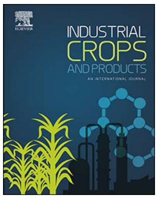
Industrial Crops & Products 111 (2018) 536–543

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop



Research Paper

Manufacturing & characterization of regenerated cellulose/curcumin based sustainable composites fibers spun from environmentally benign solvents

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ARTICLE INFO

Keywords:
Curcumin
Cellulose
Ionic liquids
Fibres
Textiles
Food packaging

ABSTRACT

We report a novel manufacturing method for bio renewable regenerated cellulose fibres modified with curcumin, a molecule is known for its medicinal properties. Ionic liquid namely 1-Ethyl 3-Methyl Imidazolium diethyl phosphate (emim DEP) was found to be capable of dissolving cellulose as well as curcumin. Regenerated cellulose/curcumin composites fibres with curcumin concentration ranging from 1 to 10 wt% were manufactured using dry jet wet fibres spinning process using three different winding speeds. All the cellulose and curcumin composite fibres showed distinct yellow colour imparted by curcumin. The resultant fibres were characterised using scanning electron microscopy (SEM), infrared spectroscopy, mechanical testing, and X-Ray diffraction studies. Scanning electron microscopy of cellulose/curcumin fibres cross-section did not show curcumin aggregates in cellulose fibres indicating uniform dispersion of curcumin in cellulose matrix. The cellulose chain alignment in cellulose/curcumin composite fibres resulted in tensile strength ranging from 223 to 336 MPa and Young's modulus ranging from 13 to 14.9 GPa. The mechanical properties of cellulose/curcumin composite fibres thus obtained are better than some of the commercially available regenerated cellulose viscose fibres. The wide-angle X-ray diffraction analysis of cellulose/curcumin composite fibres showed good alignment of cellulose chains along the fibre axis. Thus, our findings are a major step in manufacturing strong cellulose fibres with a pharmacologically potent drug curcumin which in future could be used for medicinal, cosmetic and food packaging applications.

1. Introduction

Among different bio renewable materials, cellulose is one of the most common natural polymers found in higher plants, algae, bacteria, fungi and marine animals. It is a linear polymer that consists of two glucose sugar units that are linked by β-1, 4 glycosidic linkage to form a dimer known as cellobiose (Eichhorn et al., 2010; Kontturi et al., 2006). The length of cellulose chains can be very different due to the number of repeating units of glucose (from 20 to 10 000 or more), also called degree of polymerization or DP (Sidhu et al., 1998). Several studies have shown that cellulose and its derivatives have a good biocompatibility and in addition, can be regarded as slowly degradable materials (Czaja et al., 2007; Granja et al., 2005; Martson et al., 1999; Miyamoto et al., 1989; Müller et al., 2006). Due to its excellent mechanical and barrier properties, biocompatibility and low cost, cellulose is used in many biomedical applications, like orthopedic devices and tissue engineering (Granja et al., 2001; Poustis et al., 1994; Svensson et al., 2005) and is an excellent candidate for food packaging (de Moura et al., 2012; Imran et al., 2010).

Several studies have indicated that some herbal supplements contain phytochemicals that are able to prevent various relevant and widespread pathologies, including diabetes, cancer and autoimmune diseases (Aggarwal et al., 2008; Kaefer and Milner, 2008; Mahmood et al., 2015). Among these many studies have reported that curcumin, a polyphenol derived from *Curcuma longa*, commonly called turmeric, has excellent pharmacological properties like antimicrobial, antiviral, anti-inflammatory and anti-tumor activities (Ramsewak et al., 2000; Ruby et al., 1995). Previous studies on wound healing in diabetic rats as well as genetically diabetic mice have shown the efficacy of curcumin treatment both by the oral and topical application. There was an

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https://doi.org/10.1016/j.indcrop.2017.09.041
Received 22 February 2017; Received in revised form 10 September 2017; Accepted 20 September 2017

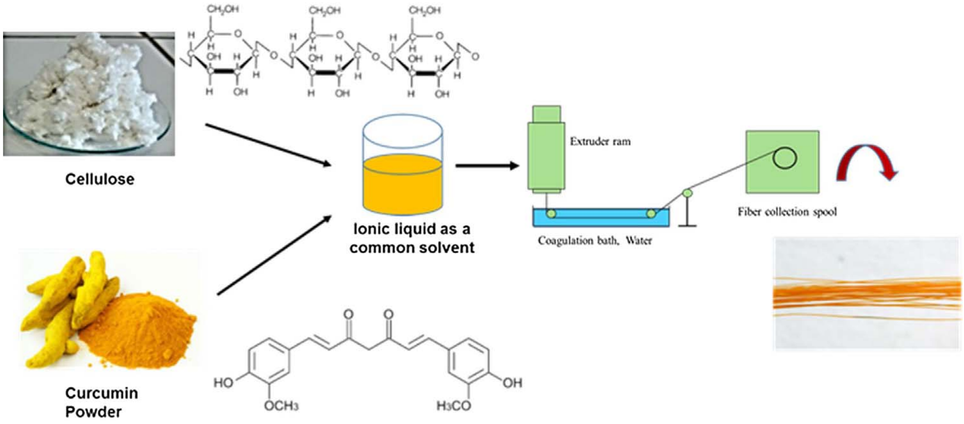

Fig. 1. Schematic representation of the preparation of cellulose/curcumin composite fibres.

improved neovascularization, earlier re-epithelialization, increased migration of various cells including fibroblasts, and dermal myofibroblasts, when curcumin was used to treat the wounds of animals. (Sidhu et al., 1999; Sidhu et al., 1998). Furthermore, curcumin has been widely used as an active component in the food industry to create new packaging films with antioxidant and antimicrobial activities (Sonkaew et al., 2012; Vimala et al., 2011).

