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Preparation and characterization of cellulose composite hydrogels from tea residue and carbohydrate additives

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ABSTRACT

Composite hydrogels were prepared from tea cellulose in ionic liquid of 1-allyl-3-methylimidazolium chloride and effect of κ-carrageenan, chitosan, guar gum and soluble starch on characteristics of the prepared hydrogels were investigated. The prepared hydrogels were characterized *via* Fourier transform infrared, thermogravimetry analysis, differential scanning calorimetry. Sodium salicylate was used as the model drug to compare the swelling, drug loading and releasing kinetics of the prepared hydrogels. Thiazolyl blue tetrazolium bromide assay and relative growth rates were adopted to evaluate cell cytotoxicity and biocompatibility of the prepared hydrogels. Chitosan and guar gum could improve thermostability and mechanical characteristics of the composite hydrogels, while κ-carrageenan or soluble starch could improve equilibrium swelling ratio, sodium salicylate loading and releasing. Guar gum and chitosan could increase permeation resistance and were beneficial for release control of the hydrogels. Addition of chitosan, κ-carrageenan, guar gum and soluble starch were proven cell compatibility and non-cytotoxicity.

1. Introduction

In recent years, utilization of the cellulosic raw materials for various applications has attracted great interest (Thakur, Thakur, & Gupta, 2013). The main reason is that the utilization of farm by-products can significantly reduce amount of waste. (Dos Santos et al., 2013). Cellulose is a long linear chain of polysaccharide, composed of β-D-glucopyranose units joined by β-1,4-glycosidic linkage, which is difficult for processing in most solvents because of its insolubility due to its strong intra- and inter-molecular hydrogen bonding (Klemm, Heublein, Fink, & Bohn, 2005). Rogers and Seddon (2003) detailedly reported and explained that cellulose at room temperature exhibited soluble in ionic liquid of 1-butyl-3-methylimidazolium chloride. From then on, ionic liquid has entered people's vision as a green, recyclable and efficient solvent for cellulose processing. In particular, ionic liquid of 1-allyl-3-methylimidazolium chloride ([AMim]Cl) has been used to dissolve cellulose (Wu et al., 2004) and prepare cellulose-based materials (Hu, Wang, & Huang, 2013; Ma, Zhou, Li, Li, & Ou, 2011). It is no doubt that cellulose is not suitable for many requirements prior to special treatment. Modified cellulose with other kinds of polysaccharide show different promising characteristics, for examples, the cellulose-based hydrogels with antibacterial and gene transfection characteristics (Song, Sun, Zhang, Zhou, & Zhang, 2008; You, Zhao, Cao, Zhou, & Zhang, 2014), the cellulose nanocrystals pre-grafted by polymerizable groups with better stretching characteristics and higher water swelling ability (Yang et al., 2015), composite hydrogel prepared from pineapple cellulose with definite adsorption and release ability of sodium salicylate *via* dissolution in [AMim]Cl ionic liquid with polyvinyl pyrrolidone (Hu, Hu, Zeng, Zhao, & Huang, 2010). As a worldwide beverage, tea products are consumed in huge amount. In 2014, Amount of tea production in the world achieved 5,026,000 tons, including 1,980,000 tons from China. Production of tea beverage and instant tea produce a lot of residue composed of cellulose. However, most of tea residuals are discharged as waste at the present. Therefore, treatments for abundant of tea residue in tea processing become the serious problem to solve. This research mainly focused on the preparation of composite hydrogels from tea cellulose (TC) in ionic liquid of [AMim]Cl. Effect of four kinds of polysaccharides including κ-carrageenan (CA), chitosan (CH), guar gum (GG) and soluble starch (SS) on characteristics of the prepared hydrogels were compared based on characterization, swelling kinetics, releasing kinetics, cell cytotoxicity and cell compatibility.

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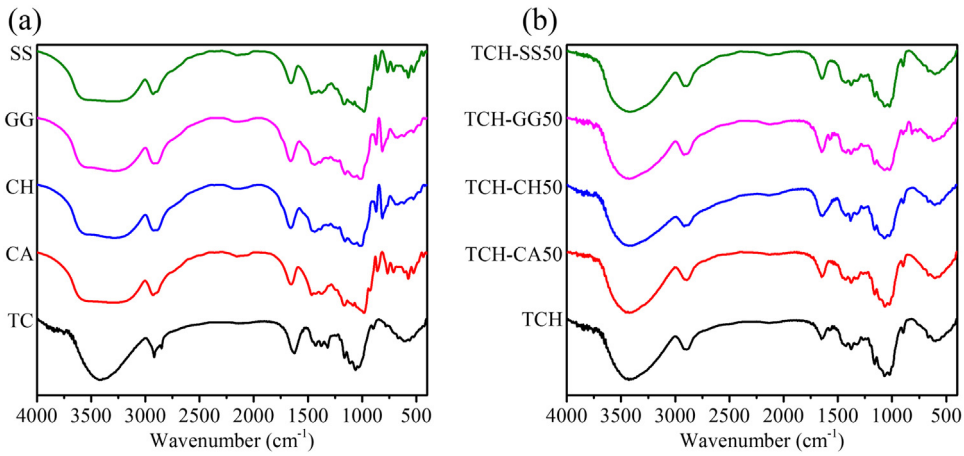

Fig. 1. FTIR characteristics of additives, tea cellulose powder (a) and the corresponding hydrogels prepared from tea cellulose and additives (b).

