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ABSTRACT

HCl, H_2SO_4 and potassium persulfate (PPS) were studied as catalysts of the process of citric acid (CA) crosslinking on locust bean gum (LBG). The copolymer (CA-c-LBG) obtained was characterized by its viscosity, pH, FTIR, NMR and SEM. It was found that the protonation of the hydroxyl groups at C_6 atom of mannose and galactose in LBG and the hydrogen atoms of CA carboxylic group was accelerated. The best catalytic effect was obtained in presence of HCl.

Keywords: locust bean gum, citric acid, crosslink, HCl, H_2SO_4, PPS.

INTRODUCTION

Locust bean gum (LBG) is a natural gum which often used in pharmaceutics. It is a biodegradable, biocompactible, non-toxic and low cost material. Its processing is environmentally-friendly. Furthermore, it is locally available. LBG is derived from the endosperm of galactomanan from the family of leguminosae. It consists of mannose and galactose (4:1). The hydroxyl groups at the C_6 atom of mannose and galactose have the potential to protonate and react with free radicals [1 - 3]. LBG is used as a binder, a thickener, a suspending agent, and a matrix of a drug delivery system [4]. Modifications of its chemical structure cause changes in its physical characteristics such as viscosity, solubility and pH. Carboxymethylation of locust bean gum is carried out aiming its penetration into polymer network microspheres used for controlled drug delivery [5]. Microwave assisted synthesis of acrylamide grafted locust bean gum is conducted and its application to drug delivery is studied [6].

Citric acid is one of polyanions that can react with polysaccharides. Butane tetracarboxylic acid (BTCA), ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid, are other polyanions [7]. The hydrogen atoms of CA carboxylic group can form free radicals [8]. The carboxylic group in CA has three pKa (3.128; 4.761; and 6.396). The low pKa value observed under acidic conditions indicates a greater potential of protonation. The latter can affect all carboxylic groups of CA [4, 9]. CA/SHP (sodium hypoposphite)-cellulose crosslinking system and citric-acid-derived photo-cross-linked biodegradable elastomers are investigated [10, 11].

HCl, H_2SO_4, and potassium persulfate (PPS) are acidic catalysts often used in chemical reactions. HCl and H_2SO_4 are strong acids of pKa values of -7 and -5, correspondingly. Acids of low pKa values increase the acid strength, the anions nucleofilicity, and ROH reactivity, while PPS as a catalyst dissociates to form sulfate free radicals [9, 12]. In this study, the catalyst accelerates the process of crosslink by creating acidic conditions needed for the protonation forming of free radicals. HCl and H_2SO_4 have been used as catalysts of the esterification of *Jatropha curcas* oil and *Thevetia peruviana* seed oil [13, 14]. PPS has been used as acatalyst of jute fabric modification by methacrylic acid and cellulose based materials grafting [15, 16]. The present investigation is focused at the joint catalytic effect of HCl, H_2SO_4, and PPS on the process of CA crosslinking on LBG.

EXPERIMENTAL

Materials

Locust bean gum (Viscogum) (*Cargill*, France), citric acid monohydrate (Merk KgaA, Darmstadt, Germany), hydrochloride acid (Sigma-Aldrich Chemie, GmbH, USA), sulfuric acid (Sigma-Aldrich Chemie, GmbH, USA), and potassium persulfate (Sigma-Aldrich Chemie, GmbH, USA) were the materials used in this research.

Manufacture of CA-c-LBG

LBG (1.1 g) was swollen in 50 ml of distilled water in a glass bowl. The LBG was left to swollen. Then CA (4.4 g) and a catalyst (HCl, H_2SO_4, or PPS) were added stirring and irradiation by UV 254 (shortwave 8 watt CH-4132 Muttenz, Camag, Switzerland) were applied to reach homogenization. The CA-c-LBG copolymer was precipitated with acetone, washed with an acetone-distilled water (1:1) mixture, and dried at ambient temperature.

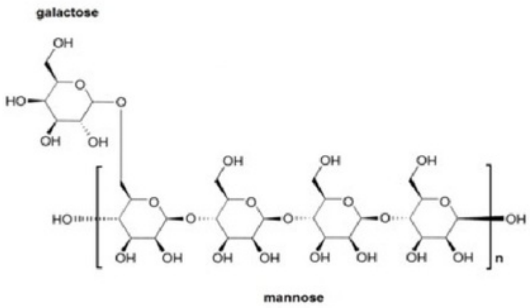


Fig. 1. Chemical structure of LBG.

It was then characterized by its viscosity, pH, FTIR, NMR, and SEM. The viscosity was determined by Brookfield viscometer (Model LVDV-I Prime, AP6510416, Brookfield Engineering Labs, Inc., Middleboro, MA, USA). The measurement was carried out using 50 mL of CA-c-LBG dissolved in distilled water until reaching a volume of 300 mL, a spindle (S61) and rotation at 100 rpm.

