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Preparation of hydrophilic luffa sponges and their water absorption performance

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ABSTRACT

Hydrophilic luffa sponges are prepared by grafting polymerization of acrylamide (AM) on luffa cylindrica and subsequent partial hydrolysis under alkaline conditions. Attenuated total reflection infrared spectroscopy is used to verify the composition of the grafted (luffa-g-PAM) and hydrolyzed (luffa-g-(PAM-*co*-PAANa)) samples. Alkalization conditions, including aqueous NaOH concentrations, alkalization temperature, and time, are studied extensively. Optimized conditions are then obtained. The grafting percentage (GP) of polyacrylamide increases with the feed ratios of [AM]/[OH] and [Ce]/[OH], reaction temperature, and time. Furthermore, the GP can reach up to 160%. Pristine, alkalized, grafted, and hydrolyzed luffa sponges show rapid absorption kinetics, and the pseudo second-order rate equation is applied to describe their kinetic procedure. Reaction conditions, such as [AM]/[OH], [Ce]/[OH], reaction temperature and time, influence the water absorption capacities of grafted and hydrolyzed samples. The hydrolyzed luffa sponges particularly exhibit high water absorption capacities of 75 g g^{-1}. The absorption mechanism is also discussed.

1. Introduction

Natural cellulose fibers from different biorenewable resources have recently attracted the attention of the research community around the world because of their biodegradability, easy availability, environmental sustainability, flexibility, easy processing, and impressive physico-mechanical properties. Natural cellulose fiber-based materials can be applied in many fields, ranging from automobile to biomedical dressing (Thakur & Thakur, 2014).

Sponge gourd, also known as luffa cylindrica, is a fibrous vascular system that forms a ripe fruit when dried and is a subtropical plant abundant in Asia and central and southern America. Sponge gourd consists of fibrous cords that are disposed in a multidirectional array. The fibers of the sponge gourd are composed of 65.5% cellulose, 17.5% hemicellulose, and 15.2% lignin (Siqueira, Bras, & Dufresne, 2010). Various works are focused on the surface chemical modifications of luffa fibers, composites, water aging, and their influence on mechanical and hydrothermal properties, such as polyester/luffa composites (Ghali et al., 2011). Boynard and D'Almeida (2000) and Boynard, Monteiro, and d'Almeida, (2003) characterized the change of fibrous morphology and structure and used it as a reinforcement component in polyester. They found that untreated luffa sponge does not increase the mechanical properties of resin compared with alkali-treated luffa sponge but changes the fracture mode. Seki et al. analyzed the change of morphology and composition by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectrometry, and thermogravimetric analysis. The effect of water aging on the mechanical properties of luffa cylindrica-polyester composites was also investigated. The experiment on water aging (50 °C for 170 h in 5% NaOH solution) showed that the tensile strength, flexural strength, interlaminar shear strength, and tensile elongation at the break values of the composite decreased to −28%, 24%, 45%, and 31%, respectively; however, the tensile modulus and flexural modulus had insignificant changes(Seki et al., 2012). Botaro, Novack, and Siqueira (2012) treated luffa sponges with a different chemical modification and then reinforced the vinylester thermoset matrix. The resultant composite supported by fibers esterified with benzophenone tetracarboxylic dianhydride showed a 50% increase in tensile strength. Ghali, Msahli, Zidi, and Sakli (2009) used NaOH or NaOH/H_2O_2 to treat luffa fibers and analyzed the change of fibrous

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structures by using SEM and XRD. They found that the samples alkalized at 120 °C for 3 h in a NaOH/anthraquinone solution exhibited good cleaning and high crystallinity index. Tanobe, Sydenstricker, Munaro, and Amico (2005) conducted different chemical treatments on luffa fibers and found that the physical properties of luffa fibers were enhanced.

Recently, Chen, Shi, Gorb, and Li (2014) studied the relationship between the structure of luffa sponge and its mechanical properties at hierarchical levels. The result showed that the Young's modulus and fracture strength of single fiber were around 2.3 GPa and 103 MPa, respectively; and the mechanical performance of the block samples from the hoop wall is superior to that from the core part; and the inner surface of segment samples exhibited higher Young's modulus, strength and strain energy absorbed than that of the core part. Fan et al. (An et al., 2015) reported the crushing behaviors of luffa sponges and found the luffa sponge in axial, radial, and circumferential directions showed quasi-linear deformation and anisotropic responses. The ultra-thin and stiff inner surface dominates the crushing capabilities, leading to elastic deformation, yielding deformation plateau and densification. They considered the luffa sponge was composed of an ultra-thin and stiff membrane surrounded by a thick and soft supporting matrix. They also found that crushed luffa cylinders restored their geometric shape completely and the load-bearing capacity could be partly restored when luffa sponge was immersed into water; but damage of the inner surface layer during the water immersing/drying cycles weakened the strength of the fibers; removing the inner surface layer, the sponge were able to completely restore their large quasi-linear deformation during water immersing/drying cycles.