2. Materials and methods

2.1. Materials

Oolong tea was obtained from the Department of Food Science of South China Agricultural University (Guangzhou, China). κ-carrageenan (molecular weight from 400 kD to 550 kD and BR purity grade) was purchased from Nanjing Ao Duo Fu Ni Co., Ltd. (Nanjing City, China). Soluble starch (molecular weight 342D and AR purity grade) was purchased from Shanghai Run Jie Chemical Co., Ltd. (Shanghai City, China). Guar gum (molecular weight from 200 kD to 220 kD and AR purity grade) was purchased from Fei Bo Co., Ltd. (Guangzhou City, China). Chitosan (molecular weight from 40 kD to 65 kD and AR purity grade) was purchased from Shanghai Buo Ao Biological Co., Ltd. (Shanghai City, China). Thiazolyl blue tetrazolium bromide (3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2-H-tetrazolium bromide, MTT) was purchased from Sigma Co. (St. Louis, MO, USA). Human breast carcinoma MCF-7 cell line was obtained from American Type Culture Collection (ATCC, Rockville, MD, USA). Heat-inactivated fetal bovine serum (FBS) and Dulbecco's modified Eagle's medium (DMEM) were purchased from Gibco Life Technologies (Grand Island, NY, USA). Sodium salicylate (NaSA) was purchased from Guangzhou Chemical Co., Ltd. (Guangzhou City, China). 1-allyl-3-methylimidazolium chloride was purchased from Shanghai Cheng Jie Chemical Co., Ltd. (Shanghai City, China). Dimethyl sulfoxide (DMSO) was purchased from Sigma Co., Ltd., USA. All other chemical reagents used in the present study were of analytical grade.

2.2. Extraction of cellulose from tea residue

The tea cellulose was extracted from tea residue according to the method of Hu et al. (2010). Firstly, tea materials were extracted according to tea beverage processing by distilled water at 1/30 ratio of tea/water (g/mL) at 90 °C for 30 min. After three extractions and filtrations, the filtered tea residue was dried at 60 °C for 24 h and then ground into powder through a 60-mesh sieve. The residue powder was then degreased with petroleum ether at 1/10 ratio of materials/solvent (g/mL) for 2 h. Depigment of the residue was performed with acetone at 1/10 ratio of materials/solvent (g/mL) for 2 h in a beaker and under magnetic stirring condition respectively. The filtered residue was delignified with sodium chlorite at 1/20 ratio of materials/solvent (g/mL) at pH 4.0 and 75 °C for 2 h and then was treated with KOH (10%, w/v) at 1/20 ratio of materials/solvent (g/mL) for 10 h so as to remove semi-cellulose. The residue was washed three times with distilled water until the filtrate turned neutral, and then ethanol (95%, v/v) was used to wash the residue three times so as to prevent the sample from agglomerate after drying. After drying at 60 °C for 24 h, tea cellulose was available for hydrogel preparation.

Table 1
Formula of composite hydrogels prepared from tea cellulose and additives.

Marked Sample	Additives	Additive Amount (% of tea cellulose)
TCH	–	0
TCH-CA25	κ-	25
TCH-CA50	carrageenan	50
TCH-CA100		100
TCH-SS25	soluble	25
TCH-SS50	starch	50
TCH-SS-100		100
TCH-GG25	guar	25
TCH-GG50	gum	50
TCH-GG100		100
TCH-CH25	chitosan	25
TCH-CH50		50
TCH-CH100		100

2.3. Preparation of composite hydrogels from tea cellulose and polysaccharide additives

Tea cellulose hydrogels were prepared *via* method of heating – cooling – washing process according to the reported method (Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Kadokawa, Murakami, & Kaneko, 2008; Li, Lin, Yang, Wan, & Cui, 2009). The prepared tea cellulose (0.5 g) was mixed with four kinds of polysaccharide additives respectively according to the formula in Table 1. The mixture was stir-treated and reacted in 10 g of 1-allyl-3-methylimidazolium chloride solvent at 100 °C for 8 h in a shaker until to complete dissolution. Composite hydrogels were obtained after the reacted mixtures were cooled to ambient temperature. The excessive ionic liquid leached out from the hydrogels was rinsed out with distilled water. The prepared hydrogels were marked as Table 1 on the basis of additives.

2.4. Characterization of the prepared composite hydrogels

The prepared hydrogels were characterized by Fourier transform infrared (FTIR), thermogravimetry analysis (TGA), differential scanning calorimetry (DSC) respectively.

FTIR spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} and 32 scans were performed for each sample with IR-Solution software from FTIR spectrometer (VERTEX-33, Bruker, Germany).