



Cellulose nanofibers reinforced sodium alginate–polyvinyl alcohol hydrogels: Core-shell structure formation and property characterization



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ABSTRACT

Core-shell structured hydrogels consisting of a flexible interpenetrating polymer network (IPN) core and a rigid semi-IPN shell were prepared through chemical crosslinking of polyvinyl alcohol (PVA) and sodium alginate (SA) with Ca²⁺ and glutaraldehyde. Short cellulose nanofibers (CNFs) extracted from energycane bagasse were incorporated in the hydrogel. The shell was micro-porous and the core was macro-porous. The hydrogels could be used in multiple adsorption–desorption cycles for dyes, and the maximum methyl blue adsorption capacity had a 10% increase after incorporating CNFs. The homogeneous distribution of CNFs in PVA-SA matrix generated additional hydrogen bonds among the polymer molecular chains, resulting in enhanced density, viscoelasticity, and mechanical strength for the hydrogel. Specifically, the compressive strength of the hydrogel reached 79.5 kPa, 3.2 times higher than that of the neat hydrogel.

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1. Introduction

Hydrogels, a network of polymer chains, which can swell in aqueous solutions, hold a large amount of water, permeate to oxygen and nutrients, can be used in the fields of implantable artificial organs, drug delivery, cell encapsulation, biosensors, toxic ion removal, and water purification (Cushing & Anseth, 2007; Thakur & Thakur, 2014; Perez, Kim, Buitrago, Wall, & Kim, 2015; Thakur & Thakur, 2015). However, most hydrogels are soft. Their low mechanical strength and variable dimensions with water content changes severely restrict their range of applications (Sun et al., 2012; Zhang, Liu, Huang, Wang, & Wang, 2015). Increased attention has thus been paid to novel hydrogel architectures including core–shell and interpenetrating network (IPN) structures that offer improved mechanical performance and smaller swelling ratios (Yang, Wang, & Chiu, 2014; Zhang et al., 2015). In recent years, core-shell or IPN structured hydrogels have found use as biomaterials and adsorbents (Perez et al., 2015; Zhang et al., 2015). IPNs can be

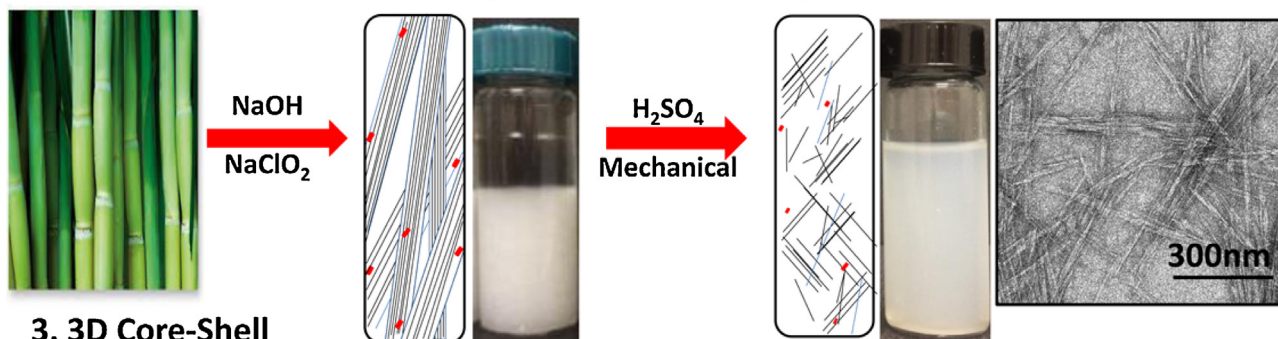
classified as semi-IPNs (SIPN) and full-IPNs. SIPNs are cross-linked linear polymer structures and IPNs consist of at least two polymers, in which one polymer network is cross-linked in the presence of the other polymer network (Dragan, 2014; Berrebi, Fabre-Francke, Lavédrine, & Fichet, 2015; Zhang et al., 2015). It has been shown that the IPN and SIPN structures can improve mechanical performance and dimensional stability of functional hydrogels (Yang et al., 2014; Berrebi et al., 2015).

Sodium alginate (SA) is a linear polymer comprising 1,4-linked-β-D-mannuronic acid (M) and α-L-guluronic acid (G) units, combined in blocks of M-M, G-G and M-G (Lee & Mooney, 2012; Bidarra, Barrias, & Granja, 2014). Due to its aqueous-solubility, biocompatibility, non-toxicity, non-immunogenicity, biodegradability, and acceptance by human body (Yang et al., 2014; Zhang et al., 2015), SA based core-shell structured polymers are particularly attractive in the textile (as a base for dyes), foods, biomedicines, pharmaceuticals and encapsulation materials, such as drug, gene, cell, enzymes, and lipids delivery (Dalmoro, Barba, Lamberti, & d'Amore, 2012; Lee and Mooney, 2012; Bidarra et al., 2014; Dragan, 2014; Dalmoro, Sitenkov, Lamberti, Barba, & Moustafine, 2016). SA is hydrophilic, absorbing water quickly. Its –COOH and –OH groups participate in hydrogen bonding and

