Composites Communications 4 (2017) 5–9

Contents lists available at ScienceDirect

Composites Communications

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

Novel sandwiched structures in starch/cellulose nanowhiskers (CNWs) composite films

Dongyan Liu[a], Yu Dong[b], Debes Bhattacharyya[c], Guoxin Sui[a,*]

[a] *Institute of Metal Research, Chinese Academy of Science, 72 Wenhua Road, Shenhe District, Shenyang City, Liaoning Province, 110016 China*
[b] *Department of Mechanical Engineering, School of Civil and Mechanical Engineering, Curtin University, Perth, WA 6845, Australia*
[c] *Centre for Advanced Composite Materials, University of Auckland, 20 Symonds Street, Auckland 1101, New Zealand*

ARTICLE INFO

Keywords:
Starch
Cellulose nanowhiskers (CNWs)
Sandwiched structures
Solvent casting

ABSTRACT

Novel sandwiched structures of cellulose nanowhiskers (CNWs) were found for the first time at the cross section of fractured starch/CNWs composite films. CNWs were obtained by hydrolysing bleached flax yarns through heating in a concentrated sulfuric acid (60 wt. %) aqueous solution at 55 °C for 60 min. Starch and starch/CNWs composite films were prepared by casting starch and mixtures of starch/CNWs homogenous aqueous suspensions, which was followed by drying at atmosphere. The CNWs' layers are sandwiched within starch matrices in a parallel direction to nanocomposite film surfaces. The layer thickness increases with an increase in the content of CNWs. The discovery of novel sandwiched structures demonstrates that both the interaction and evaporation rate of the solvent can affect the dispersion and thus play important roles in the nanoparticle dispersion. Such nanocomposite films in the presence of self-assembled multi-layer structures may further improve mechanical and gas barrier properties as a promising material candidate for food packaging applications.

1. Introduction

Starch, one of the most abundant natural polysaccharides, has been well recognised as a potential bio-polymer for environmental sustainability. It is inexpensive, biodegradable and edible with good formability of films [1]. Starch has been utilised in the packaging and coating of food products owing to its edibility and low oxygen permeability. However, its extensive application is limited due to its water sensitivity. Starch films are brittle and difficult to handle. Hence a plasticiser is required to increase the flexibility, elongation and toughness of films. Unfortunately, plasticisers generally decrease mechanical strength and gas barrier properties, resulting from the decrease in film cohesion [2]. The addition of reinforcing fillers, such as layer silicates [3], carbon nanotubes [4,5], carbon black [6] and metal or non-metal oxide nanoparticles [7], to biopolymers has proven to be effective in enhancing their thermal, mechanical and barrier properties.

Cellulose is the most abundant natural bioresource in the world. Cellulosic fibres have been used as reinforcements due to their high modulus, renewable sources, low density, biodegradability and low cost. CNWs possess high crystallinity because their amorphous phases can be mostly removed by acids during a hydrolysis process. Such reinforcements have large specific areas, and high aspect ratios leading to a high elastic modulus [8–10]. The extent of reinforcements relies on the filler dispersion into polymer matrices as well as their interfacial adhesion between fillers and polymer matrices [11]. Hence, CNWs are ideal fillers for starch matrices due to their similar chemical structures, which provide good compatibility between cellulose and starch through hydrogen bonding. Dissolving starch in a solvent (usually warm water), and then casting, dipping or spraying on a specific surface is still the main method to produce edible starch films or coating [12]. Nanocellulose shows positive effects on the properties of starch matrices due to uniform nanocellulose dispersion and good interfacial bonding between cellulose and starch [13–15]. It is conventionally recognised that the strong interface bonding between nanoparticles and matrices is attributed to good nanoparticle dispersion. Dufresne got the well-dispersed nanofillers in starch/microfibril composite films at high cellulose concentration of 20 and 50 wt.% [16]. In this study, novel layer structured CNWs closely connected within starch matrices was obtained for the first time by evaporating water from starch/CNWs solution at room temperature. Very recently, Chen et al. [17] demonstrated that nanoparticle dispersion was dependent on the strength of nanoparticle/polymeric molecule interaction by large-scaled molecular dynamics simulations [17]. From the experiment viewpoint, this paper offers strong support, for Chen's simulation work [17] in relation to layer

---

[*] Corresponding author.
E-mail address: gxsui@imr.ac.cn (G. Sui).

http://dx.doi.org/10.1016/j.coco.2017.03.001
Received 27 September 2016; Received in revised form 1 March 2017; Accepted 9 March 2017

structures formed in starch/CNWs films by using solvent casting. The formation of layered structures is crucial to tailor the dispersion of nanoparticles into polymer matrices, which could be achieved by controlling the interfacial strength and solvent evaporation rates. Our pioneering study sheds light on the further investigation of the interactions between components in starch/CNWs composites in order to understand the fundamental mechanism of such interactions.

2. Materials and methods

2.1. Materials

Normal maize starch (average granule size: ~20 μm) was purchased from Penford NZ Ltd., New Zealand, which consists of 25% amylase and 75% amylopectin. Raw flax yarns were supplied by Jayashree Textiles, Kolkata, India. Sodium hydroxide and sulphuric acid with the concentration in range from 95–97% were supplied from Ajax Finechem Pty Ltd., Taren Point, Australia and, ECP Ltd., New Zealand, respectively.

2.2. Preparation of nanocellulose and composite films

The extraction of nanocellulose was similar to the process reported in the previous literature [18]. Briefly, the flax yarn was mixed with a concentrated sulfuric acid aqueous solution at 60 wt.% and stirred vigorously at 55 °C for 1 h, which was followed by the centrifugation and neutralisation to remove free acid. Subsequently, freeze drying was utilized to obtain loose cellulose whiskers.

