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# Synthesis of carboxylated locust bean gum hydrogels by ionizing radiation

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## HIGHLIGHTS

- Carboxylation of LBG by TEMPO mediated oxidation described.
- Preparation of CLBG hydrogels in paste like conditions, and in the presence of acetylene gas explained.
- Influences of the degree of carboxylation and dose rate on the gelation of CLBG examined.

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## ABSTRACT

In the present study, a locust bean gum (LBG) was carboxylated by a technique known as TEMPO mediated oxidation. Characterization of the carboxylated LBG (CLBG) was performed by spectroscopic and chromatographic techniques. The CLBG was then irradiated with gamma rays utilizing a  $^{60}\text{Co}$  gamma-ray source at the dose rates of 30 Gy/h and 300 Gy/h up to 10 kGy in very concentrated solutions called as “paste-like” and in the presence of acetylene. Sol–gel analysis was carried out in order to determine the polymer-to-gel conversion ratios. It was found that the swelling capacity of the hydrogels prepared in the presence of acetylene increased with dose from 19,000% to 34,000%. The gelation percentage was observed to increase rapidly up to 5.0 kGy, which then continued to increase at a slower rate. Despite low gelation, the crosslink density of the CLBG hydrogels prepared in the paste-like state was observed to be high.

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## 1. Introduction

Superabsorbent polymers (SAPs) are moderately crosslinked, 3-D, hydrophilic network polymers that can absorb and conserve considerable amounts of aqueous fluids even under certain heat or pressure. Because of the unique properties superior to conventional absorbents, SAPs have found potential applications in many fields such as hygienic products, disposable diapers, horticulture, gel actuators, drug-delivery systems, as well as water-blocking tapes coal dewatering, water managing materials for the renewal of arid and desert environment, etc. (Buchholz and Peppas, 1994). Majority of the studies in literature have involved SAPs that are prepared using synthetic monomers and polymers. Moreover, recent trend throughout the world has been toward the use of naturally available resources (e.g. polysaccharides) and avoidance of synthetic polymers wherever possible. Therefore, studies on the interactions between natural polymers and radiation, and preparation of crosslinked natural polymers have gained momentum.

Galactomannans are neutral polysaccharides that occur in substantial amounts in the endosperm of the seeds of some leguminous plants. Of numerous galactomannans known, locust bean gum (LBG) (also known as carob gum, carob bean gum, carobin, E410) is the most used one in various applications in food, pharmaceutical, and chemical industries as thickening agents or stabilizers owing mainly to the high viscosity they possess at low concentrations.

It is very well known that polysaccharides in dry form or in solution degrade when exposed to ionizing radiation (Choi et al., 2002; Wasikiewicz et al., 2005). Results reported so far on the radiation-induced degradation of polysaccharides have indicated that the chain scission yield depends strongly on the relative concentration of the polymer. Recently it has been found that when the concentration of a polysaccharide is increased beyond the state of viscous solution to the paste-like state, the crosslinking effect starts to dominate, and polymers that tend to undergo chain scission turn into cross-linking type (Fei et al., 2001; Yoshii et al., 2003; Zhao et al., 2003; Ramnami et al., 2004).

Recently a process has been reported to modify natural polymers (e.g. hydrocolloids such as CMC, gum arabic, dextran, gelatine, etc.) in solid state by high energy radiation (Al-Assaf

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et al., 2006, 2007a, 2007b) to obtain hydrogels. The new method allows the controlled modification of the structure of polysaccharides and other related materials in the solid state using ionizing radiation in the presence of a mediating alkyne gas. The method has been applied to a range of polysaccharides of differing origin and structure, to proteins either directly derived from animal connective tissue sources such as collagen, gelatin, or from human and animal products, such as casein, or combinations of one or more such polysaccharides with proteins of plant origin. These polymers, when irradiated in the presence of acetylene gas, undergo crosslinking and hence lead to the formation of macromolecules with increased molecular weights and functionalities. Highly branched polysaccharide structures can produce a 4-fold increase in molecular weight with doses up to 10 kGy and hydrogels with doses up to 50 kGy, whereas straight chain structures can yield a similar change with doses as low as 1–3 kGy. Proteins require doses up to 25 kGy to achieve similar results.

No study has been carried out on the preparation of hydrogel systems using the LBG polymer, in the paste-like state or by the assistance of substances like acetylene. This study aimed to synthesize carboxylated LBGs (CLBGs), to prepare superabsorbent polymers (hydrogels) by using the so-synthesized CLBGs in the paste-like state or by the assistance of acetylene, to characterize the synthesized polymers, and to determine their usability in the area of agriculture by investigating their water uptake properties.

