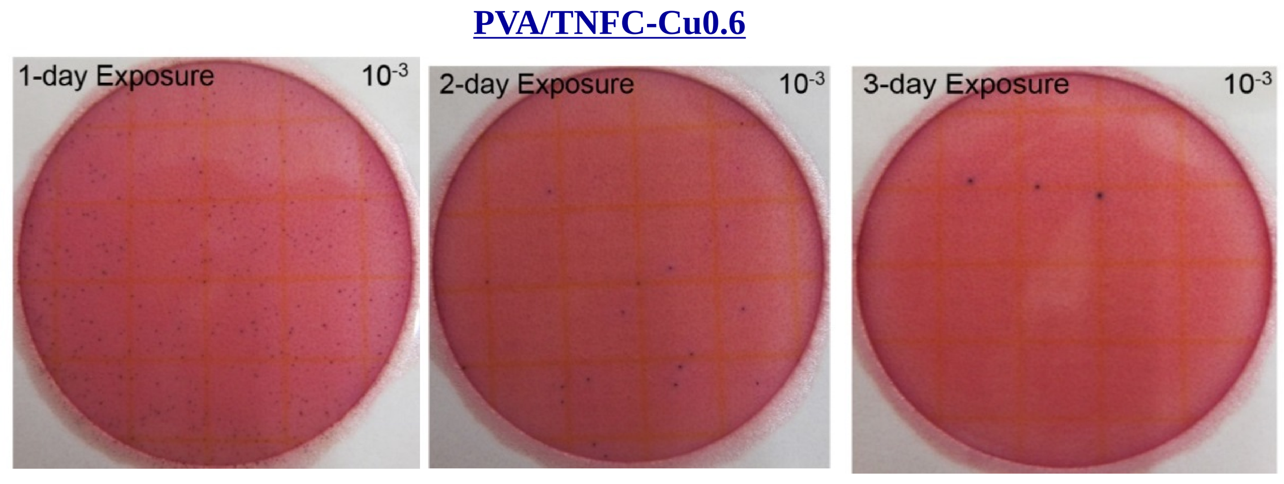
Fig.4: (a) Microbial reduction induced by PVA containing hybrid cellulose-copper nanoparticles after various exposure time. The asterisks refer to significant level regarding antimicrobial efficacy of PVA/CMC-0.6 compared to PVA/TNFC-Cu0.6 at the same exposure time: $p < 0.05$ (*), $P < 0.01$ (**); (b) The amount of copper leaching from the films in the medium.

Bacterial reduction increased over time and had similar trend with the rate of copper ion leaching from both PVA composite films as shown in Fig. 4.

Note: approximately 90% less cellulosic material was needed to stabilize the same copper when using TNFC template compared to CMC template to get similar film antimicrobial performance.

