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SYNTHETIC ROUTE TO OBTAIN SUPER ABSORBENT POLYMER OF POLY(VINYLGLYOXYLIC ACID) TO POSSIBLE APPLICATION FOR BIOMEDICAL USE

G.M. Estrada-Villegas (D), C. E. Nascimento and A. B. Lugao*
Nuclear and Energetic Research Institute IPEN-CNEN, Sao Paulo, SP 05508-000 Brazil ablugao@gmail.com

Abstract - Recently, PVA poly (vinyl alcohol) was modified with glyoxylic acid to induce formation of cyclic acetals to obtain poly(vinylglyoxylic acid) (PVGA), but the chemical crosslinking reaction to obtain the superabsorbent polymers (SAP), decrease the water absorption capacity. In order to crosslink PVGA without decrease the superabsorbent behavior, another synthesis route has be studied. Non-crosslinked PVGA was mixture with glutaraldehyde (GA) to induce chemical crosslinking and do not use the crossover points of the acid functional groups instead, the residual OH groups in PVGA chains. They can recombine to generate crosslinking chains without decrease of super absorption because the free acids group's are not involved. The superabsorbent hydrogel can cover growing demands of medical devices for the treatment of highly exudate wounds.

Keywords: *Crosslinking, poly(vinylglyoxylic acid), wound dressing, super absorbent polymer.*

Introduction

Superabsorbent hydrogel materials act as permeable physical barriers against moisture and oxygen, and protect wounds from microorganism (1). For the stimulation of wound healing, a passive dressing is essential for maintaining optimal moisture (2-3). Due to characteristics of the different types of wounds and healing stages, there is no one single dressing that can be applied in all situations efficiently (4). In order to promote healing of different stage of a wound, it is possible to develop and to optimize biocompatible dressing materials in terms of their physico-chemical properties, e.g. moisture absorption and permeation capacities (5).

Use of biodegradable polymers can induce and stimulate the wound healing process through reparation of damaged tissues and skin regeneration (6). Crosslinking polymers are three-dimensional networks that can swell in contact with water or biological fluids. These copolymers have been employed in the pharmaceutical and biomedical area, especially for wound management, tissue engineering, drug delivery, and organ transplant (7). In addition, novel biomaterials based on synthetic polymers (non-toxic and biodegradable) were obtained through radiation processing (8).

Commercial superabsorbent polymers (SAP) are crosslinked networks of ionic polymers, capable of absorbing large amounts of water and retaining absorbed water under pressure. The maximum water retention capacity of these products is about 400 times their weight. However, polymer fragments can be cytotoxic and non-biodegradable thus are persistent in the environment (9).

There are polymers that promise better features in terms of flexibility and low cost from natural and synthetic polymers as starch and PVA.

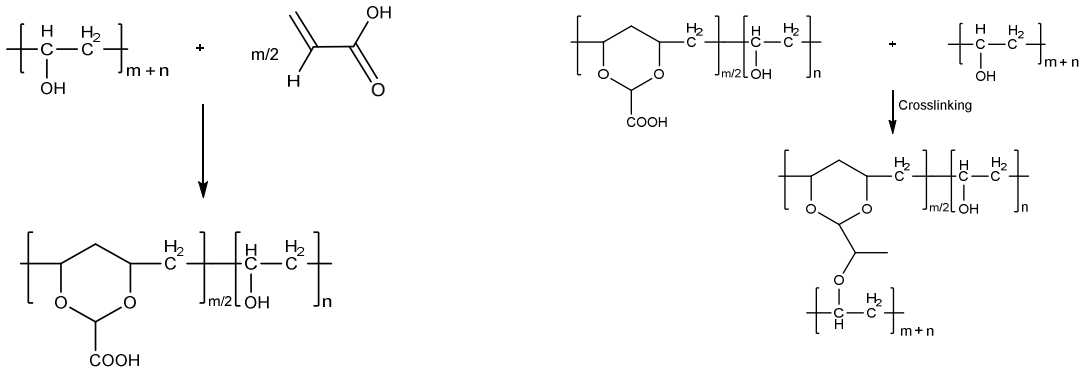
In present work, we have studied the synthesis of PVGA at basic pH from poly (vinyl alcohol) and chemically crosslinked with glutaraldehyde for preparation of pH-sensitive and superabsorbent hydrogel network for potential use as super absorbent wound dressing material. As far as we know, this is the first report of PVGA system chemically crosslinked with a bi-functional aldehyde to be investigated and characterized as pH sensitive hydrogel.

