Selective localization of cellulose nanocrystals in the biodegradable poly(vinyl alcohol)/poly(ε-caprolactone) blend composites prepared by Pickering emulsions

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HIGHLIGHTS

- CNCs can be used as emulsifier to stabilize emulsions of two polymer solutions.
- Rheological responses can be used as probe to detect morphology of emulsions.
- Pickering emulsion can be used as template to prepare ternary nanocomposites.
- This work provides new approach of regulating selective localization of CNCs.

ARTICLE INFO

ABSTRACT

Cellulose nanocrystal (CNC) particles were used as the solid emulsifier to stabilize poly(ε-caprolactone) (PCL) solution-in-poly(vinyl alcohol) (PVA) solution emulsions (oil-in-water), with the objective to prepare ternary nanocomposites using as-obtained Pickering emulsions as the templates. The morphology of emulsions and mechanical properties of nanocomposites were studied, aiming at establishing a convenient route to regulate selective localization of CNCs and multiphase structures. The results show that emulsion stability depend strongly on CNC loadings and PVA concentrations in continuous phase. The evolution of multiphase morphology of emulsions from locally coalesced droplet structure to interfacial saturation one, and finally to droplet-particle interfacial flocculation, shows scaling characteristics with increasing CNC loadings, and can be detected through rheological way. The interfacial localization makes CNCs show excellent reinforcement to ternary nanocomposites because of their two-phase bridging effect. This work provides an interesting strategy of fabrication of the CNC reinforced polymer blend composites with controllable multiphase structures.

1. Introduction

Cellulose nanocrystal (CNC) is one of the most interesting members in the cellulose material family. It commonly shows rod-like structure, with controllable geometrical aspect ratio, which depends on the cellulosic source and the hydrolysis conditions [1]. Higher degree of crystallinity and rigid structure of molecular chain make it present very extraordinary mechanical strength and modulus. Besides, CNC is easily modified through chemical or physical approaches because of an abundance of hydroxyl groups at its surface. Therefore, its surface properties, such as the surface energy or charge characteristics can be tuned conveniently according to requirements of applications [2]. All those features, together with the biodegradable characteristics and

abundant resources of CNC, make it become a promising nanofiller in polymer nanocomposite field. Accordingly, CNC has been incorporated into a wide range of polymers so far, with clear objective to develop new nanocomposites with sustainable characteristics, or with outstanding mechanical strengths [2–4].

However, the reinforcement of CNC to the polymers is commonly accompanied by an evident decrease of toughness of nanocomposite systems. To balance the overall mechanical properties of CNC filled polymer nanocomposites, introducing the third component, such as the rubbery polymers or the polymers with higher ductility, into the systems, is a common route [5–10]. For instance, the presence of natural rubber phase could improve the impact toughness of the CNC filled unsaturated polyester composites evidently [5], and the addition of

small amount of poly(butylene succiate) (PBS) could increase the elongation levels of polylactide (PLA)/CNC nanocomposites remarkably because PBS has far better ductility than PLA [9]. Therefore, the ternary systems, namely the immiscible polymer blend nanocomposites reinforced with CNCs, have attracted much interest in recent years because their properties can be regulated more easily.

Of particular interest around these ternary nanocomposites is the distribution of CNC particles in the blend matrices because their localization is crucial to the formation of final phase morphology of blend matrices, and to the emulsification of phase interface, as well as to the dispersion of CNC particles and their percolation structure, which determine the final performance of ternary systems. Favis and coworkers reported that CNC particles perfectly segregated into the polyamide11 (PA11) phase in the ternary PLA/PA11/CNC nanocomposites because CNC showed far better affinity to PA11 [11]. After surface treatment with poly(ethylene) oxide (PEO), CNC particles located in the PLA phase preferentially [12]. They attributed the altered localization of CNC particles to the far improved PLA-CNC compatibility because the surface PEO chain of CNC is miscible with PLA. Similar selective localization was also reported on the CNC filled poly(β-hydroxybutyrate)/poly(ε-caprolactone) blend composites [6].

Actually, the selective localization of CNC particles follows the same mechanisms with those of other types of nanoparticles in an immiscible polymer blend system, as revealed by numerous studies [13–27]. In brief, CNC particles prefer to be dispersed in the more compatible phase if the two polymers have far large difference in their polarities (but with the same level of viscosities) during melt processing. Otherwise, they may be localized on the phase interfaces (the two polymers have poor affinities to the hydrophilic CNCs (repulsive effect), or both are somewhat compatible with the CNCs and have a close viscosity level) or locate in the less viscous phase (the two polymers show the same level of affinities to CNC particles, but have large difference in their flowability). This selective localization behavior favors the improvement of phase morphology of blend matrices, which is associated with two types of possible mechanisms [6]. *Type I*: those nanoparticles localized on the phase interfaces act as the role of compatibilizer, emulsifying phase interfaces and reducing overall mixing free-energy [24]. This is also called thermodynamic compatibilization. *Type II*: those particles dispersed in the less viscous phase can alter the viscosity ratio between two polymers, preventing coalescence of discrete domains during melt mixing, which is called kinetic compatibilization [18,19]. Clearly, for the CNC filled polymer blend nanocomposites, controlling selective localization of CNC particles is a good strategy to regulate their final morphology and properties.

