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## Uniform nanoparticle coating of cellulose fibers during wet electrospinning†

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This work outlines a newly developed method that allows electrospun cellulose fibers to be coated with nanoparticles during dry-jet wet electrospinning. Cellulose fibers were wet electrospun from a room temperature ionic liquid solvent into a coagulation bath containing an aqueous suspension of magnesium hydroxide nanoparticles to prepare composites of nanofibers coated with functional nanoparticles. Flame retardant cellulose–magnesium hydroxide coated composite fibers were prepared to demonstrate this novel electrospinning method. The placement of the nanoparticles exclusively on the surface of the cellulose fibers dramatically impacted the functionality of the fibers. Electrospun cellulose fibers exhibited an onset of combustion in air at 239 °C and a maximum mass loss at 302 °C. Cellulose fibers with Mg(OH)<sub>2</sub> nanoparticles (<50 nm avg. diameter) inside them exhibited an onset of combustion at 267 °C and a maximum mass loss at 315 °C. Cellulose fibers with the same nanoparticles uniformly coated on their surfaces exhibited an onset of combustion at 276 °C and a maximum mass loss at 318 °C. When larger Mg(OH)<sub>2</sub> nanoparticles (>100 nm avg. diameter) were used, the onset of combustion was 185 °C and the maximum mass loss was at 216 °C when nanoparticles were inside the fibers, and the onset of combustion was 263 °C and the maximum mass loss was at 317 °C for Mg(OH)<sub>2</sub> nanoparticle coated cellulose fibers. Simple flame tests showed a similar trend, with nanoparticle-coated fibers being fire resistant and fibers with nanoparticles inside burned rapidly upon exposure to an open flame.

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### 1. Introduction

Electrospinning was first reported in 1934,<sup>1</sup> and eventually experienced a rapid increase in development in the 1990's, which continues today.<sup>2,3</sup> A major technological advance for electrospinning came with the discovery and the expansion of a class of solvents known as room temperature ionic liquids (RTILs).<sup>4,5</sup> These novel solvents are liquid salts that can be custom-designed to exhibit a large number of chemical, physical, and electrical properties.<sup>6–9</sup> RTILs make it possible to electrospin certain polymers that are insoluble in conventional solvents. The most prominent example is the wet

electrospinning of cellulose into a coagulation bath using dialkylimidazolium-based RTILs.<sup>6,10,11</sup> Unlike traditional electrospinning, this wet electrospinning of cellulose from RTIL results in cellulose fibers that slowly solidify in a coagulation bath in which RTIL is replaced by a co-solvent such as water, acetone, or alcohol, resulting in a hydrogel. This co-solvent is then removed from these hydrogel fibers by either standard desiccation or freeze-drying. While this method for the wet electrospinning cellulose nanofibers from RTILs has been widely reported, the exploitation of the gelled intermediate state of the fibers prior to hydrogel formation, present immediately after wet electrospinning into the coagulation bath, has not been described.

Here we report a novel technique for the synthesis of nanofiber composites in which functional nanoparticles (NPs) are embedded into the surface of wet electrospun cellulose fibers. Cellulose dissolved in the RTIL 1-ethyl-1-methylimidazolium acetate ([EMIM][Ac]) was electrospun into an aqueous coagulation bath that contained a suspension of two types of fire-retardant magnesium hydroxide NPs. This resulted in effective surface coating of fibers with nanoparticles, producing significantly different properties than fibers electrospun from a solution of [EMIM][Ac]-cellulose containing Mg(OH)<sub>2</sub> NPs.

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## 2. Experimental methods

### 2.1 Materials

Cellulose pulp (degree of polymerization approx. 1100) was obtained from Weyerhaeuser Co. (2449 Stagecoach Rd, Oglethorpe, GA 31068). The RTIL 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]), was obtained from Sigma-Aldrich (St. Louis, Missouri, USA). Magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) NPs (average particle size  $<50$  nm as determined by BET (performed by manufacturer)) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Milk of magnesia (CVS brand,  $80 \text{ mg mL}^{-1}$   $\text{Mg}(\text{OH})_2$  in water) was purchased from a local CVS pharmacy (average particle size  $>100$  nm having an average agglomerate size of  $\sim 2 \mu\text{m}$  as determined by electron microscopy). All solvents were purchased from Fisher Scientific (Pittsburgh, Pennsylvania) and used without further purification.

