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Simultaneous enhancement of toughness, strength and superhydrophilicity of solvent-free microcrystalline cellulose fluids/poly(lactic acid) fibers fabricated *via* electrospinning approach

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ABSTRACT

In this paper, solvent-free microcrystalline cellulose fluids (MCCFs) with liquid-like behavior were synthesized for the first time through surface grafted polyethylene glycol-substituted tertiary amines into microcrystalline cellulose (MCC) followed by fabricating MCCFs based polylactic acid (PLA) fabric (PLA/MCCFs) *via* electrospinning method. Owing to low viscosity of MCCFs at room temperature, the addition of MCCFs not only hardly affected the viscosity of electrospinning solution, but also improved the thermal stability of as-prepared PLA fibers. Interestingly, it was amazingly found that surface micropore morphology of PLA fabric diminished, and even disappeared with the content of MCCFs increasing during solvent evaporation process, which may be ascribed to the rapid migration of MCCFs into micropore before solidification. More importantly, the tensile strengths of PLA/MCCFs fabric with 10 wt% content of MCCFs achieved as high as 13.68 MPa, which was 3.18 times as much as that of 4.3 MPa for pure PLA fabric meanwhile the elongation at break of PLA/MCCFs fabrics increased from 13.19% for pure PLA fabric to 48.84% for PLA/MCCFs fabric with 15 wt% content of MCCFs. Beyond above mentioned, the water contact angle for pure PLA fabric was 127° (hydrophobicity), whereas other samples were close to 0° with addition of MCCFs, displaying the super-hydrophilicity. It was possibly inferred that MCCFs quickly migrated towards to the surface of fibers rather than staying inside of the fibers during the electrospinning process, leading to positive effect on the hydrophilicity of the PLA fibers. Finally, it is anticipated that this strategy for fabricating PLA fiber using this novel MCCFs as filler will pave the way for developing high performance PLA composites with desirable properties in the future.

1. Introduction

Nowadays, owing to the requirement of environment protecting and sustainable development of nature resources, cellulose as most rich renewable polymer resources available on earth has been attracted extensive research interest in academia and industry [1–6]. Moreover, due to these advantages of biocompatibility, biodegradability and sustainability of cellulose and its derivatives [7], they have broad application prospects in medical [8], cosmetics [9], engineering materials [1], food industries [3] et al. Microcrystalline cellulose (MCC) as a type of biodegradable materials is mainly derived from sub products of α-cellulose extracted from wood pulp. In recent years, MCC is widely employed in medicine [8], food [2] and reinforcement materials [10] on account of its advantages of renewable resources, inexpensive, low density, biodegradability et al. Especially, it should be to point out that MCC as a type of biopolymer reinforcement fiber can take place of others inorganic filler to prepare environment friendly polymer composites. Oksman et al. [11] fabricated PLA/MCC composites using a

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twin-screw extruder with improved tensile modulus at MCC content of 25 wt%, which is 1.4 times than that of pure PLA. Mubarak et al. [12] prepared MCC filled low-density polyethylene (LDPE) composites by melt blend extrusion with enhanced the impact strength with 10 wt% loading, which is two folds that of pure LDPE. Although some efforts have been made to improve the mechanical properties of MCC based polymer composites, it is still not possible to maximize the potential of MCC enhancement. Generally, the MCC is insoluble in water and other organic solvents that easily aggregate together during melt extrusion polymer blends or solution casting on account of intermolecular hydrogen bonding interaction of MCC limited its application [4]. Various physical and chemical methods have been used to improve the compatibility between the polymer matrix and MCC fiber [1,8,13]. As well known, MCC and its derivatives exhibit solid-like behavior without solvent existence and cannot flow like viscous liquids at room temperature.

In 2009, Perriman et al. [14] firstly reported a type of solvent-free liquid protein fluids with liquid-like behavior without solvent fabricated by ion exchange reaction of cationized ferritin with an anionic polymeric surfactant. Afterwards, a novel of DNA oligonucleotide fluids was successfully synthesized through ion exchange reaction with a polyethylene glycol-tailed quaternary ammonium cation [15]. Notably, it is different from the above mentioned works that an acid-base reaction method was developed by Tan et al. [4] to prepare alginate fluids through only using polyethylene glycol-substituted tertiary amines reaction with alginate. Inspired by the above methods, in our previous works, we synthesize self-suspended chitosan derivative *via* ion-exchange reaction that was used as coating to obtain enhanced wettability and antibacterial cotton fabrics [16]. Due to these advantages of its low viscosity, low surface energy, well dispersion as well as amphiphilicity in water and organic solvent [4,16], this novel kind of natural polymer fluids can effectively solve the particle dispersion and improve the interfacial interaction between polymer matrix and particles. Therefore, it is desirable that this strategy for fabricating biopolymer fluids will expand to other natural polymer.