The pH of CA-c-LBG was determined by a pH meter (Model in by Metrohm Herisau Switzerland). The electrode of the pH meter was adjusted to pH 7.

FTIR analysis was performed using UATR PerkinElmer Spectrum Version 10.4.3. Liquid state ^1H was applied to characterize of LBG and CA-c-LBG using liquid state NMR spectroscopy JEOL RESONANCE

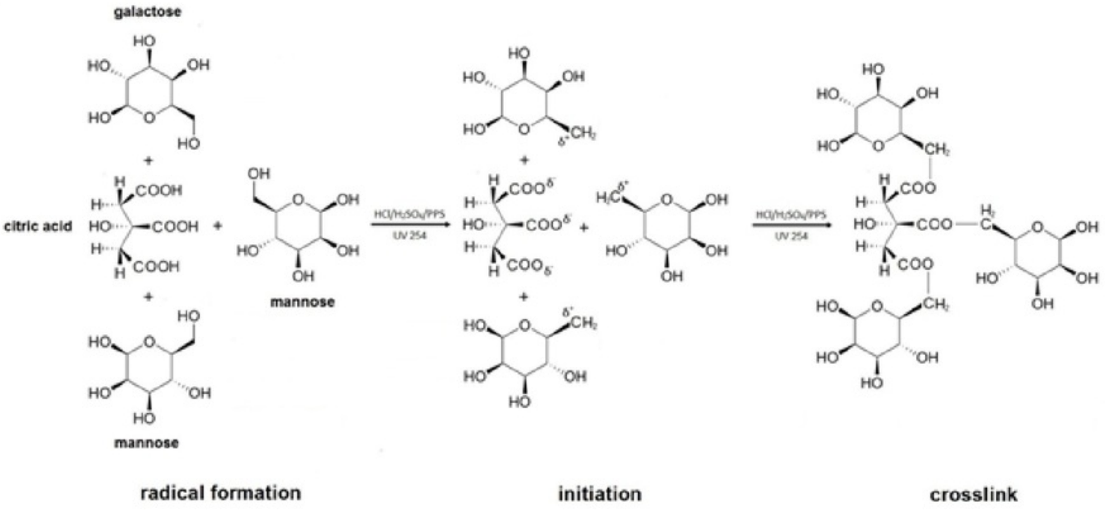


Fig. 2. Mechanism of crosslink of CA on LBG.

Table 1. Detail LBG, CA, catalyst, UV irradiation, pH, λ C=O, form of peak.

batch code	LBG (g)	CA (g)	catalyst	viscosity (cP)	UV irradiation (min)	pH	λ C=O (cm^{-1})	form of peak
C_{LBG}	1.1	-	-	9.36	-	4.80	-	-
C_1	1.1	4.4	-	8.76	-	1.95	1714.82	strong
C_2	1.1	4.4	-	8.74	75	1.95	1714.01	strong
C_{HCl}	1.1	4.4	0.75 mL	10.90	75	< 1 (0.80)	1743.92	strong
$C_{H_2SO_4}$	1.1	4.4	0.75 mL	10.60	75	< 1 (0.70)	1734.38	weak
C_{PPS}	1.1	4.4	0.75 g	6.12	75	1.10	1736.24	medium

ECZ 500R spectrophotometer (Japan).

SEM analysis was carried using the system JSM-6510LA, JEOL, Tokyo.

RESULTS AND DISCUSSION

CA crosslinking on LBG follows the esterification reaction mechanism. The latter is shown in Fig. 2. The catalyst (HCl/H_2SO_4/PPS) used creates acidic conditions and attacks mannose and galactosa (LBG). As a result, the hydroxyl groups at the C_6 atom of mannose and galactose are protonated. The hydrogen atoms of CA carboxylic group are also protonated providing free radicals. The carbonyl groups (C=O) is the specific group responsible for CA crosslinking on LBG to give (CA-c-LBG).

The results of the viscosity measurements are listed in Table 1. The copolymer CA-c-LBG obtained in absence of a catalyst has viscosity lower than that of LBG. This is due to the release the crystal water in this case. The copolymer obtained in presence of HCl and H_2SO_4 has viscosity higher than those of the copolymer prepared with the participation of PPS and LBG. This is explained with CA protonation leading to higher bonding and hence to trapping more water.

The pH measurement results are also shown in Table 1. The addition of CA as a crosslinking agent causes pH decrease. This is attributed to the acidic character of the catalyst addition decreases pH as well as HCl and H_2SO_4 are strong acids.