### 2.2 Preparation of electrospinning solution

Finely divided cellulose pulp (310 mg) was added to [EMIM][Ac] (19.7 g) to prepare a 1.55 wt% cellulose solution in RTIL. The mixture was mechanically stirred using a magnetic stir bar in a temperature controlled oil bath at  $80^\circ\text{C}$  for 8 h until a homogeneous solution was formed.

Cellulose- $\text{Mg}(\text{OH})_2$  solutions were prepared, following a similar method as used to prepare the cellulose solution in RTIL, with the addition of  $\text{Mg}(\text{OH})_2$  NPs. Specifically,  $\text{Mg}(\text{OH})_2$  NPs were added to [EMIM][Ac] and stirred for 10 min to yield a uniform dispersion. The cellulose pulp was then added, and the solution was then stirred at  $80^\circ\text{C}$  for 8 h until the cellulose dissolved completely. Cellulose-milk of magnesia solutions were prepared following the same method, however the milk of magnesia was freeze-dried prior to addition to the RTIL, which resulted in a certain degree of nanoparticle agglomeration. Both  $\text{Mg}(\text{OH})_2$  solutions (0.5 wt%) were further homogenized with ultrasonication in a Bransonic bath sonicator for 30 min at room temperature.

### 2.3 Electrospinning procedure

A previously reported dry-jet wet electrospinning technique was modified to produce micron-scale cellulose fibers as shown in Fig. 1.<sup>6,10</sup> The RTIL-cellulose solutions both with and without  $\text{Mg}(\text{OH})_2$  NPs were placed into a 5 mL syringe and connected to the spinneret (MECC, Ogori, Fukuoka, Japan) using PTFE tubing. The spinneret was fitted with a stainless steel needle with an internal diameter of 0.94 mm. The needle was connected to a high voltage power supply (CZE1000R, Spellman, Hauppauge, New York, USA), which is capable of generating a DC voltage up to 30 kV. Electrospun cellulose fibers were collected in a deionized aqueous coagulation bath to remove [EMIM][Ac] and solidify the fibers. In some cases the bath contained a suspension of  $\text{Mg}(\text{OH})_2$  particles in order to coat the surface of the cellulose fibers as they formed during the coagulation/solvent exchange. For the  $\text{Mg}(\text{OH})_2$  NP bath, approximately 300 mg of  $\text{Mg}(\text{OH})_2$  NPs were added to 100 mL deionized water to form a  $3 \text{ mg mL}^{-1}$   $\text{Mg}(\text{OH})_2$  NP coagulation bath. In the case of the milk of magnesia solution, a coagulation

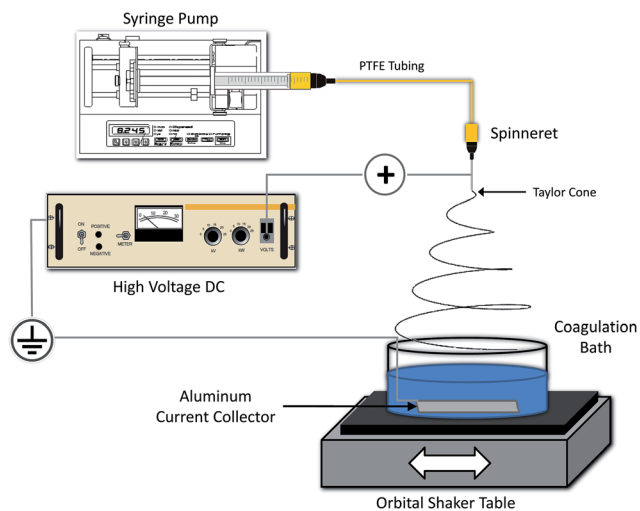


Fig. 1 The electrospinning setup for wet electrospinning of cellulose. The coagulation bath was placed on an orbital shaker table to aid in solvent exchange and to maintain the  $\text{Mg}(\text{OH})_2$  nanoparticle suspension when added.