4. Representative examples of the results of bacterial enumeration of survival *E.coli* DH 5α

PVA/TNFC-Cu0.6



PVA/CMC-Cu0.6

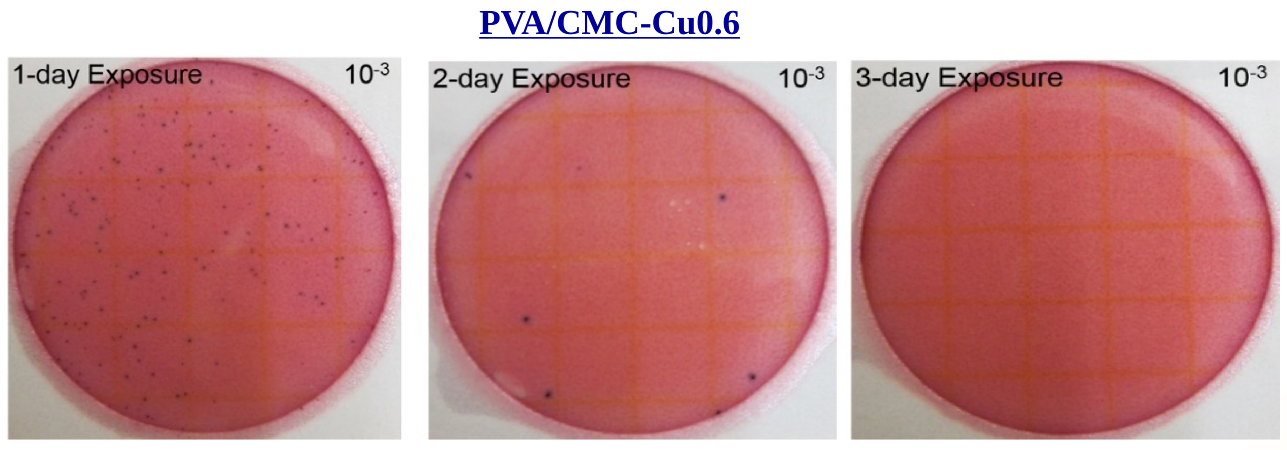


Fig. 5: Bacterial enumeration of the *E coli* culture exposed to PVA/TNFC-Cu0.6 film (above) and PVA/CMC-Cu0.6 film (below) after various exposure time.

Figure 5 shows that survival *E.coli* population on PVA/CMC-Cu0.6 film are lower compared with PVA/TNFC-Cu0.6 film at the same exposure time.

5. Crystalline structure of copper nanoparticles within the films

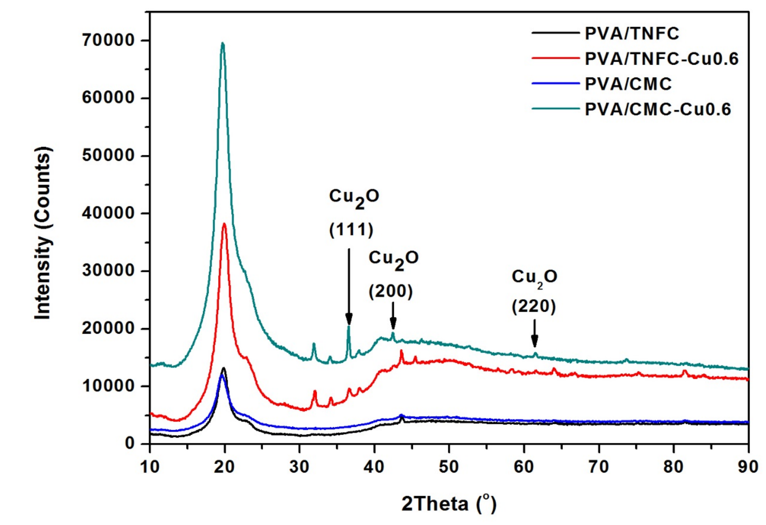


Fig.6: XRD patterns of PVA composite films.

It is reported by Park et al. (2012)[1] that Cu_2O and Cu (I) ions are more toxic than CuO and Cu (II) ions.

Figure 6 displays that the intensity of characteristic peaks for crystal Cu_2O within PVA/CMC-Cu0.6 film is much stronger than that in PVA/TNFC-Cu0.6, suggesting higher amount of crystal Cu_2O was present in PVA/CMC-Cu0.6 film, this may explain why PVA/CMC-Cu0.6 inactivated more *E.coli* as shown in Fig. 5.

