



## Research Paper

# Enhanced flame-retardant properties of cellulose fibers by incorporation of acid-resistant magnesium-oxide microcapsules



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## ABSTRACT

Magnesium oxide (MgO) microcapsules were synthesized via in-situ emulsion polymerization as confirmed by Fourier transform infrared spectroscopy and scanning electron microscopy. Pure MgO and the MgO microcapsules were separately incorporated into cellulose fibers by blend wet spinning. Inductively coupled plasma-emission spectroscopy results revealed that cellulose fibers modified with the MgO microcapsules contained more Mg<sup>2+</sup> than those modified by pure MgO, indicating more acid resistance. The flammability and thermal degradation of modified cellulose fibers (cellulose-Mg fibers) were studied by calorimeter (CONE), thermogravimetry (TGA), and the determination of the limiting oxygen index (LOI). The minimal LOI value obtained for the cellulose-Mg fibers was 35, being much higher than that of the unmodified cellulose fiber (19). The heat release rate of the cellulose-Mg fibers was significantly lower than that of the non-doped ones. The TGA curves showed that the generated residues increased from 13.79% (cellulose fiber) to 30.26% (cellulose-Mg fiber).

## 1. Introduction

In the recent years, the awareness of fossil fuel shortage and environmental pollution incited scientists to develop sustainable solutions such as the exploitation and utilization of regenerated cellulose fibers. Indeed, regenerated cellulose fibers (viscose fibers) represent the most important derivatives of biomass and present the advantages of being both natural and fossil-based fibers positioning cellulose fibers as one of the most potential alternative sources of biopolymers (Matkó et al., 2005; Singh, Simmons, & Vogel, 2009). Viscose fibers are versatile materials found in many areas of application such as textile, building, public transportation, and electrical equipment due to their multiple properties that are suitable for the industry and the end-user such as low cost, non-toxicity, recyclability, biodegradability, excellent air permeability, and ecological advantage (Dittenber & GangaRao, 2012; Matkó et al., 2005; Santamala et al., 2016). However, cellulosic textiles such as the ones made of viscose fibers are easily flammable and the related fires are difficult to extinguish due to the low value of the limiting oxygen index (LOI) of cellulose fibers of only 19% (Tomak & Cavdar, 2013). Fortunately, various filler-functionalized polymer composites presenting enhanced compatibility, photocatalytic property and lipophilicity had been synthesized through different methodologies (Choi et al., 2012; Han et al., 2014; Reddy,

Hassan, & Gomes, 2015; Reddy et al., 2016; Reddy, Lee, & Gopalan, 2007; Son, Raghu, Reddy, & Jeong, 2016).

To overcome this disadvantage, filler-functionalized viscose fibers were obtained by the incorporations of different types of flame-retardants into spinning solution. Flame retardants can be categorized as inorganic and organic flame-retardants depending on their chemical nature (Lv et al., 2014). For examples, organic flame-retardants containing halogen, nitrogen, and phosphorus compounds, and cyclo-triphosphazene were extensively employed to impart flame retardancy to cellulose fibers (Gaan & Sun, 2007; Horrocks, 2011; Jiang, Jin, & Park, 2015; La Guardia & Hale, 2015). The incorporation of the named flame-retardants prevented the formation of levoglucosan and other flammable volatiles by promoting the formation of char when burning. However, the use of these conventional flame retardants are harmful to the environment and toxic to human beings due to the generation of toxic gases after combustion (Cheema, El-Shafei, & Hauser, 2013; Xu et al., 2014). In contrast to organic flame-retardants, inorganic flame-retardants presented more advantages such as excellent thermal stability, no volatilization and therefore long-term effect, and non-toxicity (Gashti, Alimohammadi, & Shamei, 2012; Lee et al., 2011; Lv et al., 2014; Zhang & Horrocks, 2003). In particular, it was reported that metal ions could influence the kinetics of thermal decomposition and pyrolysis behavior of cellulose fibers by decreasing

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the production of levoglucosan and flammable volatiles while increasing the yields of the generation of char, water, and other low molecular-weight compounds (Collard, Blin, Bensakhria, & Valette, 2012; Hajibeygi, Shabaniyan, Omid-Ghallemohamadi, & Khonakdar, 2017; Xu et al., 2014; Yaman, 2004).

