

In situ chitosan gelation initiated by atmospheric plasma treatment



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ARTICLE INFO

Article history:

Received 3 October 2013

Received in revised form

19 December 2013

Accepted 21 December 2013

Available online 6 January 2014

Keywords:

DBD plasma

Chitosan

In situ gelation

Hydrogels

Swelling

ABSTRACT

This work reports on the feasibility of atmospheric dielectric barrier discharge (DBD) plasma as a novel synthetic pathway for the liquid phase gelation of chitosan. The DBD plasma chitosan gelation process did not significantly alter the chemical structure of the biopolymer as confirmed by FTIR study. However, the oxidation processes and local heating effect associated with the solvent evaporation during the plasma treatment could provoke both reaction of chitosan degradation and the cleavage of β -1-4-glycosidic linkages with the concomitant generation of aldehyde groups able to crosslink via Schiff-base with amino groups from other chitosan molecules. Shear viscosity measurements suggested the formation of chitosan fragments of lower molecular weight after the plasma treatment of 1% (w/v) chitosan and fragments of higher molecular weight after the plasma treatment of 2% (w/v) chitosan. The crosslinking density of hydrogels generated during the *in situ* DBD plasma chitosan gelation process increased as a function of the treatment time and concentration of chitosan. As of consequence of the increase of the cross-linking density, the equilibrium swelling ratio and water content decreased significantly.

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1. Introduction

Chitosan, a polysaccharide-based cationic copolymer of β -(1 \rightarrow 4)-linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose, is able to react with many negatively charged surfaces/polymers and also to chelate metal ions. In alkaline solutions above pH 6.5, chitosan forms a hydrated gel-like precipitate due to neutralization of the amine groups and elimination of the repulsive interchain electrostatic forces, allowing intensive hydrogen bonding and hydrophobic interactions. Gelation of cationic chitosan solutions can be achieved even at acidic pH by the addition of polyanions. Gel formation can be further induced by low molecular counterions such as β -glycerophosphate, polyphosphates, sulphates and by crosslinking with dialdehydes such as glyoxal (Khalid, Ho, Agnely, Grossiord, & Couarraze, 1999; Patel & Amiji, 1996), formaldehyde (Singh, Narvi, Dutta, & Pandey, 2006) and in particular glutaraldehyde (Aly, 1998; Denkbaz, Seyyal, & Piskin, 2000), despite that the dialdehydes could exhibit problems related to physiological toxicity (Leung, 2001; Murata-Kamiya, Kamiya, Kaji, & Kasai, 1997). Owing to its

unique properties such as biodegradability, biocompatibility, high charge density and non-toxicity, the chitosan has great potential for biomedical and pharmaceutical applications either as covalently or ionically cross-linked hydrogel (Bai-Shuan, Chun-Hsu, & Shr-Shin, 2008; Berger et al., 2004; Jahren, Butler, Adams, & Cameron, 2010; Mei-Chin et al., 2009; Muzzarelli, 2009, 2010) as well as blended with other polymers to modulate swelling and mechanical properties (Berger et al., 2004), or combined with thermo-responsive polymers to exhibit stimuli-responsive properties (Lee, Wen, Lin, & Chiu, 2004; Prabakaran & Mano, 2006; Sai-bo et al., 2010).

Recently, *in situ* forming hydrogel systems based on liquid phase plasma polymerization (Baroch, Anita, Saito, & Takai, 2008; Joshi, 2010) have been reported. Liquid phase plasma polymerization can be performed without the use of chemical initiators or/and even without cross-linking agents, offering multiple advantages over the conventional hydrothermal and chemical polymerization methods. Precursors or monomers with a high vapour pressure can also be used since no volatile compounds are needed in contrast with the plasma polymerization in gas phase. Different experimental configurations can be employed for the generation of non-thermal plasmas in liquid and/or in contact with liquids, e.g. direct liquid phase discharges, discharges in the gas phase with liquid electrode(s), and discharges in bubbles in liquids. Discharges in liquids and in contact with liquids generate UV radiation, shock waves and reactive species than could promote oxidative and degradation

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processes of pollutants, biological material and are also very effective in modifying material surfaces (Baroch et al., 2008; Bruggeman & Leys, 2009; Joshi, 2010). Glow discharge electrolysis and liquid phase capillary discharge have been used to obtain functionalized polymer surfaces with tailored chemical functionality such as carboxylic groups (Gao et al., 2008; Joshi, Dieter-Schulze, Meyer-Plath, Wagner, & Friedrich, 2009; Joshi, Friedrich, & Wagner, 2009). In addition, a specific solution plasma system was introduced as a method for the preparation of low molecular weight chitosan and chito-oligosaccharides (Montembault, Viton, & Domard, 2005; Prasertsung, Damrongsakkul, Terashima, Saito, & Takai, 2012). In this work, a novel *in situ* liquid phase dielectric barrier discharge (DBD) plasma method for the synthesis of chitosan hydrogels, emphasizing the influence of the plasma treatment time and chitosan concentration on physico-chemical characteristics of the generated hydrogels is proposed. The study performed herein would be of relevance for plasma assisted gelation of chitosan also on polymer or textile substrates.

2. Experimental

2.1. *In situ* plasma gelation of chitosan

A dielectric barrier discharge (DBD) reactor operating at atmospheric pressure was used in this work (Fig. 1). Gas mass flow metre and controllers (Bronkhorst, Ruurlo, Netherlands) were used in order to introduce helium gas ($5 \text{ L}_n \text{ min}^{-1}$) in the reactor chamber. A 100 kHz signal was generated with a GF-855 function generator (Promax, L'Hospitalet de Llobregat, Spain) connected to a linear amplifier AG-1012 (T&C Power Conversion Inc., Rochester, NY, USA).