## 2. Experimental

For the preparation of the CLBGs, a 0.5 g of LBG was suspended in a 250 ml of deionized water overnight and then stirred at 60 °C for 2 h. The solution was then cooled to room temperature, and catalytic amounts of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and NaBr were added. The oxidation reaction was initiated by the drop wise addition of a NaOCl solution (the active Cl value was 11%) at 4 °C. In order to obtain various oxidation ratios, 4.5, 7.0, 13.5, 18.0 or 35 ml of the NaOCl solution was added into the mixture. NaOCl/primary alcohol mol ratio was 1.2, 1.9, 3.6, 4.8 or 9.3, respectively. For the selective oxidation of polysaccharides, pH should be around 10.2 (Ponedel'kina et al., 2010). The pH in this study was kept in between 9–10 during the reaction by adding a 0.5 M of aqueous NaOH solution. When the pH decrease was very slow, the reaction was quenched by adding MeOH. Finally, the CLBG was precipitated by the use of acetone. The chemical structures of LBG and fully CLBG are given in Fig. 1.

For the preparation of the CLBG hydrogels in the paste-like state, solutions of 20% (w/v) LBG and CLBG were placed in tightly closed tubes and irradiated at a dose of 5.0 kGy in a Gammacell 220 type <sup>60</sup>Co-gamma irradiator at room temperature, in air. Sol-gel analysis and swelling experiments were performed using the sintered Gooch crucible apparatus showed in Fig. 2 (Hayrabolulu, 2011).

In order to prepare the CLBG gels in the presence of acetylene gas, a 0.5 g of the ground dry carboxylated polymer samples were

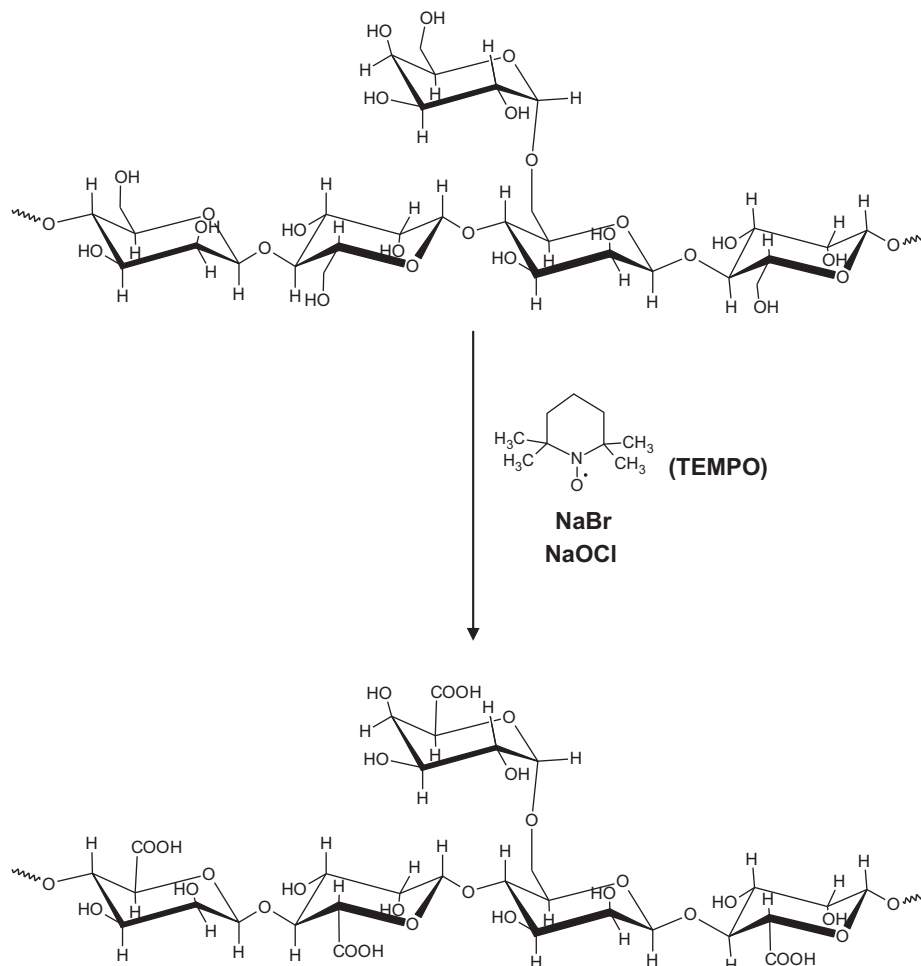


Fig. 1. Chemical structure of LBG and CLBG.

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