Gao et al. (Han et al., 2014) treated the young immature luffa sponge with aqueous solutions of 0% (Control), 0.5% and 1.0% of chitosan, and then enclosed in plastic boxes with polyethylene film bags and then stored in darkness at 25 ± 1 °C and 90–95% relative humidity (RH). The results showed this method effectively retained postharvest quality and extended shelf life of sponge gourd. Wang, Shen, Zuo, Huang, Zhou, and Xie (2015) investigated and analyzed the compressive behavior of luffa sponge and luffa-filled tubes through finite element analysis (FEA) and its model. They found that the optimal density of the luffa as filler for the luffa-filled tubes was equal to the optimal density of the luffa sponge; it increased with the increase of the thickness to diameter ratio of the tube.

Siqueira et al. (2010) prepared macroscopic lignocellulosic fibers and cellulosic nanoparticles, i.e. microfibrillated cellulose (MFC) and whiskers. These nanoparticles as reinforcing phase in nanocomposites are expected to open high value valorization of these fibers. Jayamani et al. (2014) analyzed mechanical and acoustical properties of the epoxy/luffa composites. They found that the tensile and yield strengthes of the NaOH-treated fiber composites were increased, but the untreated fiber composites had a better sound absorption coefficient, and the higher fiber contents and lower binder concentrations produced higher sound absorption coefficients.

Nevertheless, the fiber mesh of luffa sponge is a good support-based netting system for water absorption. Boynard and D'Almeida, (1999) studied the water absorption behavior of luffa sponge-polyester composites, which fitted well with Fick's model. Ghali et al. (2011) studied the hydrothermal behavior of luffa sponge-polyester composites and found that alkalized treatment increased the water absorption of luffa fibers, whereas acetylation treatment decreased the moisture absorption. The water absorption behavior of composites follows Fick's law at an early stage, and the external loading and flexural loading accelerated the water diffusion process in composite materials. Gupta, Agarwal, Singh, and Pathania (2013) and Gupta, Pathania, Agarwal, and Sharma (2014)) utilized the acrylic acid and methyl acrylate/acrylamide (MA/Am) grafted on the luffa sponge, but the water absorption capacity and moisture absorbance of grafted samples were less than that of raw fiber.

In this paper, hydrophilic luffa sponges are prepared under different conditions and their water absorption properties are investigated. The water absorption mechanism is also discussed.

2. Experimental

2.1. Chemicals and materials

Luffa sponge, as shown in Fig. S1, was purchased from Hengshui, Hebei province, China. Sodium hydroxide and nitric acid were purchased from Beijing Chemical Works. Acrylamide (AM) and ceric ammonium nitrate (CAN) were purchased from Aladdin and acrylamide was further purified by recrystallization from chloroform and then dried in a vacuum desiccator. Ceric ammonium nitrate and nitric acid were used directly without purification. And then the nitric acid was diluted into 0.01 M nitric acid solution. High purity nitrogen gas was obtained from Changchun Juyang Air Products Inc.

2.2. Alkalization of pristine luffa sponges

The pristine luffa sponges were washed by hot water before pretreatment to remove the dirt on the surface and dried to constant weight at 70 °C. The above luffa sponges were treated using NaOH aqueous solution with variable concentration, temperatures and time to eliminate wax and gummy substance, followed by washing the sponge in deionized water to reach neutralization and drying to a constant weight at 70 °C and named as alkalized luffa.

2.3. Grafting polymerization of acrylamide on alkalized luffa sponges

In a three-necked flask, a fixed amount of alkalized luffa sponge was stirred with a magnetic stirring bar in 50 mL of 0.01 M nitric acid solution for 5 min at 25 °C and then kept for 1 h under nitrogen atmosphere. Then, the calculated amount of CAN dissolved in 30 mL of 0.01 M nitrate acid solution and 70 mL of 0.01 M nitric acid solution with predetermined amount of AM were added into above mixture under stirring at 25 °C for 24 h. The as-prepared sample was washed with deionized water at least ten times to remove the unreacted chemicals. The sample was obtained after drying at 70 °C in an oven to a constant weight and named as grafted luffa (luffa-g-PAM).

The grafting percentage (GP) and the grafting efficiency (GE) were calculated using the following formulas

$$GP = (W_2 - W_1)/W_1 \times 100 \tag{1}$$

$$GE = (W_2 - W_1)/W_0 \times 100 \tag{2}$$

where W_0, W_1 and W_2, were the masses of monomer (AM), alkalized luffa and grafted luffa, respectively.

2.4. Hydrolysis of grafted luffa sponges

The above dried grafted luffa sponge was added into 600 mL of 1 M NaOH aqueous solution and stirred with a magnetic stirring bar at 50 °C for 12 h. Finally, the sample was washed with deionized water at least ten times to reach neutralization and dried at 70 °C in an oven to constant weight and named as hydrolyzed luffa (luffa-g-(PAM-*co*-PAANa)). The hydrolysis degree of samples is about 21%. The calculated details can be found in Supporting information.

Lignin is one kind of capturing agent for radical groups and will decreases initiation efficiency. Removal of lignin and hemicellulose are necessary through alkalization treatment. In current work, cellulose is dominant component with many –OH groups attached