Obtaining PLA fibers and fibrous membrane is an interesting research subject because it has many advantages of biodegradability [17], biocompatibility and excellent processability [1,18], which can be extensively used in tissue engineering, wound dressing and packaging et al. [13,19,20]. Unfortunately, there are still some typical deficiencies mainly including low flexibility, poor thermo-mechanical properties, slow crystallization rate, seriously restricted its applications [21]. Accordingly, MCC can have potential use as reinforcement filler to improve the mechanical property of PLA biocomposites by mean of various methods. Gaitán et al. [10] used electrospinning method to fabricate PLA/MCC fabrics for achieving a 476% increase in tensile strength with only addition of 1 wt% of MCC. Aouat et al. [22] prepared PLA/MCC multifilament fibers *via* melt-spinning process in the presence of PLA-grafted maleic anhydride with 23% and 63% increase of Young's modulus and maximum tensile strength, respectively, in comparison with PLA/MCC fabrics. Although some effects have been made to enhanced mechanical and thermal properties of PLA fibers, it still faces great difficulties due to the incompatibility between the PLA matrix and MCC as well as a poor dispersion of the MCC within the PLA matrix during the spinning.

In this paper, this work was aimed at fabricating solvent-free MCCFs through surface grafted polyethylene glycol-substituted tertiary amines into MCC followed by preparing PLA/MCCFs fabrics *via* electrospinning method. Such design is in triple purpose. Polyethylene glycol-substituted tertiary amines of MCCFs surface not only enhance the interfacial compatibility between PLA and MCCFs but also achieve well dispersion in PLA matrix. Further, inherent low viscosity and fluidity of MCCFs are conducive to improve the toughness and wettability of PLA/MCCFs fabrics. Meanwhile, the size distribution, thermal stability and morphology of pure PLA and PLA/MCCFs fabrics were also analyzed.

2. Experiment

2.1. Materials

Microcrystalline Cellulose (MCC) was purchased from National Pharmaceutical Group Chemical Reagent Company. Polyethylene Glycol (PEG)-substituted tertiary amines ($C_{18}H_{37}NH(CH_2CH_2O)_n(CH_2CH_2O)_mH$, m + n = 30, named as M-1830) was purchased from Zhejiang Haian Pharmaceutical Co., Ltd., China. PLA (Mw = 200,000Da) was obtained from Zhejiang Hisun Co., Ltd., China. Other reagents of chemically pure grade were purchased from National Pharmaceutical Group Chemical Reagent Company.

2.2. Preparation of MCCFs

Firstly, the sodium hydroxide was dissolved in isopropanol aqueous solution (mole ratio of reactants is 1:20:3). Next, 1 g of MCC was swelled in premixed alkali/isopropanol aqueous solution for 2 h at 30 °C, and then added 3 g chloroacetic acid into the solution with stirring for 3 h at 50 °C. The pH value of the solution was adjusted to 6–7 followed by filtering with 85% alcohol aqueous solution over three times, and dried at 50 °C for 24 h to obtain carboxymethyl cellulose. Subsequently, 1 g carboxymethyl cellulose, 0.5 ml pyridine and 30 ml thionyl chloride were charged into a beaker with three flasks for stirring for 24 h at 65 °C. After the solvent were removed by a rotary evaporator followed by adding 4 g M-1830 and 40 ml N, N-dimethylforma mixture with stirring for 24 h at 65 °C. Finally, the mixed solutions were dialyzed in deionized water for 5 days, then dried at 60 °C for 36 h under vacuum to obtain MCCFs. The preparation route was pictured in Scheme 1.

2.3. Fabrication of electrospun PLA/MCCFs fibers

The mixture of chloroform/DMF (4:1) was used as the solvent for dissolving PLA. Initially, PLA pellets of 8 wt% was dissolved in mixture at room temperature with stirring for 8 h, then MCCFs were dispersed in above mixture solution by the weight of 5 wt%, 10 w%, 15 wt% relative to PLA, corresponding to PLA/MCCFs-5%, PLA/MCCFs-10%, PLA/MCCFs-15%, respectively. Next, 5 ml of PLA/MCCFs suspension was fed into the syringe with controlling the feed rate at 0.35 mm/min. A voltage of 20 KV power generated positive DC voltage and controlled the electrospinning process. The positive electrode of high-voltage power supply was directly connected to the needle and the negative electrode was connected to the plate collector. The fibrous mats were typically collected on a stainless steel plate and wrapped with an aluminum foil with a distance of 10 cm from the needle to the collector plate. Finally, the PLA/MCCFs fabrics were detached from the plate and dried at 50 °C for 2 h (see Fig. 1).

2.4. Characterization

Fourier-transform infrared (FT-IR) spectra of all samples were studied by a Nicolet iS10 spectrometer (Nicolet Instrument Corporation) in the range 400–4000 cm^{-1} and scanning time of 64 using KBr powder for the original MCC and KBr disk for the MCCFs, respectively. Infrared spectra of MCCFs/PLA specimens were obtained from attenuated total reflection infrared spectroscopy (ATRIS) (a Nicolet NEXUS 670) in the range 400–4000 cm^{-1} and scanning time of 64. X-ray diffraction (XRD) was performed using a Bruker D2 diffractometer in the 2θ range from 5° to 80°. Polarizing optical microscope (POM) (OLYMPUS BH2) was used to observe the morphology of original MCC. Firstly, a small amount of MCC powder was placed on glass slide, and then transferred them to the thermal platform of Polarizing Microscope, finally the morphology of powder were observed at room temperature. Scanning electron microscopy (SEM, JEM 1200EX) was carried out to analyze the surface morphology of samples at accelerating voltage of 80 kV. The