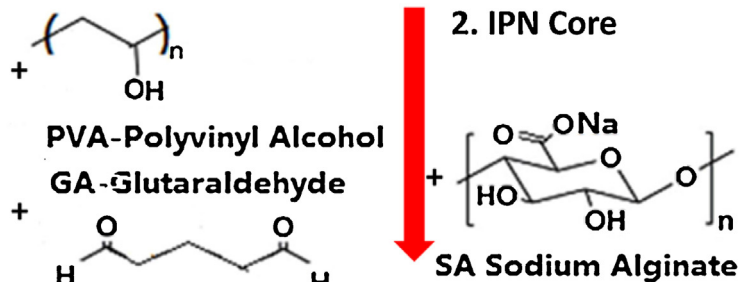
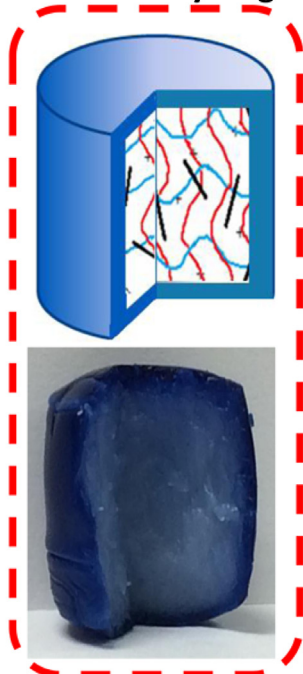
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1. Cellulose Extraction and Preparation of CNFs Suspensions



3. 3D Core-Shell Structured Hydrogel



2. IPN Core

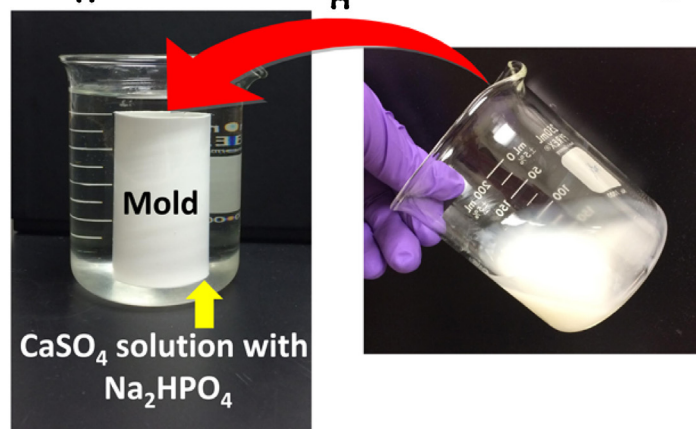


Fig. 1. Scheme for preparation of 3D core-shell structured PSG-CA-CNFs hydrogel.

van der Waals force; therefore, it is an excellent natural adsorbent and is commonly used for removal of water pollutants, such as heavy metal ions, dyes, fertilizers, microorganisms and enzymes (Aftab, Akhtar, & Jabbar, 2014; Mohammed, Grishkewich, Waeijen, Berry, & Tam, 2016). At a pH level of 4, the maximum amount of $-\text{COOH}$ in G units is deprotonated to $-\text{COO}^-$, which permits facile cross-linking by multivalent cations, such as Ca^{2+} , to form SIPN by chelation (Sun et al., 2012; Bidarra et al., 2014; Dragan, 2014; Samanta & Ray, 2014). Usually, the SA- Ca^{2+} structure is formed only in the shells of hydrogels (Dragan, 2014). Compared to the rigid SA, PVA, with one $-\text{OH}$ group in each repeating unit, is more flexible (Cho et al., 2009). Therefore, PVA can be blended with SA to improve the flexibility of SA matrixes. PVA/SA blends exhibit a good compatibility in aqueous solutions (Cho et al., 2009), and they can be chemically crosslinked with glutaraldehyde (GA), a commonly used crosslinking agent, to form IPN (Jao, Chen, Lin, & Yang, 2009).

Although core-shell structures can significantly enhance the toughness of hydrogels by three-dimensional physical and/or chemical cross-linkages (Cushing & Anseth, 2007; Perez et al., 2015), the mechanical behavior of most hydrogels is still not satisfactory for some applications. To further improve performance, adsorption capability and dimensional stability, cellulose nanofibers (CNFs) extracted from energycane bagasse were used

to reinforce hydrogels (Thakur & Thakur, 2014). Compared to other nanofillers, such as resin, metallic, or silica nanoparticles, as well as carbon nanotubes, CNFs are attractive, due to the characteristics of biocompatibility, availability, low density, non-toxicity, hydrophilicity, biodegradability and high crystallinity (Dash, Foston, & Ragauskas, 2013; Ummartyotin & Manuspiya, 2015). Because of the hydrophilic nature of PVA and SA, CNFs could crosslink with the PVA/SA matrix to stabilize the hydrogel (Ummartyotin & Manuspiya, 2015). Moreover, CNFs with high tensile modulus can act as decelerators of propagating cracks and retard the failure of the hydrogel (Shin, Spinks, Shin, Kim, & Kim, 2009). Several researchers have studied the cellulose nanocrystal based hydrogel. Mohammed et al. (2016) reported cellulose nanocrystal-alginate hydrogel beads used in wastewater treatments. Han, Lei, & Wu (2013) investigated cellulose nanoparticle reinforced PVA-borax hydrogels and stated that the compressive stress of the hydrogel at the 90% strain level could achieve 20 kPa.

However, to the best of our knowledge, we are unaware of any work on the crosslinking PVA and SA using GA and calcium sulfate with the presence of CNFs based on core-shell and IPN structure. In the present study, novel hydrogels with core-shell structures were fabricated by casting PVA/SA-GA complexes (IPN core) in CaSO_4 solution to form robust Ca^{2+} -SA shells. The objective was to deter-

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