Since the last decade, our team intensely investigated biomass fibers and more specifically flame-retardant cellulose fibers. We provided evidences supporting that metal ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Zn}^{2+}$  enhanced the flame retardant property of cellulose fibers when incorporated by ion exchange and grafting (Shi et al., 2017; Xu et al., 2014; Zhang et al., 2011, 2016). Recently, literature articles reported that nanometer magnesia presented attractive properties for our research interests. Indeed, nanometer magnesia was halogen-free and non-toxic, exhibited higher refractory insulation and generated only a low amount of smoke during combustion. Moreover, mixtures containing nanometer magnesium, sawdust, and shavings are commonly used to manufacture refractory materials for light and sound insulation applications and are also found in adiabatic refractory fiber boards and metal ceramic (Najafi, 2016a, 2016b; Qiu, Peng, Yue, Guo, & Zhang, 2016). Unfortunately, our previous attempt for incorporating metal ions was not satisfying because of the low grafting ratio, inefficient ion exchange rate, and complicated grafting process. Alternatively, the blend wet spinning is a simple and direct method. However, when incorporating a flame retardant in fibers by blend wet spinning, one is mainly confronted to the limited reaction of the additive, namely the flame retardant, with the coagulating bath. In fact, magnesium oxide was seriously eroded by sulfuric acid when a spinning solution of cellulose penetrated the coagulating bath. Besides, the microencapsulation technique proved to be an effective protection method of sensitive molecules such as fragrances, antimicrobial agents, dyes, and phase-change materials among others (Gashti et al., 2012; Hu, Yao, Liu, Ao, & Zhang, 2009; Jimenez, Bellayer, Revel, Duquesne, & Bourbigot, 2013; Liang, Neisius, & Gaan, 2013). Furthermore, in-situ emulsion polymerization, the most widely used method in industry, which was employed to synthesize poly(styrene)-graphene nanocomposite, polystyrene/carbon nanotube composites and multifunctional core-shell structures such as  $\text{SiO}_2$ /Poly(3-aminophenylboronic acid) and iron oxide-conjugated polymer composite (Hassan, Reddy, Haque, Minett, & Gomes, 2013; Khan, Reddy, Snguanwongchai, Haque, & Gomes, 2016; Reddy et al., 2007; Reddy, Park, Sin, Noh, & Lee, 2009; Zhang, Lee, Reddy, Gopalan, & Lee, 2007). Until now, microencapsulation specifically applied for the protection of sensitive flame-retardant additives was rarely reported in the open literatures (Dong et al., 2016; Jiang et al., 2015; Lee et al., 2011; Liang et al., 2013; Reddy et al., 2007; Savas, Deniz, Tayfun, & Dogan, 2017; Yang, Wang, Huo, Wang, & Cheng, 2015).

Herein, the system composed of styrene and acrylic-acid copolymer was employed to prepare acid-resistant magnesium oxide (MgO) microcapsules due to their thermodynamic stability and acid resistance. Then, we doped cellulose fibers with MgO via a blend wet spinning process by the consecutive addition of neat MgO nanoparticles and then MgO microcapsules. It was worth noting that an excessive incorporation of MgO and MgO microcapsules could decrease the mechanical properties of the cellulose fiber, therefore, the additive amounts of MgO and MgO microcapsules were limited. The flame-retardant property and thermal degradation of the obtained cellulose fibers were investigated by inductively coupled plasma-emission spectroscopy (ICP-ES), limiting oxygen index (LOI), cone calorimeter (CONE) and thermo-gravimetric analyzer (TGA). The results showed that the flame-retardant performance of the prepared cellulose fibers was significantly improved through incorporation of MgO. In addition, MgO microcapsules were more efficient than the neat ones in promoting the flame retardancy of the cellulose fibers due to their better acid resistance.

## 2. Experimental

### 2.1. Materials

Cellulose fibers (viscose fibers) were purchased from Hailong Industrial Co., Ltd. (Shandong, China). Sodium hydroxide (NaOH) and sodium dodecyl sulfate (SDS) were obtained from China Pharmaceutical Group Chemical Reagent Co., Ltd. (Shanghai, China) and used without any prior purification steps. Styrene (St) was obtained from China Pharmaceutical Group Chemical Reagent Co., Ltd. (Shanghai, China) and distilled under reduced pressure before use. Acrylic acid (AA) was obtained from China Pharmaceutical Group Chemical Reagent Co., Ltd. (Shanghai, China) and subjected to an activated-carbon adsorption before use. 1-((Cyano-1-methylethyl)azo)formamide (CABN) and MgO (99.9%) were purchased from Aladdin and used directly without prior treatment.

### 2.2. Methods

#### 2.2.1. Preparation of magnesium oxide microcapsules

The schematic diagram of the preparation of the MgO microcapsules is shown in Fig. 1. The MgO microcapsules were synthesized by a typical water-in-oil emulsion method. The external phase of the microcapsule was composed of the copolymer of St and AA. Briefly, St (5 g) and AA (10 g) were separately homogenized under magnetic stirring at 40 °C for 2 h and then mixed together under magnetic stirring at 40 °C for another 3 h. The internal phase contained pure MgO and SDS. More specifically, pure MgO (7.5 g) was dispersed in deionized water

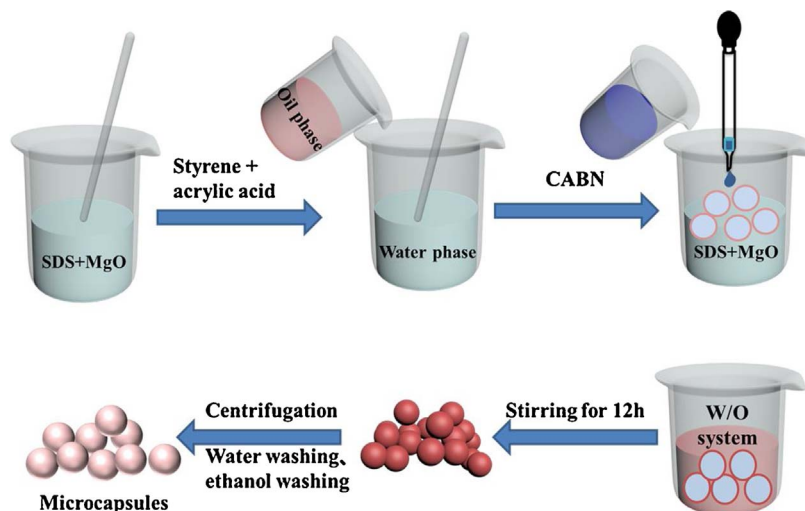


Fig. 1. Scheme of synthesis of magnesium oxide microcapsules.

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