Ionic liquids (ILs) are a new class of benign solvents that can be liquid at room temperature (usually $T_{melt} < 100$ °C) (Holbrey and Rogers, 2002). Over the past 20 years many studies have shown the countless properties of ionic liquids, in particular their low volatility that makes them benign solvents as compared to traditional volatile and aggressive solvents used for dissolving cellulose (Carbon disulphide, sulfuric acid etc). ILs have good chemical and thermal stability, high ionic and thermal conductivity, high heat capacity and easy recyclability. All these properties can reduce many health and environmental related issues when ILs are used as solvents for the dissolutions of natural polymers like cellulose, lignin, starch and chitin (Pu et al., 2007; Silva et al., 2011; Wang et al., 2012; Wu et al., 2009). There are several ILs that can directly dissolve cellulose upon heating, such as 1-allyl-3-methylimidazolium chloride (AMIM-Cl) and 1- ethyl-3-methylimidazolium acetate (EMIM Ac) (Haward et al., 2012; Wu et al., 2009). Furthermore, in recent years there has been a great interest of the international scientific community on ILs, used as pharmaceutical ingredients that can modify the pharmacokinetics and pharmacodynamics of drugs (Moniruzzaman et al., 2010; Stoimenovski et al., 2010).

In biomedical applications and tissue engineering, there is need for soft polymers which show more compatibility with the soft tissue as compared to the stiff ones (Foster, 2017). While taking this into account, cellulose is not only biocompatible and green, but also has advance applications while working under biological conditions (Zainuddin et al., 2017a; Ravikumar et al., 2017).

In view of its bio-applications, and to reap the benefits of a pharmacological drug, we have incorporated curcumin at different percentage by weight in a matrix of cellulose dissolved by ionic liquid to manufacture curcumin incorporated fibres. The focus of current work is to develop a simple but effective manufacturing method which will allow continuous manufacturing of strong cellulose/curcumin fibres. The strong cellulose/curcumin fibres thus obtained has the potential to be woven into bandages and to use in drug, food and cosmetic industry for various low cost affordable health care.

2. Materials and methods

Cellulose pulp sheets (A4 size cardboard sheets) with a degree of polymerization of 890 DP were purchased from Rayonier (Jacksonville, US). Curcumin in powder, purity about 95%, was purchased from https://supplementsyou.com/(Jersey, United Kingdom). The ionic liquid 1-ethyl −3-methylimidazolium diethyl phosphate (emim DEP, > 95%) was obtained from Iolitec, and used without further purification.

2.1. Cellulose/curcumin fibres formation

The cellulose pulp sheets were finely chopped into (1×1 cm^2) small pieces using scissors and grinded into filaments using a Bosch MMB43G3BGB Glass Jug Blender. To prepare cellulose/curcumin composite fibres, 4% of cellulose (with respect to the mass of the ionic liquid) was dissolved in emim DEP. The solution preparation was carried out in a fume hood using a magnetic stirrer hotplate from Fisher Scientific (Loughborough, UK) with an oil bath heated at 80 °C. The viscous solution was stirred for 6 h until there was a complete dissolution of cellulose. When the cellulose was dissolved 0 wt%, 1 wt%, 5 wt% and 10 wt% of curcumin (with respect to the mass of cellulose) was added to the 4 wt% cellulose/emim DEP solutions. The cellulose/emim DEP with 0 wt%, 1 wt%, 5 wt% and 10 wt% of curcumin was transferred into a 20-ml Luer lock syringe (Terumo, UK). The solution in the syringe was degassed in a vacuum oven at 60 °C overnight to remove any bubbles before spinning. A lab-built spinning facility, which consists of a syringe pump, a deionized water bath and a winding drum with a monitor, was used for the dry-jet wet fibre spinning of cellulose (Fig. 1). The cellulose/curcumin/emim DEP solution was injected into the water bath at a fixed extrusion velocity ($V1 = 2.9 \times 10^{-2}$ m/s), while the winding drum and electric motor were continuously winding the fibres at varying winding velocities (V2) of 1.5×10^{-1} m/s, 2.9×10^{-1} m/s and 4.8×10^{-1} m/s downstream. After spinning, the fibres were immersed in deionized water for 2 days, with a change of water every 24 h, and then rolled and dried in a fume hood for a further 48 h. According to (Haward et al., 2012), the fibres spun under high extension rate within the air gap tends to align better and shows high crystallinity. Following the similar trend, here we have investigated the fibres spun with the higher draw ratio.

In the fibre spinning process, the air gap between the die and the roller was maintained at d = 3 cm. Here, the draw ratio, DR = V2/V1 is the degree of stretching applied to the fluid filament within the air gap. Here, V1 is the average velocity at which fluid is ejected from the die. V2 is the velocity at which fibre is taken up on the spool. $V1 = Q/\pi r^2$, where Q is the volume flow rate and r is the die radius. (Haward et al., 2012).

2.2. Characterization techniques

2.2.1. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to study the morphology of the fibres obtained and to measure the diameters of the fibres. The samples (1 cm^2) were vacuum-coated with 10 nm thick layer of gold using an EMS 7620 Mini Sputter Coater/Glow Discharge System and were observed with Jeol JSM-5510 (Jeol Ltd., Japan). For each