bath of 100 mL was used with a  $\text{Mg}(\text{OH})_2$  concentration of  $20 \text{ mg mL}^{-1}$ . A small sheet of aluminum foil ( $20 \mu\text{m}$  thick) was electrically grounded and placed as the current collector on the bottom of the coagulation bath (inside of vessel). The coagulation bath was placed on top of a bench-top orbital shaker in order to both aid in the coagulation process by gently moving the solution and to maintain the uniform  $\text{Mg}(\text{OH})_2$  suspension during the electrospinning process. The distance between the needle tip and the surface of the water in the coagulation bath remained constant at 10 cm. The electrospinning solution was fed at a constant rate using a mechanical syringe pump (NE-1000, New Era Pump System Inc., Wantagh, New York, USA) at  $60 \mu\text{L min}^{-1}$ . The applied voltage was optimized to obtain sufficient spinnability of continuous fibers, ranging from 15–20 kV. Fibers collected in the coagulation bath formed an entangled web of flexible fibers, some of which had  $\text{Mg}(\text{OH})_2$  inside them, and some of which were coated with  $\text{Mg}(\text{OH})_2$  NPs. These fibers were recovered and washed with distilled water five times to remove traces of [EMIM][Ac] and excess  $\text{Mg}(\text{OH})_2$  NPs not fully embedded in the fiber surfaces. The resulting fiber mats were freeze-dried to form a loose structure similar to a cotton ball (see ESI†).

### 2.4 Electron microscopy

Samples were imaged using a field emission scanning electron microscope (FE-SEM) Zeiss SUPRA-55 (Oberkochen, Germany). All samples were sputter-coated with 1 nm of gold/palladium (Denton Vacuum Desk IV, Moorestown, NJ) prior to imaging. Images were obtained at a working distance of 2.8–4.1 mm using an acceleration voltage of 1 kV.

### 2.5 X-ray spectroscopy

The presence of  $\text{Mg}(\text{OH})_2$  NPs on the surface of coated fibers was confirmed with a Bruker D8-discover X-ray diffractometer using graphite monochromated  $\text{CuK}_\alpha$  radiation.

## 2.6 Thermal analysis

Thermogravimetric analysis (TGA) was performed using a computer-controlled TA Instruments TGA Q50 (New Castle, Delaware, USA) under an ambient air atmosphere at a heating rate of 10 °C per min.

## 3. Results

Using a modified dry-jet wet electrospinning method (Fig. 1) cellulose fibers were electrospun into a coagulation bath containing distilled/deionized water both with and without the addition of Mg(OH)<sub>2</sub> NPs for external fiber coating. For comparison, cellulose fibers that contained Mg(OH)<sub>2</sub> NPs inside of the cellulose fiber were also prepared. This resulted in neat cellulose fibers, cellulose fibers with Mg(OH)<sub>2</sub> inside them, and cellulose fibers coated with Mg(OH)<sub>2</sub> (Fig. 2). Electrospinning was carried out at an acceleration potential of 15–20 kV and a flow rate of 60 μL min<sup>-1</sup> at a fixed distance of 10 cm between needle tip and the surface of the aqueous coagulation bath, which contained Mg(OH)<sub>2</sub> NPs in the case of coated fibers.

The cellulose and cellulose–Mg(OH)<sub>2</sub> NPs composite fibers were collected, washed with distilled water to remove loosely bound magnesium hydroxide in the case of coated fibers, and freeze-dried to obtain “cotton ball” fiber meshes (see ESI†) for characterization. SEM was carried out to characterize the fibers produced by this method (Fig. 3 and ESI†).