The incident power in the plasma reactor was kept constant at 40 W. A matching network and two transformers (HR-Diemen S.A., Sant Hipòlit de Voltregà, Spain) were connected to the amplifier output in order to increase the voltage up to $\approx 20 \text{ kV}$. The distance between the two electrodes was kept constant approximately at 5 mm. A small amount (approximately 4 ml) of chitosan solution was poured into a polystyrene Petri dish and has been placed between the electrodes. The 1% and 2% (w/v) solutions of medium molecular weight chitosan (190–310 kDa determined by viscosity, Sigma Aldrich) and degree of deacetylation of 85% were freshly prepared under an overnight stirring in a 1% (v/v) acetic acid. Thereafter, the chitosan solutions were filtered off through a $0.45 \mu\text{m}$ Millipore filter to eliminate impurities. *In situ* DBD plasma chitosan gelation was carried out during 15, 25 and 35 min.

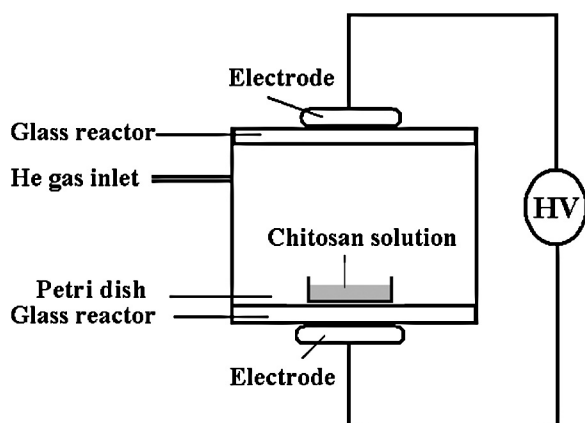


Fig. 1. Experimental set-up for *in situ* liquid phase preparation of chitosan hydrogels initiated by DBD plasma.

2.2. Characterization of chitosan hydrogels

2.2.1. Qualitative evaluation of gelation/crosslinking efficiency

The qualitative gelation/crosslinking efficiency of chitosan hydrogels has been evaluated by their re-solubilisation rate in aqueous solution of acetic acid (1%, v/v) at room temperature ($22 \pm 2^\circ\text{C}$). The weight change (%) of hydrogels was monitored as a function of the immersion time (15 min, 1, 4 and 24 h) in fresh acetic acid (1%, v/v) solution.

2.2.2. Quantitative evaluation of gelation/crosslinking efficiency

The equilibrium swelling ratio, ESR (%) measured gravimetrically was calculated according to the equation:

$$\text{ESR (\%)} = \left[\frac{W_s - W_d}{W_d} \right] \times 100 \quad (1)$$

where W_d is the weight of dried chitosan hydrogels, and W_s is the weight of chitosan hydrogels immersed in acetic acid (1%, v/v) water solution for 24 h.

The equilibrium water content, EWC (%) was calculated from the equation:

$$\text{EWC (\%)} = \left[\frac{W_e - W_d}{W_e} \right] \times 100 \quad (2)$$

where W_d is the weight of dried chitosan hydrogels, and W_e is the weight of chitosan hydrogels in the equilibrium swollen state i.e. after 24 h immersion in aqueous acetic acid solution at room temperature. The equilibrium water content actually stands for the equilibrium content of aqueous acetic acid solution in chitosan hydrogel.

2.2.3. FTIR analysis

The infrared (IR) spectra were recorded by a Nicolet AVATAR 360 FTIR spectrometer operating in the transmission mode. KBr pellets were prepared with a powdered freeze dried chitosan hydrogels, whereas the FTIR of plasma treated solutions were prepared using a horizontal ATR unit for liquids. In the same way, FTIR spectra of chitosan films obtained by simple casting method (60°C overnight) were also prepared for comparative purposes. Spectra were normalized to the band at 1070 cm^{-1} corresponding to C–O stretching vibration in chitosan. Background was extracted by means of linear backgrounds performed between 1800 and 1463 cm^{-1} , 1463 and 1354 cm^{-1} , 1354 and 1278 cm^{-1} , 1278 and 1216 cm^{-1} , and 1216 and 850 cm^{-1} . A total of 32 scans were recorded for each measurement at a resolution of 4 cm^{-1} .

2.2.4. SEM analysis

The morphology of chitosan hydrogels (air-dried at room temperature or freeze dried) was studied by scanning electron microscopy (model Hitachi S-3500N). The swollen gel was quickly frozen with liquid nitrogen and then freeze-dried for 24 h prior to SEM observation. Samples were coated with Au/Pd (thickness coating $\sim 20 \text{ nm}$) in a sputtering device Polaron SC500 prior to SEM observation.

2.3. Characterization of plasma treated chitosan solutions

2.3.1. Shear viscosity measurement

Shear viscosity of untreated and plasma treated chitosan solutions were measured by AR-G2 Magnetic Bearing Rheometer (TA Instruments, USA). Cone geometry with a cone angle of 4° and radius of 40 mm was used for the measurements at a gap size of $105 \mu\text{m}$. The shear rate ranged from 0.01 to 100 s^{-1} , with 5 data points acquisition per decade. All experiments were conducted at temperature of 25°C . Steady-state shear viscosity is reported as a function of shear rate applied.

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