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Water-Induced shape memory effect of nanocellulose papers from sisal cellulose nanofibers with graphene oxide

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ABSTRACT

A novel water-induced shape memory nanocomposites were prepared by introducing graphene oxide (GO), which was based on microcrystalline cellulose nanofibers (MSF-g-COOH) extracting from sisal fibers. The results showed that the water-induced shape memory properties of MSF-g-COOH were significantly improved by the strong hydrogen bonding interaction between MSF-g-COOH and GO, It leads to some additional physically cross-linked points in MSF-g-COOH. On the other hand, at 0.5 wt% GO loading, tensile strength and Young modulus of the nanocomposite increased from 139 to 184 MPa, and from 5.77 to 8.54 GPa, respectively, compared to those of pure MSF-g-COOH. Furthermore, a water-induced model was proposed to discuss the water-induced shape memory behaviors of the MSF-g-COOH/GO nanocomposites. This study provides a framework for developing a cellulose based shape memory polymers (CSMPs) and better understanding the shape recovery mechanism in water-induced CSMPs.

1. Introduction

Shape memory polymers are one of the most important building blocks for smart material, which were applicated in various areas, such as drug release systems, lenses, smart fabrics and optical fibers to solar cells (Fang et al., 2015). The main feature of shape memory materials is that it possesses the ability to recover their original shape from transient deformation state or shapeless structure when a particular stimulus is applied (Behl, & Lendlein, 2007). Current studies show that temperature, ligh,electricity, pH and immersion in water were used as the stimulus (Hu et al., 2015), directly or indirectly actuation of the shape memory effect (SME). The shape-memory effect mainly depends on the movement of molecular architecture rather than a specific chemical structure in the repeating units (Dagnon et al., 2013). Shape memory materials has been intensively studied, while shape memory polymers (SMPs) were the mainstream study direction in last decade (Huang et al., 2010). Many polymers were used for the preparation of shape memory materials such as poly(ε-caprolactone) (PCL), poly(ester-urethane)s (PURs), Polylactic acid (PLA), Polymethyl methacrylate (PMMA) (Liu, Li, Yang, Zheng, & Zhou, 2015; Wang, Bai et al., 2015; Wang, Heim, Xu, Buntkowsky, & Zhang, 2015; Wu, O'Kelly, & Chen, 2013; Wang, Lu, Liu, & Leng, 2014). However, these SMPs are generally elastomers that consist of cross-linked polymer networks. And heating is used as a recovery trigger (Yu, Ge & Qi, 2014). Generally, the thermal switching temperature induced SMPs beyond the range of body temperature which limited the application in biomedicine.

Natural cellulose is used as raw material to prepare biomass shape memory polymer (BSMP) especially suitable for biomedical application (Kaushik et al., 2015). There were good biological compatibility and some strong hydrogen bond interaction between cellulose molecules. Beyond that, water was usually used as the stimulus to induce the SME under the lower transition temperature (Michal, Spencer, & Rowan, 2016), which have significantly broadened the possibilities for applications of SMPs.

Plants are natural unique hierarchical biocomposites obtained by nature, and are essentially made of cellulose, hemicellulose, lignin, waxes, pectin and trace elements (Zhu, Fang et al., 2016; Zhu, Lan, Tan, Sui, & Yang, 2016; Zhu, Song et al., 2016). Due to the dwindling of fossil resources, cellulose biomaterials are researched as replacements for petroleum, coal products and reduces consuming nonrenewable resources existing (Zhu, Fang et al., 2016; Zhu, Lan et al., 2016; Zhu, Song et al., 2016). Hence, renewable and sustainable eco-friendly materials are necessary and important. In the next place, the remarkable mechanical properties of biological materials reside in specific

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molecular mechanistic phenomena and in their complex hierarchical architecture (Zhu, Fang et al., 2016; Zhu, Lan et al., 2016; Zhu, Song et al., 2016). Cellulose offers many advantages such as biodegradable, non-toxic, low cost, and excellent performance physical and chemical properties. In nature, cellulose linear main structure is consist of β-1,4-linked D-glucose units which were packaged for the orderly arrangement to form crystalline cellulose (Nakamura et al., 2014). Cellulose chains have stable β-glycosidic bonds with massive hydroxyl groups on the surface and intermolecular hydrogen bonds in the crystal. Thus, cellulose can be a good choice as substrate material of water-induced shape-memory polymer. Therefore, the water-induced shape-memory materials have an attractive prospect in potential biomedical applications, such as site-specific delivery capsule, removable stents and self-retractable (Michal et al., 2016).

Currently, due to its nanoscale dimensions, extremely high specific surface area and remarkable mechanical properties, graphene oxide (GO) has evolved into an ideal candidate for the reinforcing phase in polymer nanocomposites to improve the mechanical properties (Xu & Gao, 2015). Furthermore, GO possesses well dispersion in the polar and nonpolar solvents because of the rich oxygenated functional groups(hydroxyl, epoxy, and carboxylic groups) on the basal plane of GO (Dong et al., 2016). Therefore, the performance of other polymers can be enhanced because GO was modified on the polymers through covalent or noncovalent interaction just as hydrogen bonding interaction (Zhang et al., 2014).

