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Chitosan/titanium dioxide nanocomposite coatings: Rheological behavior and surface application to cellulosic paper

Yanjun Tang[a,b,c,*], Xiulan Hu[a], Xinqi Zhang[a], Daliang Guo[a], Junhua Zhang[a], Fangong Kong[d]

[a] National Engineering Laboratory of Textile Fiber Materials and Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China
[b] Key Lab of Biomass Energy and Material, Nanjing 210000, Jiangsu Province, China
[c] Key Laboratory of Renewable Energy, Chinese Academy of Sciences, Guangzhou 510070, China
[d] Key Lab of Pulp and Paper Science & Technology of Ministry of Education, Qilu University of Technology, Jinan 250353, China

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ABSTRACT

Incorporation of nanofillers into a polymeric matrix has received much attention as a route to reinforced polymer nanocomposites. In the present work, an environmentally friendly chitosan (CTS)/titanium dioxide (TiO_2) nanocomposite coating was designed/prepared and subsequently employed for imparting antibacterium and improved mechanical properties to cellulosic paper *via* surface coating. Effect of TiO_2 nanoparticle loadings on the rheological behavior of nanocomposite coatings was investigated. Surface application of CTS/TiO_2 nanocomposite coatings to cellulosic paper was performed, and the antibacterial activity and mechanical properties of surface-coated cellulosic paper were examined. Results showed that the increased TiO_2 nanoparticle loadings decreased the viscosity and dynamic viscoelasticity of the as-prepared coatings, and improved the antibacterial activity and mechanical properties of surface-coated cellulosic paper. The optimum loading of TiO_2 nanoparticles was identified at 10%. This work suggested that CTS/TiO_2 nanocomposite coatings may have the potential to be used as a promising antibacterial protective coating for paper packaging.

1. Introduction

Due to the increasing awareness of infectious diseases caused by different microorganisms, the development and application of functional antibacterial materials received great attention. Among these antibacterial materials, antibacterial cellulosic paper is generally considered to be one of the most promising candidates largely because of its inherent advantages of cellulosic paper, particularly environmental benefits (Liu, Lin, Chen, & Huang, 2016). In general, antibacterial paper holds great promise for many applications, *e.g.*, food wrappers, hospital paper, indoor environmental protection paper, and sanitary paper (Ling, Luo, Luo, Wang, & Sun, 2013; Nechita, Bobu, Parfene, Dinica, & Balan, 2015). In this context, it is thus of great practical interest to develop an efficient process for imparting antibacterial properties to conventional cellulosic paper.

In general, cellulose-based antibacterial paper can be produced *via* direct wet end addition of antibacterial agents, surface coating and impregnation (a material with antibacterial property is made to permeate the fiber structure, rather than merely coat on the surface) (Shen, Song, Qian, & Ni, 2011a; Shen, Song, Qian, & Ni, 2011b; Shen et al., 2016). Nevertheless, the properties of antibacterial cellulosic paper were highly dependent upon the used chemicals. Over the past few years, various antibacterial agents including inorganic bactericide, organic bactericide and natural bactericide have been applied in the production of antibacterium cellulosic paper (Hassabo, Nada, Ibrahim, & Abou-Zeid, 2015). As a matter of fact, chitosan, known to have high antimicrobial activity, has been widely used as antibacterial components for a wide range of application because of its biodegradable, non-toxic and non-allergenic natures (Liu et al., 2013; Zhang, Yu, Long, Yang, & Wang, 2016). In particular, the application of chitosan-based nanocomposite in cellulosic paper has gained increasing attention because it is capable of imparting the cellulosic paper with reinforced mechanical properties in addition to antimicrobial activity. For instance, Ling et al. (2013) studied the production of Ag NP quaternized carboxymethyl chitosan/organic montmorillonite (QAOM) nanocomposite using an environmentally friendly pro-

* Corresponding author at: National Engineering Laboratory of Textile Fiber Materials and Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China.
E-mail address: tangyj@zstu.edu.cn (Y. Tang).

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cess and its application to cellulosic paper *via* surface coating and wet-end addition process, respectively. The results revealed that the presence of QAOM nanocomposites not only imparted the cellulosic paper with desired antimicrobial activity, but positively affected the tensile, tear, and bursting strength of the finished paper. Moreover, it was also suggested that the antibacterial capacity of cellulosic paper produced by surface coating was notably stronger than that derived from wet-end addition process. Nechita et al. (2015) evaluated the potential of two (bio) active compounds, *i.e*., quaternary ammonium salts (QAS) and quaternary chitosan (QCh) as the component of antimicrobial coating for packaging paper applications. The results indicated that the QAS immobilized on ZnO particulates showed good antimicrobial activity against both gram-positive bacteria and fungi, and the QCh films were proved to be very effective for bacterial inhibition and paper strength improvement, but less effective against fungi. Lv et al. (2014) reported that a novel chitosan based polymer with long side chains (2,3-epoxypropyltrimethyl ammonium chloride (ETA) modified chitosan-graft polyacrylamide, typically denoted as CTS-ETA-g-PAM), was designed/developed and employed to modify the pulp fibers. The results showed that the used CTS-ETA-g-PAM led to the improvement of the mechanical properties of the handsheets, and the loading of CTS-ETA-g-PAM was found to exert a strong influence on the antibacterial activities. These works provided evidence that tailored chitosan-based nanocomposites may have a great opportunity to improve the antibacterial activity and mechanical properties of cellulosic paper.