The simple solution casting process was used for the preparation of starch/CNWs composite films. Starch, glycerol, and nanocellulose aqueous suspension were mixed together in order to obtain homogeneously dispersed composite films. The plasticiser and filler contents were fixed at 35 wt.% for glycerol, 5, 10, 15, and 20 wt.% for CNWs, based on dry starch matrices. The mixture was then heated above the gelatinisation temperature for 30 min with aid of agitated stirring. After the mixture was cooled down, it was cast on a polystyrene Petri dish, prior to drying at room temperature until it was easily peeled off.

2.3. Characterisation

The structure of hydrolysed flax cellulose was investigated using a transmission electron microscope (TEM – Philips CM 12, Holland). A droplet of the diluted suspension was stained by allowing the grids to float in a 2.0 wt% uranyl acetate solution for 1 min before observation. The fracture surfaces of starch and starch/nanocomposite films were examined by a field-emission scanning electron microscope (FE-SEM, Philips XL30s FEG). Fourier transform infrared spectroscopy (FTIR, ATR-FTIR, Nicolet 8700, USA) was employed to evaluate chemical structures of starch and composite films.

3. Results and discussion

3.1. Morphology

TEM micrograph of CNWs is shown in Fig. 1. The rod-like CNWs with diameters of 10–30 nm and lengths of 300–500 nm were obtained by the acid hydrolysis of bleached flax yarns. The incorporation of sulphate groups along cellulose surfaces could result in a negative charge of the surfaces. This anionic stabilisation via attraction/repulsion forces of electrical double layers might be the reason for CNWs to form a stable and uniform aqueous suspension. The formation of starch/CNWs mixture was then obtained by heating the mixtures above 85°C. However, CNWs could be rearranged with the water evaporation under room temperature during the film formation.

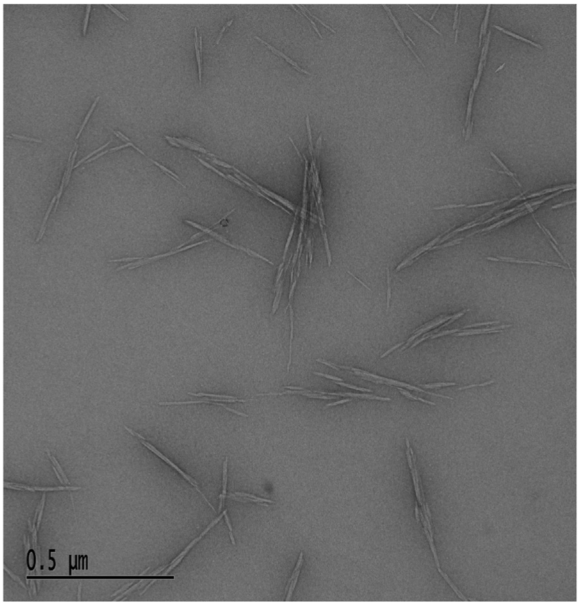

Fig. 1. TEM micrograph of CNWs via the hydrolysis of bleached flax yarns.

All composite films appear to be smooth, uniform and transparent. Fig. 2 shows fracture surfaces of pure starch, starch/CNWs composites and pure cellulose films. Compared to pure starch shown in Fig. 2(a), starch/CNWs composites possess the formation of clear CNWs layers. CNWs layers become thin and discontinuous at the low concentration, as evidenced by single layer and double close layers for 5 and 10%, respectively. The distance between CNWs layers is around 1 μm. The thickness of CNWs layer significantly increases with increasing the cellulose contents up to 15 and 20%. The whiskers can be clearly detected under the high magnification for starch composites reinforced with 15 wt% CNWs. However, the distance between the layers is independent on the cellulose concentration. Fracture surfaces of pure CNWs films demonstrate layered CNWs structures of CNWs that are closely connected. These results signify totally different morphology from previously reported research. Sain et al. reported that 10 wt.% cellulose nanofibers shown as white spots uniformly distributed in potato starch films [19]. Aggregates of cellulosic crystals were present at the fractural surface of pea starch-based nanocomposite films when the crystals content reaches 15 and 20 wt.% [13]. Cao et al. also obtained the homogeneously embedded flax cellulose nanocrystals in the plasticised starch at the concentrations of 10–30 wt.% cellulose nanocrystals via drying the composites in a vent oven at 50 °C [20]. These morphologies have been recognized as the strong interactions between the cellulose and starch matrix. From our experimental results, the formation of the above mentioned layered CNWs results from minor interactions between CNWs and slow water evaporation rate. The determination of associated factors to control the CNWs dispersion in starch matrices are currently under way in our research group and will be reported in the near future.

The chemical structure of CNWs in composites was evaluated by FTIR analysis. Fig. 3 shows FTIR spectra of pure starch, starch/CNWs composite film, as well as pure CNWs. The wide peak at around 3258 cm^{-1} and sharp peak at around 997 cm^{-1} were attributed to the stretching vibrations of the hydrogen bonding of –OH groups and C–O stretching vibrations in starch. All samples show similar spectra in Fig. 3(1), resulting from similar structures of starch and cellulose. Pure starch presents single peak at 3258 cm^{-1} from OH-stretching. This peak moves to the higher wave number with an increase in CNWs content from 3262 to 3279 cm^{-1} for 5 and 20 wt%, respectively. A small peak at the left shoulder appears when the CNWs content is higher than 15 wt %, clearly shown as the characteristic peak for CNWs. From Fig. 3 (2), the spectra have no apparent peak shifting for pure starch and starch/CNWs composites at lower wave numbers. A decrease in the peak intensity of starch at 1074.6 cm^{-1} and an increase in the peak intensity of cellulose at 1105.5 cm^{-1} become manifested, which suggests that the