Electrospinning from a mixed solution of [EMIM][Ac]–cellulose–Mg(OH)<sub>2</sub> NPs resulted in fibers that had a relatively small number of 5 nm Mg(OH)<sub>2</sub> NPs on their surfaces, which had migrated to the surface during electrospinning. Most of the NPs, however, are distributed throughout the interior of the fibers and can be seen where NP clusters at surface cracks and defects along the fiber (Fig. 3A and B). Micron scale aggregates of particles, some of which are formed during the drying of the milk of magnesia suspension prior to blending with the [EMIM][Ac]–cellulose solution, were detrimental to fiber strength and the spinnability of the solution. In contrast, fibers produced by electrospinning an [EMIM][Ac]–cellulose solution into an aqueous Mg(OH)<sub>2</sub> NP suspension resulted in a complete coverage of the fiber surfaces with 5 nm Mg(OH)<sub>2</sub> NPs (Fig. 3C and D). The NPs physically adhere to the cellulose fibers when

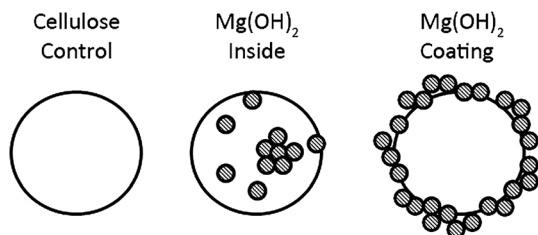


Fig. 2 Schematic of fiber cross-sections showing distributions of Mg(OH)<sub>2</sub> NPs. Large micron size clusters can be found within the fibers which are electrospun from a mixture of [EMIM][Ac]–cellulose–Mg(OH)<sub>2</sub> (center). Such large clusters quickly precipitate and also do not readily attach to the fiber surface in fibers electrospun from [EMIM][Ac]–cellulose into a coagulation bath containing Mg(OH)<sub>2</sub> NPs (right).

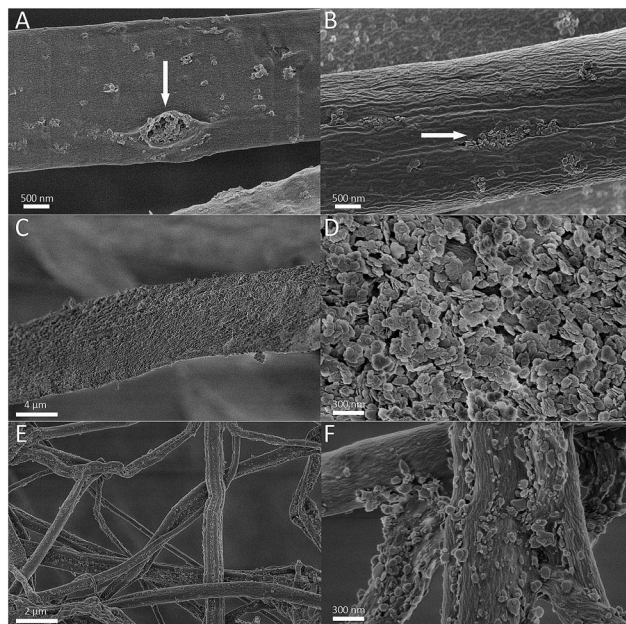


Fig. 3 Electron micrographs of cellulose–magnesium hydroxide fiber composites. (A and B) Fibers electrospun from an [EMIM][Ac]–cellulose–Mg(OH)<sub>2</sub> NPs mixture into a water coagulation bath showing a small number of Mg(OH)<sub>2</sub> NPs on surface and internal clusters exposed at defect sites and cracks along the fibers (arrows); (C and D) fibers electrospun from an [EMIM][Ac]–cellulose solution into a water–Mg(OH)<sub>2</sub> NP coagulation bath showing a large number of Mg(OH)<sub>2</sub> nanoparticles on their surface; (E and F) fibers electrospun from an [EMIM][Ac]–cellulose solution into water–milk of magnesia coagulation bath showing a reduced quantity of Mg(OH)<sub>2</sub> NPs on their surface, due to the larger NPs being removed during the washing steps.