The infrared data obtained in the course of the copolymer analysis is shown in Table 1 and Fig. 3. It is well recognized that ketone, aldehyde, ester groups are outlined in FTIR spectra at 1715 cm^{-1}, 1725 cm^{-1}, and 1735 cm^{-1}, respectively. CA crosslinking on LBG in catalyst absence creates ketone groups at 1714.82 cm^{-1} (C1) and 1714.01 cm^{-1} (C2) (Fig. 3a). This is the case observed under less acidic conditions, where the protonation is not well expressed. An ester group is created in presence of a catalyst. It is observed at 1743.92 cm^{-1} (C_{HCl}), 1734.38 cm^{-1} (C_{H2SO4}), and 1736.24 cm^{-1} (C_{PPS}) (Fig. 3b). The stretching peak at about 3300 cm^{-1} refers to a hydroxyl group (OH). It is found in presence of LBG only. The spectrum of CA-c-LBG, shows stretching vibrations at 2950 cm^{-1}and 1643 cm^{-1} referring to C-H and C-C. The peak there out lined at 1735 cm^{-1} refers to is an ester group. The latter is an indication that CA crosslinking has occurred on LBG. The copolymer prepared in presence of HCl shows the best spectrum (Fig. 3c). The carbonyl group appears as a strong peak at 1743.92 cm^{-1}. The spectrum of the copolymer obtained in presence of H_2SO_4 shows a damaged stretching peak of hydroxyl group and aweak carbonyl group peak (Fig. 3b). This indicates that H_2SO_4 effect is very strong and which why damages the chemical structure. The spectrum of CA-c-LBG prepared in presence of PPS shows a carbonyl group peak lower than those observed in case HCl and H_2SO_4 are used as catalysts (Fig. 3b). This is attributed to protonation which is not well expressed as those previously discussed.

The ^1H NMR spectra stretching peak at $\delta = 4.080$-3.046 ppm in presence of LBG only indicates CH and CH_2 of mannose and galactose [17] (Fig. 4a). A pair of twin peaks at $\delta = 2.927$ ppm and $\delta = 2.896$ ppm, and $\delta = 2.744$ ppm and $\delta = 2.713$ ppm, correspondingly, appear in the spectrum of the copolymer (Fig. 4b). In

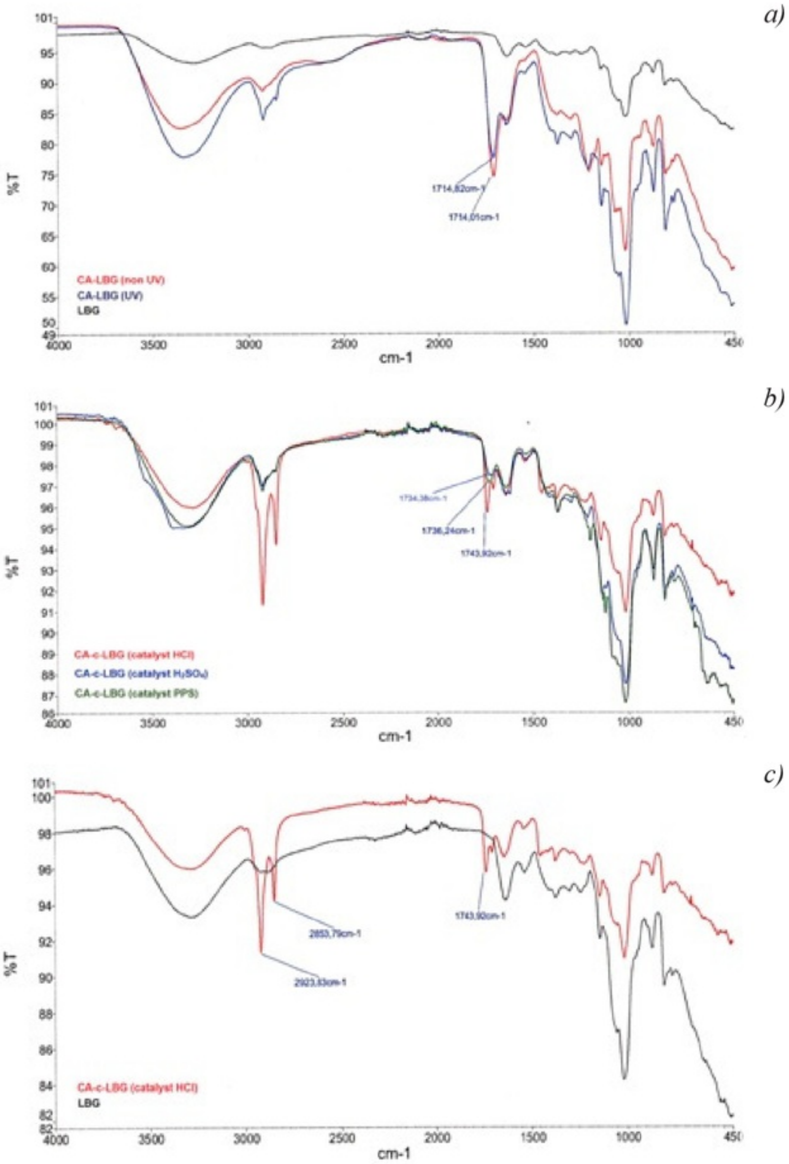


Fig. 3. FTIR spectra of CA-c-LBG without catalyst (a), with catalyst (b), and the best catalyst (c).