6. Thermal property

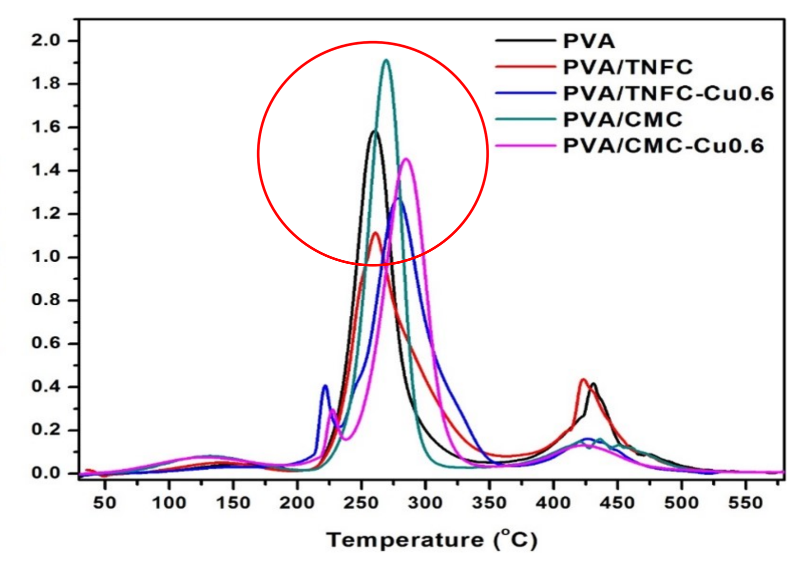


Fig.7: DTG curves of PVA composite films (the decomposition temperature corresponding to the maximum weight loss (*indicated by red circle*) of PVA, PVA/TNFC, PVA/TNFC-Cu0.6, PVA/CMC, PVA/CMC-Cu0.6 was 260, 263, 278, 269, and 285 ℃, respectively).

Figure 7 shows that the maximum decomposition temperatures of PVA/TNFC-Cu0.6 and PVA/CMC-Cu0.6 have increased by 18 ℃ and 25 ℃ over pure PVA, respectively.

7. Dynamic mechanical property

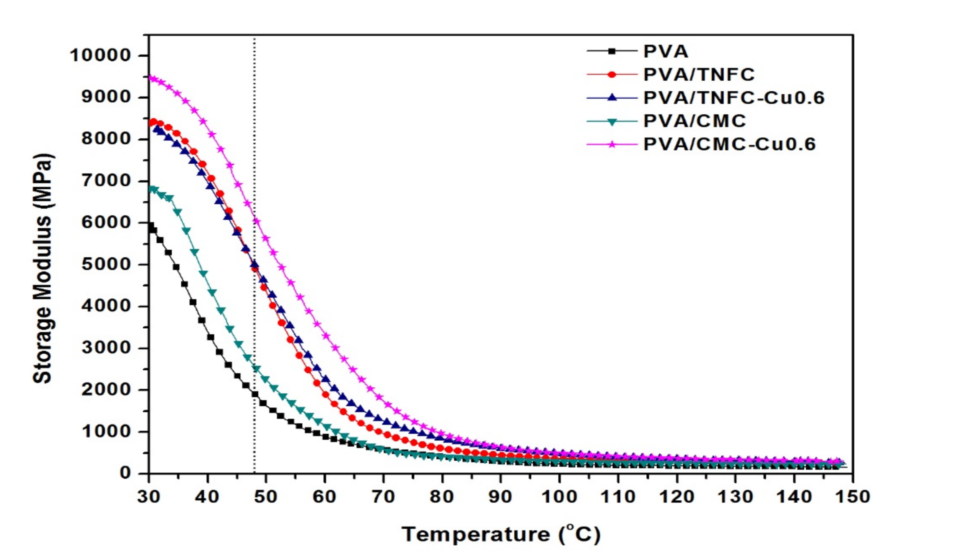


Fig.8: Storage modulus as function of temperature for PVA composite film.

Figure 8 displays that storage modulus for both PVA/TNFC-Cu0.6 and PVA/CMC-Cu0.6 has significantly enhanced.

CONCLUSIONS

1. The optimum copper loading for antimicrobial efficacy in the PVA/TNFC matrix is 0.6 wt.%.
2. Both PVA composite films containing 0.6 wt.% copper possessed strong antimicrobial activities against *E.coli* DH 5α, over 99.99 % of *E.coli* were inactivated after 3-day exposure to either PVA/TNFC-Cu0.6 film or PVA/CMC-Cu0.6 film.
3. Approximately 90% less cellulosic material is required when using TNFC as copper template compared to CMC template to get similar film antimicrobial performance.
4. Antimicrobial activities depend not only on the amount of copper ion release, but also on oxidation states of copper.
5. The incorporation of the hybrid cellulose-copper nanoparticles improves the thermal stability and enhances the film mechanical performance.

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[1]Park et al. *Environmental Science & Technology*, 2012, *46*(20), 11299-11304.