they enter the bath. The fibers are in a tacky intermediate state between an ionic liquid solution and a cellulose hydrogel. It is this initial tackiness of the RTIL that allows the particles to adhere, and as the RTIL is replaced with water the particles

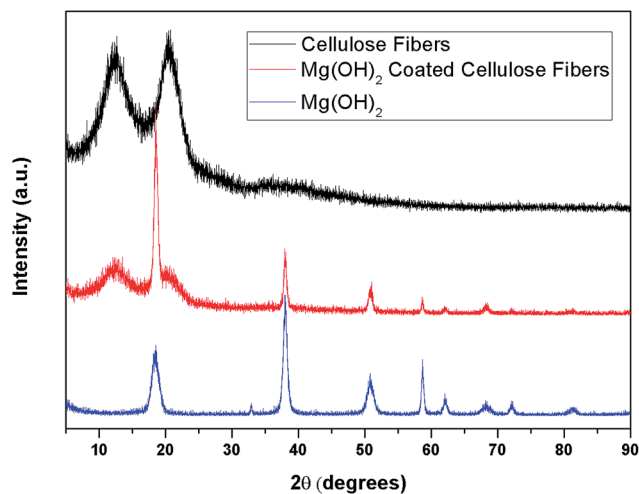


Fig. 4 X-ray diffraction spectra for electrospun cellulose fibers (top), Mg(OH)<sub>2</sub> NPs (bottom), and Mg(OH)<sub>2</sub> NPs coated cellulose composite fibers (middle).

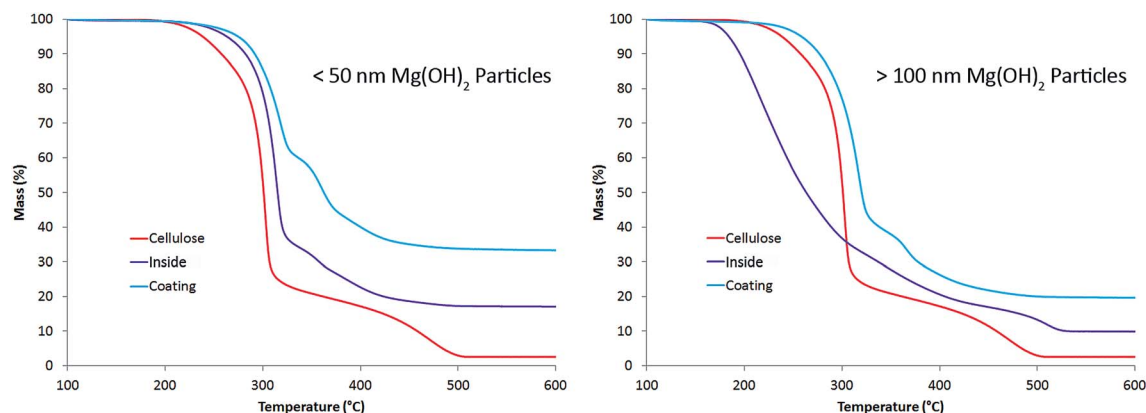


Fig. 5 TGA of electrospun cellulose nanofiber composites. Smaller  $\text{Mg}(\text{OH})_2$  nanoparticles (left) delayed combustion both inside and as a coating. Larger  $\text{Mg}(\text{OH})_2$  nanoparticles (right) accelerated combustion when placed inside the fibers, and delayed combustion when coated on the surface of the fibers.

Table 1 First derivative of mass loss data for smaller  $\text{Mg}(\text{OH})_2$  particles (left) and larger  $\text{Mg}(\text{OH})_2$  particles (right)