Experimental

Synthesis of PVGA

To 100 mL of 6.5% wt aqueous solution of PVA (99% hydrolyzed, Mw 110,000) 35 mL aqueous solution of glyoxylic acid pH 4 were added drop by drop over 2 hours at 60 °C. The acetylation degree depended on the reaction conditions.

However, in the **Chemical Crosslinking** step could take place reaction of PVGA with the derivative glyoxylate; this reaction causes a loss of water absorption. The following scheme describes the crosslinking event.



Scheme 1 Synthesis of Poly(vinyl glyoxylic acid) by cyclic acetal formation and chemical crosslinking of PVGA. The molecule can lose the water absorption by crosslinking with glyoxilic acid

This reaction could be controlling employing a mixture of glyoxylate salt and glyoxylic acid because the carboxylate salt has lower reactivity than the free acid. Esterification or transesterification reactions with free residual hydroxyl or carboxylic groups from PVA and PVGA, can form crosslinks between the hydroxyl and the acetalized glyoxylate derivative. The selectivity of acetalization above esterification is important to the overall success of the invention, because uncontrolled crosslinking by esterification or transesterification of derivative glyoxal will reduce the water absorption of the final PVGA. Additionally, employing a mixture of glyoxylate salt and glyoxylic acid in the reaction with PVA provides a balance of acid catalyzation reaction with selectivity for acetalization over esterification (9). For these reason we added NaOH to glyoxilic acid until pH 4.

Crosslinked PVGA hydrogels.

5 g of anterior PVGA and 0.3, 0.75, 1.0 and 2.0 % w/v of glutaraldehyde (GA) were mixed in a petri box and stirred. After stirred, the solution was homogenously heated at 60 °C by 1 h. For all gels test of gel fraction and swelling were done. An aqueous solution of 6.5 % PVA was crosslinked at similar GA concentration of PVGA for comparison

Gel fraction

Samples of each hydrogel were taken and dried at 60 °C until constant weight, then packed in stainless steel screen (500 meshes), immersed in distilled water and kept in an autoclave at 120 °C for 2 h. Next, the samples were dried until constant weight; thereafter, the % gel fraction was calculated according to Eq. (1), and the final result takes into account the average value of the assays based on the triplicate:

$$\text{Gel fraction (\%)} = Wd/Wi \times 100 \qquad (1)$$

where Wd is the mass of the dried sample after extraction and Wi is the mass of the dried sample before extraction.

Swelling assay

The swelling assays were performed by immerging each previously weighed specimen into distilled water at room temperature and evaluating its weight after different periods of immersion time (from 30 min to 24 h or beyond this time, if necessary) until the sample reaches the equilibrium swelling. Before weighing each swollen specimen, this was withdrawn from the water recipient, quickly blotted with an absorbent paper to

remove excess of superficial water and weighed. The swelling percentage was calculated according to Eq. (2), and the result takes into account the average value of the assays based on the triplicate of specimens.

Swelling (%) = Ws -Wd/Wd (2)

where Ws is the mass of the swollen hydrogel and Wd is the mass of the dried sample before immersion in the water.

FT-IR-ATR

FTIR-ATR (Attenuated Total Reflection) spectra were taken using a Perkin-Elmer Spectrum 100 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) with 64 scans

Results and Discussion.