In the present work, an environmentally friendly CTS-based nanocomposite coating was designed/developed. In the coating formulations, CTS was used as the main antimicrobial component and modified starch served as the binders instead of petroleum-based latex binders. More importantly, TiO_2 nanoparticles, one of the most potential ultraviolet (UV) light-sensitive inorganic bactericide with intrinsic photoelectric properties (Geng, Filipe, & Pelton, 2008), was employed as a functional nanofiller in this nanocomposite coatings. For a deep understanding of coating properties, the rheological behavior of the obtained CTS/TiO_2 nanocomposite coatings was investigated. Subsequently, surface application of CTS/TiO_2 nanocomposite coatings to cellulosic paper was conducted, and the change in related properties of the products was identified. In general, the developed CTS/TiO_2 nanocomposite coatings were effective in imparting the cellulosic paper with high antibacterial activity and improved mechanical properties, thus showing great potential for antibacterial packaging application.

2. Experimental

2.1. Materials

Chitosan (CTS, degree of deacetylation ≥90%) was provided by Shanghai Zhanyun Chemical Co., Ltd., China. Titanium dioxide (TiO_2) nanoparticle with an average particle size of 25 ± 5 nm was obtained from Xuancheng Jing Rui New Materials Co., Ltd, China. Modified starch (MS) with a solid content of 52% was supplied by Hangzhou Paper Technology Co., Ltd., China. The glycerol, acetic acid and sodium dodecanoate (SD) were purchased from Hangzhou High Precision Refining Chemical Co., Ltd., Sinopharm Chemical Reagent Co., Ltd. and Hangzhou Mike Chemical Reagent Co., Ltd., China, respectively. Cellulosic paper with a basic weight of 70 g/m^2 used as substrates for surface coating was supplied by Asia Pulp & Paper Co., Ltd.

2.2. Preparation of CTS/TiO_2 nanocomposite coatings

The CTS/TiO_2 nanocomposite coating was prepared schematically according to the experimental procedure as presented in Fig. 1. Various nanocomposite coatings were prepared by varying the loadings of TiO_2 nanoparticles on the premise of the fixed solid content of 8% for all coating samples. A typical run was done based on the procedure as presented in the literature (Zhang, Xiao, & Qian, 2014), 7.98 g CTS (dry weight) was initially added into 183 mL acetic acid solution (2%, v/v) in a round-bottom flask and then kept stirring (IKA RW 20) at 320 rpm for 30 min to form a suspension, followed by 2 mL glycerol addition into the system and further stirring for 20 min. Afterwards, CTS/MS suspension was obtained through adding 8.04 g MS to the above suspension and continuous stirring for 40 min. Meanwhile, TiO_2 nanoparcticle was dispersed in 2% (v/v) acetic acid in the presence of SD. Subsequently, the TiO_2 nanoparcticle suspension was totally transferred to the above CTS/MS suspension. In order to evaluate the influence of TiO_2 nanoparticles addition on the coating rheological behavior and the overall properties of surface-coated paper, various loading levels (based on total dry weight of CTS and TiO_2) of TiO_2 nanoparticles at 5, 10, 15, 20% were present into the above suspension. The mixed suspension was continuously stirred at 500 rpm for 60 min.

2.3. Preparation of surface-coated paper

As also demonstrated in Fig. 1, the prepared nanocomposite coatings with different loadings of TiO_2 nanoparticles were coated on the commercially available cellulosic paper using a laboratory scale K303 multicoater (RK Print Coat Instruments Ltd., UK) at a constant sizing speed of 15m/min. Afterwards, the surface-coated paper was dried at room temperature for 24 h. The total coating amount of CTS/TiO_2 on the surface of blank paper was controlled at about 5 g/m^2.

2.4. Measurement of rheological behavior of CTS/TiO_2 nanocomposite coatings

The rheological behavior of CTS/TiO_2 nanocomposite coatings was measured by using a Physica MCR301 advanced cylinder rotary rheometer (Anton Paar, Austria) at 25 °C. The steady shear rheological curves of CTS/TiO_2 nanocomposite coatings were measured at a shear rate range of 0.1–1000 s^{-1}. The oscillatory shear measurement was performed at a given strain level of 1.0%, which was within the linear viscoelastic region as determined by dynamic strain sweep experiments. The storage modulus (G') representing the elastic properties, and the loss modulus (G'') standing for the viscous properties, were employed to describe the viscoelasticity of CTS/TiO_2 nanocomposite coatings (Peng, Ren, & Sun, 2011).

2.5. Measurement of mechanical properties of surface-coated paper

The measurement of tensile and tear index for the blank paper and CTS/TiO_2 coated paper was performed following the relevant TAPPI test methods, using a tensile tester (D-KZ 300) and tear strength meter (J-SLY1000). Furthermore, the optical properties were evaluated by measuring the brightness and opacity using a DN-B brightness tester.

2.6. Measurement of air permeability and water absorption of surface-coated paper

The air permeability of blank paper and coated paper samples was determined (SE166, L&W)in accordance with ISO 5636-2: