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Jute cellulose nano-fibrils/hydroxypropylmethylcellulose nanocomposite: A novel material with potential for application in packaging and transdermal drug delivery system

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ABSTRACT

Nowadays, bio-derived cellulose nano-fibrils based nanocomposites is gaining utmost interest in the area of barrier films for food packaging, as reinforcing filler to make biodegradable nanocomposites with different biopolymers for various applications such as transdermal drug delivery, edible packaging and tissue scaffolding. Ultrasound-assisted preparation of hydroxypropylmethylcellulose based nanocomposites with cellulose nano-fibrils were carried out following solution mixing technique. The crystalline nature of cellulose nano-fibrils has been scrutinized by X-ray diffraction study. The field emission-scanning electron micrographs of cellulose nano-fibrils revealed a network of nano-fibrillar morphology. The Fourier transform infrared spectroscopy results of cellulose nano-fibrils confirmed the removal of lignin and hemicellulose from raw jute (*Corchorus olitorius* L.) fibres. The storage modulus and tensile properties of hydroxypropyl methylcellulose films increased up to the addition of 1.00 wt% cellulose nano-fibrils. The moisture affinity of hydrophilic hydroxypropylmethylcellulose has also been reduced at 1.00 wt% cellulose nano-fibrils loading. The impact of cellulose nano-fibrils loading on the cumulative percentage of drug release from prepared nanocomposites films has been explored accordingly. By utilizing these versatilities of cellulose nano-fibrils, the fabricated nanocomposites are expected to be highly promising in the area of packaging and transdermal drug delivery system.

1. Introduction

Cellulose nano-fibrils (CNF) with at least one of its dimensions ranging between 5 and 100 nm, obtained from lignocellulose biomass/fibres or cellulosic biomass/fibres is of great interest in the field of nanotechnology today. Some sources of CNF utilized by researchers include bacterial cellulose (George et al., 2014), pineapple leaf fibres (*Ananas comosus* Merr.) (Cherian et al., 2010), wheat straw (*Triticum aestivum* L.), and soy hulls (*Glycine max* L. Merrill.) (Silvério et al., 2014; Wang and Sain, 2007; Kaushik and Singh, 2011), wood (Bilbao-Sáinz et al., 2011; Wang et al., 2014), and tunicin/tunicate (*Microcosmus sulcatus* (species)) (Azizi Samir et al., 2004; Favier et al., 1995).

Cellulose nano-fibrils has been extracted by different approaches which range from cryocrushing (Bhatnagar and Sain, 2005), high pressure homogenization (Qua et al., 2011), acid hydrolysis (Kumar et al., 2014), steam explosion (Michell, 1989), enzymic hydrolysis (Pääkkö et al., 2007), grinding (Iwamoto et al., 2007), and a combination of two or more approaches including cryocrushing and high pressure homogenization (Wang and Sain, 2007), homogenization and grinding (Iwamoto et al., 2007), refining and high pressure homogenization (Nakagaito and Yano, 2004).

The attention drawn to CNFs is as a result of its attractive properties which include high modulus, high tensile strength, and low coefficient of thermal expansion (De Moura et al., 2011). CNF has shown promising potential in several applications, such as, in oil recovery (Chen et al., 2011; Jin et al., 2011), pharmaceuticals (Lin and Dufresne, 2014), bio-scaffolds (Lin and Dufresne, 2014), foldable paper antenna (Chen et al., 2011), dye carriers (Sun et al., 2014), aerogel membranes

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for cargo carriers (Jin et al., 2011), filtration media (Asper et al., 2015; Huang et al., 2016), dental tissue regeneration, barrier films, high strength paper boards, emulsion, dispersion, biomedical (Lin and Dufresne, 2014), bioimaging (Dong and Roman, 2007), nanocomposites for gas barrier films (Nair et al., 2014), novel tablet excipient (Kolakovic et al., 2011), optically transparent functional materials (Koga et al., 2013; Nogi et al., 2009, 2013), and ultra flexible non-volatile memory (Nagashima et al., 2014).

There are three classes of nanocellulose (Lin and Dufresne, 2014) namely cellulose nanocrystals (CNC) (Kumar et al., 2014; Brinchi et al., 2013) or nanocrystalline cellulose (NCC) (Kumar et al., 2014) or cellulose nanowhiskers (CNWs) or cellulose nano-particles (Bilbao-Sáinz et al., 2011) and cellulose nano-fibrils (CNFs) also referred to as nanofibrillated cellulose (NFC) (Bhatnagar and Sain, 2005; Iwamoto et al., 2007) and bacterial nanocellulose (Juntaro et al., 2012; Lin and Dufresne, 2014). The first category is extracted by chemical method, mainly acid hydrolysis (Bilbao-Sáinz et al., 2011; Kumar et al., 2014), while the second class is extracted by mechanically disintegrating cellulose pulp in water (Bhatnagar and Sain, 2005; Iwamoto et al., 2007), and can be isolated from different sources as stated earlier. The extraction of nanocellulose using H_2SO_4 has been reported in some literature (Bilbao-Sáinz et al., 2011; Kumar et al., 2014; Youssef et al., 2015). The concentration of the acid used as reported in some literature is 63–64% (Bilbao-Sáinz et al., 2011; Kumar et al., 2014; Youssef et al., 2015). It is believed that the concentration of the acid used by previous researchers can be reduced and the process will be more environmentally friendly.

Jute is one of the most important fibres which are neglected by humans. Jute fibres possess unique properties which, if utilized effectively will not only solve problems in textiles including technical textiles, medical textiles, agrotextiles, but also in the fields of cosmetics, bioengineering, nano-composites, automobiles, aerospace, etc. The preparation of hydroxypropylmethylcellulose (HPMC) reinforced CNF from jute, which is a potential nanocomposite for advanced applications, has not been reported earlier by anyone. Some researchers tried to synthesizing CNF from jute fibres, ended up with a mixture of micro and nano-cellulose (Rahman et al., 2014; Vijay et al., 2011).