Figure 1 shows the FT-IR of PVA and PVGA. The principal absorption bands in PVA is O-H inter and intramolecular hydrogen bonds vibrations in 3500 cm^{-1}, vibrations in 2840-3000 cm^{-1} from C-H alkyl groups and one more in 1650 cm^{-1} from C=O from vinyl acetate residual group from original synthesis. PVGA spectrum shows a modification of PVA. The most important band that shows the modification of PVA is in 1660cm^{-1} that correspond to C=O vibration of carboxyl group from carboxyl cyclic acetal, another important band is at 3300 cm^{-1} that correspond to OH vibrations from carboxylic acid group, but in this case there are a overlap with band of OH from no-reacted PVA. Figure 2 shows PVA solution polymer and PVGA after modification of PVA. In this picture, is possible to see that PVGA is no crosslinked as expected.

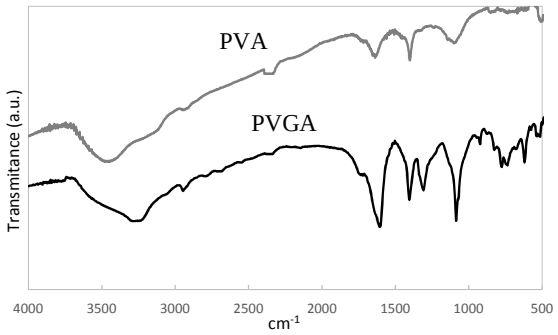


Fig.1 FT-IR of PVA and PVGA

Fig.2 PVA and PVGA

Figure 3 shows the gel fraction test of PVGA crosslinked with glutaraldehyde. There is possible to see, that fraction gel increase when increase the glutaraldehyde concentration. The maximum value of fraction gel is 90 % in a 1 % of glutaraldehyde concentration. Glutaraldehyde acts a crosslinker of PVGA as PVA. Some investigations shows that to crosslink PVA with glutaraldehyde, is necessary adds HCl as catalyst, (10) but in this case catalyst is no necessary to crosslink due to acid behavior of PVGA.

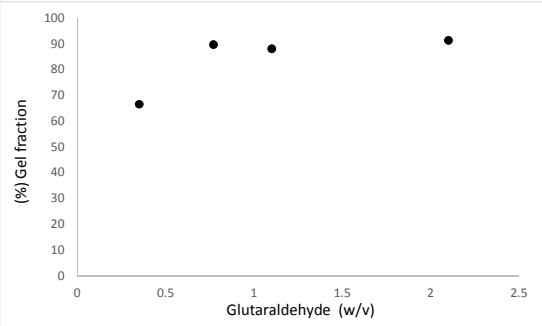


Fig.3 PVGA gel fraction at different glutaraldehyde concentration

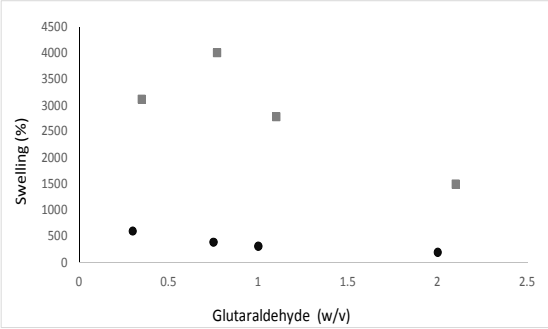


Fig. 4 PVA and PVGA maximum swelling at different glutaraldehyde concentration

Figure 4 shows the maximum swelling after 24 h. from PVA and PVGA at different glutaraldehyde concentrations. In this plot, the maximum swelling for PVA crosslinked with 0.3 % of GA is 500 %, and shows that PVA is not a SAP. However, the maximum swelling of PVGA crosslinked with GA is 4000% with 0.7 % of crosslinker agent. This behavior is improved by free carboxyl acid grup´s in PVGA. This result shows that, the crosslinking reaction occurs in OH groups that no reacted in the first step of PVA modification.

Conclusion

The pH control in the modification of PVA allows better selectivity of acetalization above esterification to obtain non-crosslinked PVGA. This PVGA can be crosslinked with another croslinked agent as GA to obtain a superabsorbent polymer. IR spectrum shows characteristic bands of PVA and it is possible to see the modification of PVA by specific band of free carboxylic acid from PVGA. Studied synthesis route to obtain SAP from biodegradable polymer could be applied as an economic wound dressing for high exudate wounds.

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