In our present study, a water-induced shape memory nanocomposite paper has been successful designed by two-dimensional (2D) layered GO nanosheets wired by one-dimensional (1D) carboxylic grafted microcrystalline cellulose nanofibers (MSF-g-COOH) (Zhu et al., 2014). The nanocomposite paper is fabricated by filtration method to form layer-by-layer structure and 1D structure cellulose inserted into the 2D GO layered unit as shown in Fig. s1 (a). This method was simple, convenient and fast to yield high quality paper (Luo, Wu, Dinh, & Chen, 2015). GO nanosheets acted as the reinforcing bars to enhance mechanical strength of nanocomposite paper. The 2 wt.% MSF-g-COOH aqueous suspensions display a gel-like behavior as shown in Fig. s1 (b). MSF-g-COOH not only can be self-aggregation by hydrogen bonding interaction used as adhesives like the concrete (Hatton et al., 2016), but also it links the MSF-g-COOH and GO nanosheets together to enhance mechanical strength and improve in response of the water. It is expected that GO/MSF-g-COOH nanocomposite paper can be applied in biomedical field due to its outstanding performance such as good hydrophilicity, biocompatible and biodegradability.

2. Experimental section

2.1. Materials

Nature flake graphite (325 mesh, 99%) was acquired from Hengrui Graphite Co., Ltd. (Qingdao, China). Sisal fibers were bought from Guangxi Sisal Company, China. $KMnO_4$, P_2O_5 and $K_2S_2O_8$ were purchased from Aladdin Chemistry Co., Ltd. $NaClO_2$, $CH_2ClCOOH$ was supplied by Sinopharm Chemical Reagent. Anhydrous ethanol, $Na_2SO_4{\bullet}10H_2O$, CH_3COOH, NaOH, CH_3CH_2OH, H_2SO_4 and H_2O_2 were purchased from Sinopharm Chemical ReagentCo., Ltd and were used without further purification.

2.2. Preparation of microcrystalline sisal fibers

The microcrystalline sisal fibers (MSF) were produced in bench-scale as follows: Firstly, the sisal fibre was cut into an approximate length of 5 cm, and wash away the grain shape lignins on the surface of sisal fibers sisal fibers by deionized water. Then, the sisal fibre were dry in an oven at 60 °C for later use. The 50 g dry fibers were boiled in aqueous solution of NaOH (4 wt.%) and $Na_2SO_4{\bullet}10H_2O$ (4 wt.%) in 500 mL autoclaves at 170 °C for 2 h. The sisal fibers were filtered and wash several times with deionized water then dried in oven at 60 °C. The dry fibers were transferred to 500 mL three-necked flask equipped with mechanical stirrer and thermometer. Then adding 12 g $NaClO_2$, 5 mL CH_3COOH and 350 mL deionized water, the mixture was heated to 80 °C and stirred for 2 h. The product was filtered and washed with water after the reaction. Finally, the MSF were dried in oven at 60 °C until constant weight.

2.3. Preparation of MSF-g-COOH

Firstly, the 3 g MSF was soaking wet by 15 mL aqueous solution of NaOH (10 wt.%), transfer it to the 250 mL three-necked round bottomed flask. Then 150 mL anhydrous ethanol was added in flask under ultrasonic dispersion for 30 min and heated to 75 °C. After that, added 1.5 g monochloroacetic acid ($CH_2ClCOOH$) under mechanical stirrer for reaction 3 h. After the reaction finishing, the precipitate of the MSF-g-COOH was collected after washing many times with distilled water by centrifugal precipitation to remove unreacted monochloroacetic acid until the pH constant at 7. The crude product was dispersed and soaked in 1500 mL distilled water for 24 h, shearing the MSF-g-COOH into small fragments by a high-shear dispersion homogenizer at 28000 rpm high speed for 30 min. The upper MSF-g-COOH dispersion was separated using a separator a high-speed centrifuge at the speed of 12000 rpm and removed sediment of unsegregated fibre. The MSF-g-COOH aqueous dispersion presenting blu-ray phenomenon was obtained and determined the content. Synthesis route of MSF-g-COOH were shown in Fig. 2s.

2.4. Fabrication of high-quality GO dispersions

The GO dispersions was synthesized using nature graphite flakes via a modified Hummers method. In more detail, the nature graphite flakes were first oxidized. Put P_2O_5 (3 g), $K_2S_2O_8$ (3 g) powder and H_2SO_4 (98%, 30 mL) into 250 mL dried round bottom flask under magnetic stirring at 90 °C. Then graphite flakes (1 g) was introduced to the above mixture and temperature was kept at 90 °C for 4.5 h. Cool to room temperature, the mixture was diluted with distilled water then washed many times and filtered to remove the residual acid, and then dried under vacuum to obtain the pre-oxidation product. The further oxidation step, the pre-oxidation graphite and 50 mL H_2SO_4 were added in a 250 mL round bottom flask under magnetic stirring in ice-water bath. Then $KMnO_4$ (3 g) was slowly added to the mixture under vigorous stirring to obtain homogeneous dispersion, while keeping the reaction temperatures lower than 5 °C for 2 h. The DI water (200 mL) was poured into the product of oxidation and kept vigorously stirring for 6 h 30% H_2O_2 was added to the mixture, redispersed and washed repeatedly with HCl solution (5%) in order to remove any other residual ions generated during the oxidation step. And then, it was washed with DI water and used a centrifuge until a neutral pH.

The graphene oxide suspension was prepared by a probe supersonic (40 kHz) to peel off from the graphite oxide in DI water for 2 h. Then the suspension was separated by repeated centrifugation at 10000 rpm/min to remove non-exfoliated graphite oxide particle. The thin thickness of graphene oxide dispersions was obtained and the content of GO was determined by evaporation water.

2.5. Preparation of MSF-g-COOH/GO nanocomposite paper

The detailed fabrication procedure of the MSF-g-COOH/GO nanocomposite is as follows. The GO solution and the MSF-g-COOH solution were diluted with 1 mg mL^{-1} and 5 mg mL^{-1} deionized water, respectively. Then, a specific amount of the two aforementioned solutions were mixed with continuous stirring and ultrasonic dispersion. So the one-dimensional structure cellulose was inserted into the two-dimensional GO layer units and formed a uniform stable solution system. Then mixed solution was to form cake shaped hydrogel through