view of the fact that an intense absorption pair of CH_2 twin peaks of CA appear at $\delta = 2.7 - 3.0$ ppm [18], it can be concluded crosslinking of CA on LBG has taken place.

The SEM image of LBG (Fig. 5a) shows bladdery and corrugated walls, while that of CA-c-LBG shows not only bladdery and corrugated walls, but also slabs attached to the wall (Fig. 5b). These slabs are attributed to CA, which in turn verifies that the process of crosslinking has taken place.

CONCLUSIONS

An acid (HCl, H_2SO_4) or potassium persulfate acting as a catalyst are expected to create acidic conditions accelerating the protonation of the hydroxyl groups

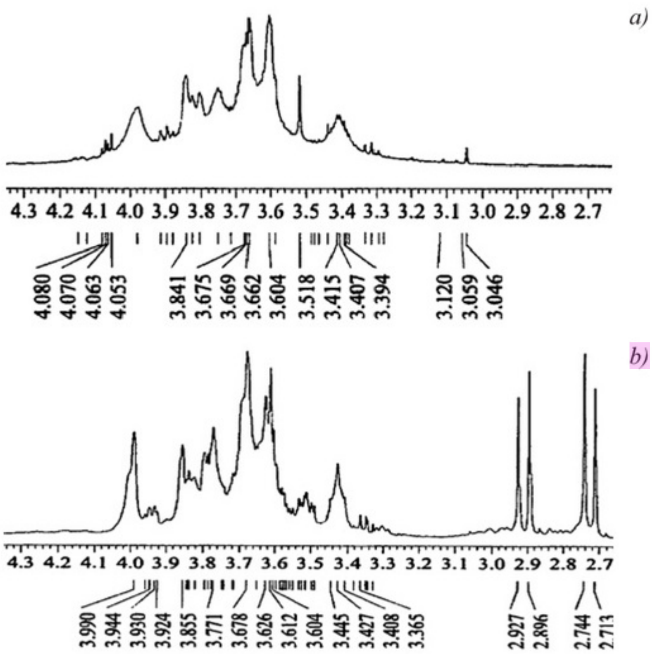
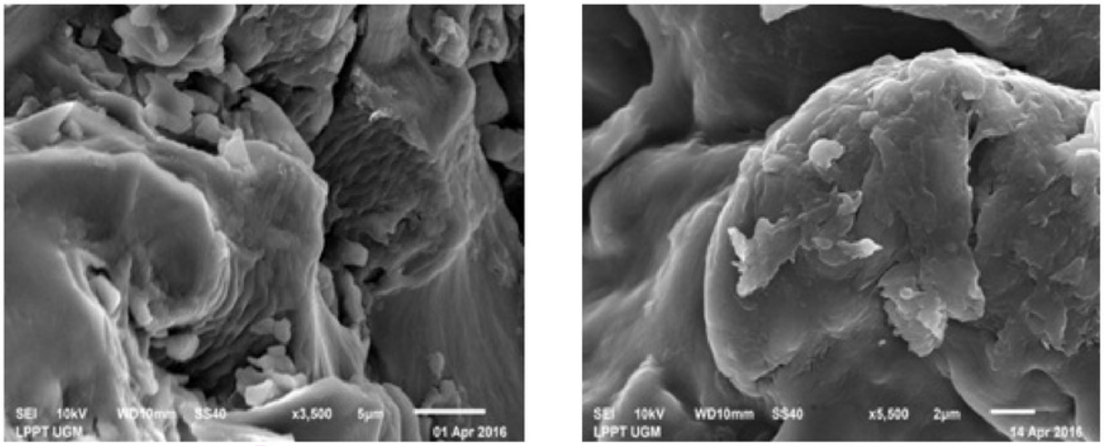


Fig. 4. 1H NMR spectra of LBG (a) and CA-c-LBG (b).



a) b)

Fig. 5. SEM images of LBG (a) and CA-c-LBG (b).

at C_6 atom of mannose and galactose in LBG and the hydrogen atoms of CA carboxylic group. HCl is found the best catalyst of CA crosslinking on LBG among the those studied.

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