Sample	Onset °C	Max °C	Residual wt%
<b>&lt;50 nm <math>\text{Mg}(\text{OH})_2</math> particles</b>			
Cellulose	239	302	0.39
Inside	267	315	11.3
Coating	276	318	31.3
<b>&gt;100 nm <math>\text{Mg}(\text{OH})_2</math> particles</b>			
Cellulose	239	302	0.39
Inside	185	216	7.4
Coating	263	317	15.9

remain physically trapped at the surface of the fibers by the immobilized cellulose chains. The coating produced had no noticeable impact on fiber strength or spinnability. Similar results were obtained when electrospinning an  $[\text{EMIM}][\text{Ac}]$ -cellulose solution into a water-milk of magnesia solution. Aqueous coagulation baths were prepared that contained  $3 \text{ mg mL}^{-1}$  of  $\text{Mg}(\text{OH})_2$  NPs and  $20 \text{ mg mL}^{-1}$  of milk of magnesia. The milk of magnesia suspension had many large particles ( $<100 \text{ nm}$ ) and so a higher concentration was chosen to ensure sufficient nanoscale particles were available to coat the fiber surfaces. In both cases, X-ray diffraction (XRD) spectral data (Fig. 4) confirmed the presence of the  $\text{Mg}(\text{OH})_2$  NPs on the surface of the coated fibers.

TGA (Fig. 5, Table 1) affords data both on the thermal stability of the fibers and on the approximate mass percent of the  $\text{Mg}(\text{OH})_2$  NPs incorporated into the cellulose nanocomposites (based on the residue that remains at  $600 \text{ }^\circ\text{C}$ ). The onset temperature of cellulose combustion in air increased, relative to neat cellulose, for both samples having  $<50 \text{ nm}$   $\text{Mg}(\text{OH})_2$  NPs on the inside or on the outside of the fiber (Fig. 5, left). The same trend was observed for the temperature at which the maximum mass loss was observed (Table 1, left). The sample with  $>100 \text{ nm}$   $\text{Mg}(\text{OH})_2$  NPs added did not follow the same trend, with the fibers with the larger  $\text{Mg}(\text{OH})_2$  NPs inside them made from an  $[\text{EMIM}][\text{Ac}]$ -cellulose- $\text{Mg}(\text{OH})_2$  mixture beginning combustion at a significantly lower temperature (Fig. 5, right).

Flame testing was carried out on the samples with  $<50 \text{ nm}$   $\text{Mg}(\text{OH})_2$  NPs by placing a compacted electrospun fiber sample horizontally in a steel clamp. Samples were weighed out such that they each contained  $100 \text{ mg}$  of cellulose (*i.e.*,  $100 \text{ mg}$  sample for the neat cellulose fibers,  $116 \text{ mg}$  for the  $\text{Mg}(\text{OH})_2$  NPs inside sample, and  $145 \text{ mg}$  for the  $\text{Mg}(\text{OH})_2$  NPs coated sample). The tip of each sample was exposed to the open flame of an ethanol lamp until sustained burning was achieved. This direct contact with the open flame was less than  $1 \text{ s}$  for the fibers of neat cellulose and with  $\text{Mg}(\text{OH})_2$  NPs (avg. diameter  $<50 \text{ nm}$ ) inside (Fig. 6A and B). In the case of the  $\text{Mg}(\text{OH})_2$  NP coated fibers it was not possible to maintain a flame and repeated exposure ( $>2 \text{ s}$  total for the picture shown in Fig. 6C) to

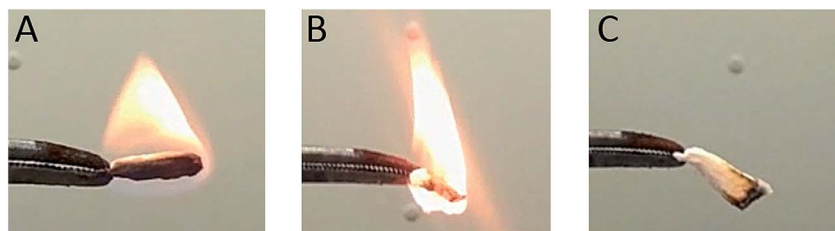


Fig. 6 Flame testing of nano fiber composites. (A) Pure cellulose,  $\text{Mg}(\text{OH})_2$  NPs inside ( $<50 \text{ nm}$  avg. diameter), and  $\text{Mg}(\text{OH})_2$  ( $<50 \text{ nm}$  avg. diameter) NPs coated electrospun fibers.



the alcohol lamp flame was required to partially burn the sample (Fig. 6C). In total the NP coated sample endured more than 12 s of direct exposure to the flame without fully burning.

