



In-situ synthesis and structural characterization of cellulose-silica aerogels by one-step impregnation

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ABSTRACT

Cellulose-silica aerogels (CSAs) are organic-inorganic hybrid composites possessing both the porous characteristics and high mechanical properties. In this paper, two kinds of CSAs were in-situ synthesized by facile one-step impregnating cellulose layers directly into silica hydrosols and alcossols, respectively. The porous microstructures and the bonding linkage were investigated by means of Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption-desorption porosimetry. The results show that the silica particles successfully in-situ crosslink on/into the cellulose matrix and maintain the porous characteristics. The regeneration of the CAs directly in the alcossols is more beneficial to realize the crosslinking between silica particles and cellulose fibrils. The silica modification tends to increase the mechanical properties over those of the CAs due to the additional effects of silica particles impregnating into cellulose matrix.

1. Introduction

Cellulose is the most naturally abundant renewable resources in the world [1–3]. The stable and high stiff cellulose fibrils are provided with reinforcement phase for plants, algae, bacteria and some marine creatures because of the actions of the intra- and inter-chain hydrogen bonding networks [3]. Cellulose aerogels (CAs), reported firstly in 1950 by A.J. Stamm [4], exhibit high strength due to the crosslinking of cellulose. Due to these unique properties, CAs might be considered as many potentially practical prospects in the fields of novel coatings [5], thermal insulation [6], biomedicine [7], et al. In addition, cellulose can be used as templates to constitute composite aerogels.

Cellulose-silica aerogels (CSAs) are organic-inorganic hybrid composites, in which celluloses constitute tough skeletons and silica gels crosslink in-situ on the cellulose fibrils. Cai [8] utilized regenerated cellulose gels prepared from the aqueous alkali-urea solution as template to fabricate CSAs by an in situ sol-gel process from organosilane. The CSAs retained the mechanical strength and flexibility, large surface area, semitransparency and low thermal conductivity of the CAs. Barud [9] prepared bacterial cellulose (BC)-silica hybrids from BC hydrogels and tetraethoxysilane (TEOS) under neutral pH conditions at room temperature. The hybrids contains 66 wt% of silica spheres and are stable up to 300 °C. Sheykhnazari [10] prepared the composites of BC

filled with silica nanoparticles to enhance the temperature of decomposition to about 370 °C as silica content increased. Litschauer [11] modified cellulose alcogels, obtained from solutions of 3 wt% cotton linters in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO), by using TEOS and 3-chloropropyltrimethoxysilane (CPTMS) as siloxane precursors. The samples are very homogeneous and possess slightly smaller pore volumes. Shi [12] fabricated CSAs by combining the NaOH/thiourea/H₂O solvent system and the immersion method. The CSAs are provided with good heat insulation performance as low as 0.026 W/(m·K). Ashori [13] obtained BC-silica nanocomposites by the solution impregnation method and then pressed them into the mats. The composites have the maximum Young's modulus (1.46 GPa) and tensile strength (113 MPa), respectively. Pinto [14] used two methods to prepare SiO₂-cellulose nanocomposites: layer-by-layer (LbL) assembly method and in situ synthesis of SiO₂ in the presence of cellulose fibers. The latter yields homogeneously coated SiO₂-cellulose nanocomposites. Gonçalves [15] dealt the surfaces of cellulose fibers with silica gel particles and then obtained superhydrophobic cellulose nanocomposites by using a multi-step nanoengineering process. Liu [16] synthesized high strength silica-cellulose composite aerogels via in situ method in the porous cellulosic hydrogel scaffolds by using water glass as silica source. Demilecamps [17] impregnated silica phase into wet cellulose to prepare CSAs by two methods: molecular diffusion and

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forced flow induced by pressure difference. The CSAs render low thermal conductivity [$0.027 \pm 0.001 \text{ W}/(\text{m}\cdot\text{K})$] and high mechanical properties under uniaxial compression.

Generally, there are two key stages in the research of cellulose, i.e. the dissolution and regeneration of cellulose [18]. In dissolution, various solvents or solvent systems have been reported, mainly including NMMO [11], ionic liquid [17], LiCl/*N,N*-dimethylacetamide (DMAc) [19], endoglucanase [20] and NaOH/urea aqueous solution [8]. The condition of cellulose in solvents decides the state of regeneration in different coagulation baths. In NaOH/urea aqueous solution, the adding of non-solvents usually disrupts alkali dissolution systems and leads to the self-association of cellulose through a rearrangement of the hydrogen bonds [18]. Hence, for cellulosic composites by in-situ impregnated method, the condition of regeneration is a balance between the rearrangement of hydrogen bonds and the grafting of composite groups.

Usually, the CSAs are synthesized by impregnating wet coagulated celluloses into silica sols [16,17] or dispersing silica nanoparticles in cellulose dissolving system [21]. In this manuscript, we used a new synthetic method of cellulose-silica aerogels (CSAs) via the sol-gel process and freeze-drying method by one-step impregnating the casting cellulose layer directly into silica aqueous and alcoholic sols, respectively. The micromorphologies and mechanical properties of cellulose-silica composite aerogels are contrastively studied. During this process, these silica sols play two roles, simultaneously. The one is as coagulation bath to realize the regeneration of cellulose. The other is as the source of silica to achieve the crosslinking of silica and cellulose.