Hydroxypropylmethylcellulose is a biodegradable and biocompatible polymer. The use of HPMC for advanced applications, such as in packaging, requires modifications such as reinforcement with nanomaterials such as CNF, which leads to improved mechanical and moisture barrier properties (inz et al., 2010, 2011; ; De Moura et al., 2011; George et al., 2014). It is reported that the addition of nanocellulose (NC) to HPMC led to an increase of 22% in tensile strength and 55% in Young's modulus and the NC only decreased 3–6% in transparency (Bilbao-Sáinz et al., 2011).

Ketorolac tromethamine (KT) is an anti-inflammatory and analgesic agent (Rokhade et al., 2006). It is a potent non-narcotic and non-opioid analgesic with cyclooxygenase inhibitory activity (Estapé et al., 1990; Mroszczak et al., 1987). It is non-addictive in nature, and no respiratory side effects (Saha et al., 2016), and other side effects such as nausea and vomiting are the prevalent side-effects in pentazocine treated patients (Estapé et al., 1990). KT has been reported to be 800 times more effective than aspirin (Saha et al., 2016).This non-steroidal analgesic, which is well absorbed after oral administration, has an excellent tolerance profile (Estapé et al., 1990). The administration of KT is done by oral, intramuscular or intravenous routes aimed at treatment of moderate to severe pain for short periods of time (biological half-life $4 \geq 6$ h). The transdermal delivery of KT would help to control the therapeutic dose and also reduce the side effects in the gastrointestinal tract (Saha et al., 2016). The investigation of drug loading and release of nanocomposites based on biopolymer bacteria cellulose has been studied (Müller et al., 2013). The use of a 3D-network of nanocellulose as a controlled drug release carrier has been reported (Huang et al., 2013). HPMC-montmorillonite based as well as other polymer nanocomposite materials have widely been studied due to its superior properties (Mondal et al., 2013b).

Nanocomposites made from cellulose regenerated polymers reinforced with naturally derived fillers such as CNF is the focal point of attraction in recent years due to its good mechanical properties, low density, biodegradability, and renewability (De Moura et al., 2011). Synthetic polymers derived from crude oil create the problem of accumulation of non-biodegradable waste (Bilbao-Sáinz et al., 2010). The use of cellulose derived polymers for the preparation of films for packaging and other advanced materials are the alternatives. The effects of incorporating different filler levels (2, 4, 6, 8, and 10%) of cellulose nanocrystals from soy hulls upon the mechanical, thermal, and barrier properties of methylcellulose (MC) nanocomposites have been previously studied (Silvério et al., 2014). The cellulose nanocrystals from soy hulls provided a reduction in water vapor permeability of up to 36.32% of the nanocomposites for 8 wt% incorporated cellulose nanocrystals in the MC. A new way of processing cellulose whisker filled electrolytes with higher mechanical stiffness than the one of highly cross-linked polyether networks has been also reported (Azizi Samir et al., 2004). Amorphous alginate-oxidized nanocellulose with good structural and mechanical strength, induced by oxidized cellulose nanocrystals having semi-interpenetrating polymer network from oxidized microfibrillated cellulose, has been also reported (Lin et al., 2012).

At present, there is lack of report on CNF derived from jute as reinforcement filler for HPMC based nanocomposites for food packaging application or for potential application as a carrier for transdermal drug delivery. In this work, a simple and effective process for isolation of CNF from jute lignocellulosic fibres using 48% acid which is much less than earlier reports has been established, and for design/fabrication of CNF reinforced HPMC. The effect of CNF loading on the mechanical, moisture barrier, water vapor transmission rate (WVTR), and transdermal drug release properties of HPMC has also been studied.

2. Materials and methods

2.1. Materials

Hydroxypropylmethylcellulose (HPMC) (50 cps) was obtained from the Central Drug House (Pvt.) Ltd., New Delhi, India. Cellulose nanofibrils were extracted from jute fibres. Caustic soda (97% pure), fused calcium chloride, sulphuric acid (98%), and hydrogen peroxide (50%) purchased from Merk Specialities Pvt. Ltd., Mumbai, India. Sodium sulphite was purchased from Qualigens Fine Chemicals, Mumbai, India. Sodium chlorite (80% pure) was purchased from Loba Chemie Laboratory Reagents & Fine Chemicals, Mumbai, India. Ketorolac tromethamine (KT) was a gift sample received from Unichem Labs Ltd., Mumbai, India.

2.2. Preparation of cellulose nano-fibrils

Jute fibres labeled as "JF" were chopped into 2–4 mm lengths and soaked in 17.5–18% NaOH solution and heated at 80–90 °C for about 2 h under continuous stirring. The fibre suspension was filtered to collect the fibres, then washed with water several times to make neutral and dried in air at 105 °C for 3 h. The dried fibres were then treated with 0.70% sodium chlorite at pH 4, at 90 °C with stirring at intervals of 5 min for 2 h. The fibres were filtered and washed with water to neutral and then antichlored with 2% sodium sulphite for 20 min. The fibres were further treated with 50% H_2O_2 using 3–6% on the weight of fibres. The treatment was carried out for 2 h at pH 10–11 and then the treated fibres were washed with water to neutral. After this, the fibres were treated with 17.50% sodium hydroxide to remove hemicelluloses from the fibres at room temperature for 1 h and then, washed repeatedly to make neutral and then dried to a constant weight at 100 °C. The purified jute cellulose fibres were labeled as "PJF".

The dried mass of PJF was then treated with 47–48% (v/v) solution