## 4. Discussion

Electrospinning of polymer fibers blended with functional nanoparticles has been widely reported in the literature.<sup>12–14</sup> The majority of these reports create these composite materials by simply mixing nanoparticles into the polymer solution prior to electrospinning. Some reports employ a more sophisticated coaxial spinning technique that allows for a core–sheath fiber to be created which concentrates the nanomaterials in the core or in the sheath layer of the electrospun fibers.<sup>10</sup> To the best of the authors' knowledge, no prior reports have described a one-step method for producing nanoparticle-coated electrospun fibers. The technique reported here was developed to allow for the formation of electrospun fibers with functional nanomaterials exclusively on their surfaces. The hypothesis of this work is that functional nanomaterials located exclusively on the surface of electrospun fibers will result in unique materials properties. This was confirmed by the observation that the Mg(OH)<sub>2</sub> NP coated cellulose fibers were consistently more resistant to combustion. In the case of the larger Mg(OH)<sub>2</sub> NPs studied (>100 nm avg. diameter nanoparticles with 2 μm avg. diameter agglomerates) from the milk of magnesia solution, mixing into the cellulose solution prior to electrospinning resulted in a significant reduction of the thermal stability of the cellulose fibers (Fig. 5). This is due to the fact that when mixed into the polymer solution prior to spinning, large micron-scale agglomerates of nanoparticles are included and this leads to large voids in the fibers produced. These agglomerates also caused interruptions during the electrospinning process by forming blockages in the syringe and spinneret. When the same particles are included in the coagulation bath, these large micron-scale agglomerates of nanoparticles have the tendency to precipitate. Even the large agglomerations of NPs that do not precipitate, it was observed that these particles are apparently too large to be incorporated into the surfaces of the coagulating cellulose fibers (Fig. 3). This coagulation occurs rather quickly once the fibers enter the coagulation bath, with the cellulose polymer chains losing mobility as the RTIL is leached out. This halts the process of nanoparticles embedding into their surfaces.

As with any composite filler, the physical voids created within the fibers by the presence of the Mg(OH)<sub>2</sub> NPs weaken the fiber strength. These voids also allow for more rapid combustion by increasing the internal surface area of the cellulose fibers. Additionally, upon exposure to elevated temperatures, the Mg(OH)<sub>2</sub> releases water vapor during the formation of MgO. This water vapor acts in concert with the increased surface area to result in a sudden onset of rapid burning of the electrospun cellulose fibers (Fig. 6B). This is in contrast to the Mg(OH)<sub>2</sub> NP coated cellulose fibers that do not support an open flame and resisted burning during sustained exposure to the flame of an alcohol lamp. The Mg(OH)<sub>2</sub> NP coated cellulose fibers had no internal voids and the water vapor released during the formation of MgO simply escaped into the

atmosphere and did not create internal pressure within the fiber (Fig. 6, right) as it had when inside of the fibers. This model system has clearly demonstrated that the location of functional nanomaterials exclusively on the surfaces of electrospun fibers resulted in unique materials properties.

## 5. Conclusions

The dry-jet wet electrospinning of cellulose from an RTIL-based solution into a coagulation bath containing a suspension of nanoparticles resulted in NP coated cellulose fibers. These NP coated cellulose fibers exhibited compositions and materials properties distinct from the fibers produced from a mixture of cellulose and NPs in an RTIL solution. Increased functionality can be obtained from fibers electrospun by this technique with the added benefit of more reliable spinning conditions. The surface coating of electrospun fibers prior to coagulation could be extended to the use of an aerosol containing the desired nanomaterial coating so long as this aerosol cloud did not interfere with the accelerating potential. Future work will focus on optimizing coating electrospun cellulose fibers with aerosolized nanomaterials. Moreover, future studies will also examine nanoparticles having a wide variety of properties including electrically conducting nanoparticles and anti-microbial nanoparticles.

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