2. Materials and methods

2.1. Materials

The cotton linter pulps were selected as cellulosic sources and purchased from Hubei Chemical Fiber Co. Ltd. (China). TEOS and water glass was supplied by Tianjin Yongda Chemical Reagent Co. Ltd. (China) and Jiangyin Xiagang Chemicals Co. Ltd. (China), respectively. Hydrochloric acid, sodium hydroxide, urea and absolute ethanol are analytical reagents and were provided by Tianjing Fuyu Chemical Reagent Co., Ltd. (China). All reagents were used as received. Distilled water was used in all experiments.

2.2. Preparation

The silica sols were synthesized using TEOS as precursor. TEOS, water and ethanol as molar ratio 1: 4: 8 were blended at 50°C under stirring. During the process, 0.2 mol/L hydrochloric acid (diluted by alcohol) was added into the solution to facilitate hydrolysis. After 30 min, the silica sols were obtained.

The cellulose solution was prepared by the method adopted by Cai [22]. Briefly, the solvent mixtures of NaOH/urea/ H_2O (7:12:81 w/w) were precooled to -12.5°C . The certain amount of the cotton linter pulps was dispersed into the solvent under vigorous stirring for 10 min. The air bubbles in the transparent cellulose solution were removed by ultrasonic treatment for 20 min. Then, the resulting cellulose solution was cast on a clear glass substrate to obtain a 0.5-mm-thick layer and directly immersed into coagulation baths at 25°C for regeneration. Here, two coagulation baths providing silica source, i.e. silica sols prepared above and commercial water glass, were chosen to form CSAs in order to compare the influences under the different solvent environments. The former was regarded as in ethanol solvent and the later in water.

After a certain amount of regenerative time, the solid films were rinsed by deionized water until to be neutral. All of specimens were dried by freeze-drying method. The films were first frozen in the cold condenser for 6 h at -50°C . The frozen specimens were subsequently transferred to a freeze-dryer and subjected to vacuum ($\sim 30 \text{ Pa}$) for



Fig. 1. The typical pictures of the CSA sample.

2–3 days. In addition, in order to determine the structural differences, the cellulose aerogel (CA) coagulated in deionized water was prepared by the freeze-drying method based on the CSAs as described above.

The CSAs specimens are coded as CSA-W/A-Y%-T. Here, W/A refers to the coagulation baths for regeneration, i.e. W to water glass and A to silica sols, respectively. Y% and T refers to the mass contents of cotton linter pulps dissolved in 100 g alkaline solution and the regenerative time in coagulation baths, respectively. For example, specimen CSA-A-3.2%-2 was synthesized by dissolving 3.2 g cotton linter pulps in 100 g alkaline solution and regenerating in silica sols for 2 h after casted. The CA specimens were coded as CA-Y%-T and the variable letters correspond to the same meanings as the ones mentioned above. The typical picture of the CSA sample and its flexuous state are shown in Fig. 1.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra in the range 4000 cm^{-1} – 400 cm^{-1} were recorded in a Tensor 27 FT-IR instrument (Bruker, Germany). The mass-loss behaviors were collected contrastively by the SDT Q600 thermo-gravimetric (TG) analyzer (USA) performed in an air atmosphere in the temperature range of 25°C – 1000°C . Phase analysis was performed by X-ray diffraction (XRD, Epyrean, Netherlands) scanning between 5° and 40° . The Microscopic morphologies of CSAs and CAs were observed by scanning electron microscopy (SEM, Hitachi-SU800, Japan) at a 15 or 20 kV acceleration voltage. Before analysis, all of the samples were sputter-coated with a thin layer of Au. Elemental analysis was made by energy dispersive spectroscopy (EDS) attached to the SEM. Transmission electron microscopy (TEM) was conducted using an H-7650 electron microscope (Japan). The nitrogen adsorption isotherms were measured with Quantachrome SI surface area analyzer (USA). The specific surface areas were determined by the standard Brunauer, Emmett and Teller (BET) analysis and the density functional theory (DFT) approach was used to analyze the pore-size distribution (PSD). The tensile measurements were performed using an Instron-5500R single column tabletop system (USA) with an 100 N load cell at room temperature. The sizes of the samples are $30 \times 22 \times 0.25 \text{ mm}^3$ and the tensile loading rate was controlled at a constant 2 mm/min until samples break. Three samples per formulation were tested and mean values calculated for Young's modulus, tensile strength and failure strain. The experimental errors were determined from standard deviation.

3. Results and discussion

3.1. XRD and FT-IR investigation

Generally, the crystal of natural cellulose is transformed from I-type to II-type during the dissolution and coagulation process, which can be explored by the method of XRD. Fig. 2 shows the XRD patterns of the CSAs and CAs under different regenerative time and cellulosic contents.

Compared with pure non-crystalline silica aerogels, CSAs are provided with the characteristic of cellulose crystalline. In Fig. 2A, the peaks at 14.6° , 16.1° and 22.4° are corresponding to the (1 - 1 0), (1 1

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