However, this is not always easy, especially through melt processing because many other factors, such as elasticity ratio between two polymer matrices [21], processing conditions [16], etc., also have possible influence on final distribution of nanoparticles. On the other hand, as the thermodynamic aspect and kinetic one compete with each other, i.e., less viscous phase has poorer affinity to CNCs, it is hard to predict final localization of CNCs [16]. Besides, final morphology of the ternary composites might not achieve its thermodynamic equilibrium state within limited melt processing time [28]. Thus, to control selective localization of nanoparticles precisely in the ternary nanocomposites is still challenging. However, from another angle of view, the ternary nanocomposites, especially those with the particles localized on the phase interfaces, can be understood as the Pickering emulsion systems, in which the particles play the role of solid emulsifier, emulsifying polymer/polymer interfaces (namely oil/oil phase interfaces). Actually CNC particles have been used to prepare Pickering emulsions widely [29]. The rod-like structure and easily tunable surface properties make them good candidate as the solid emulsifier for the Pickering emulsions, especially for the oil-in-water emulsions. In most cases, this system is very simple: the aqueous phase is water, and the oil phase is

liquid organics with lower molecular weights such as fluid wax and hexadecane, etc. [30–38] Some polymer monomers such as styrene or methyl methacrylate (MMA) [39–41] were also used as the discrete oil phase, and in this way to prepare polymer/CNC composite microspheres.

Actually, the oil/water emulsions are not limited within traditional simple systems. In a broad sense, the oil solution/water solution mixtures, in which two incompatible polymers are dissolved in the oil and water, respectively, are also included in oil/water emulsion systems. Using CNC particles as the solid emulsifier, in this case, becomes very interesting because as-obtained Pickering emulsions can be used as the templates to prepare ternary composites with easily-controlled localization of CNC particles and well-regulated phase morphology. This may open a new window for the fabrication of CNC reinforced polymer blend nanocomposites. Therefore, in this work, two types of biodegradable polymers, oil-soluble poly(ε-caprolactone) and water-soluble polyvinyl alcohol, were used to prepare the oil-in-water emulsions stabilized with CNC particles, followed by the casting and evaporation to obtain the ternary nanocomposite systems with various polymer blending ratios and CNC loadings. The phase morphologies and localization of CNCs, as well as the tensile behavior of ternary nanocomposites were then studied in detail, aiming at establishing clear technical routes to prepare the CNC filled polymer blend nanocomposites with optimized structure and properties.

2. Experimental

2.1. Material preparation

Poly(ε-caprolactone) (PCL), grade 6500, with the relative density of $1.15 \, \text{g cm}^{-3}$ and the number average molecular weight (M_n) of about 50,000 was purchased from Solvay Co. Ltd., Belgium. Polyvinyl alcohol (PVA) (grade 1750 ± 50) was purchased from China National Pharmaceutical Group Co., Ltd. Its relative density and M_n are about $1.27 \, \text{g cm}^{-3}$ and 77,000, respectively. The microcrystalline cellulose (MCC) was also a commercial product provided by Sinopharm Chemical Reagent Co. Ltd., P. R. China, with the degree of polymerization (DP) of 210–240. The average length and diameter of MCC particles are 20–100 mm and 10–20 μm, respectively.

The aqueous CNC suspensions were prepared by acidic hydrolysis of MCC. Details could be found elsewhere [42]. The average diameter and length of as-obtained CNC particles are about 10–20 nm and 200–300 nm, respectively (as shown by TEM images and DLS data, see Figs. S1 and S2 of Supporting Information). Those CNC particles show typical rigid rod-like structure with the aspect ratio of 10–30. Their transverse elastic modulus is $8.2 \pm 0.5 \, \text{GPa}$ [43,44].

The aqueous PVA solutions (5 wt% and 10 wt%) used as the continuous phase of emulsions were prepared by dissolving PVA into deionized water at 100 °C with mild stirring. The oil phase of emulsions was PCL solutions using methylene chloride as the solvent (prepared at room temperature with mild stirring). Also, two concentration levels (5 wt% and 10 wt%) were obtained for the PCL solutions. The shear viscosities of as-prepared aqueous and oil solutions, and their interfacial tensions are summarized in Table 1.

The preparation of CNC stabilized Pickering emulsions followed two steps. Firstly, aqueous CNC suspensions were mixed with PVA solution with vigorous stirring, and then rested to form stable suspensions with different CNC loadings (as-prepared CNC suspensions were very stable because of strong hydrogen bonding between hydroxyl group of CNCs and PVA chain [45]). Secondly, PCL solutions were mixed with the CNC suspensions prepared above, and emulsified using a C350-S emulsifying device (Shanghai Muxuan Co. Ltd., P. R. China) with a speed of $10,000 \, \text{rpm min}^{-1}$ for about 2 min. The Pickering emulsions with a series of oil/water (O/W) ratios (1/8, 1/4, 1/3, 1/2, 2/3, 4/3) were