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DES-ultrasonication treatment of cellulose nanocrystals and the reinforcement in carrageenan biocomposite

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ABSTRACT

CNCs are intensively studied to reinforce biocomposites. However, it remains a challenge to homogeneously disperse the CNC in biocomposites for a smooth film surface. Mechanochemical treatment via ultrasonication in deep eutectic solvent (DES) generated a stable dispersion of CNC before incorporation into carrageenan biocomposite. Shifted peaks of choline chloride (ChCl) methylene groups to 3.95–3.98 ppm in ^{1}H NMR indicated a formation of eutectic mixture between the hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) at the functional group of $CH_3\cdots OH$. The swelling of CNC in the DES was proven by the formation of intermolecular H-bond at a length of 2.46 Å. The use of DES contributed to a good dispersion of CNC in the solution which increased zeta potential by 43.2 % compared to CNC in deionized water. The ultrasonication amplitude and feed concentration were varied for the best parameters of a stable dispersion of CNC. The crystallinity of 1 wt% of CNC at 20 % sonication amplitude improved from 76 to 81 %. The high crystallinity of CNCDES resulted in an increase in film tensile and capsule loop strength of Carra-CNCDES by 20.7 and 19.4 %, respectively. Improved dispersion of CNCDES reduced the surface roughness of the biocomposite by 21.8 %. H-bond network in CNCDES improved the biocomposite properties for an ingenious reinforcement material.

1. Introduction

The integration of nanoparticles in the development of high-performance and functional biocomposite has become a prominent area of current research [1]. Cellulose nanocrystal (CNC) has been much studied recently due to its appealing intrinsic properties that contributes to outstanding functionalities such as high hydrophilicity, high tensile strength and large specific surface area [2–4]. It is also renewable, non-toxic and biodegradable [5]. Acid hydrolysis is a common method in the synthesis of CNC, leading to negatively charged surface that promote uniform dispersion in water [6]. A myriad of applications utilized CNC such as composite reinforcement [7], food industry [8], and biomedical application [9]. In the application of hard capsule, CNC has improved the mechanical strength of carrageenan biocomposite [10,11]. Despite that, surface roughness of carrageenan hard capsule is a crucial problem faced when incorporate CNC. The nanocrystals tend to aggregate through the hydrogen bonds with the presence of water [12]. This postulates to a rough surface of biocomposite, even on the nanoscale [13,14]. Actual production demands for a smooth surface of hard capsule. This is to ensure that the hard capsule meets the capsule filling machine requirement and avoids product rejection during capsule filling process. The CNC needs to be homogeneously dispersed in the biocomposite [15]. The insolubility of cellulose is attributed to the highly ordered crystalline regions, which formed by the intermolecular interactions between cellulose chains that are held together [16], leading to a poor dispersion of CNC [17]. Owing to the rod-like geometry, CNC is prone to shearing-inducing alignment and contributes to different properties with anisotropy of optical, mechanical and even the surface roughness [18].

Deep eutectic solvent (DES) is an ionic liquid (IL) analogue, which researchers have intensively explored its applications as a green solvent [19,20]. DES is formed by the complexation of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) [21], forming a eutectic mixture at ambient temperatures [22,23]. Studies on DES have

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