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Esterification of citric acid with locust bean gum

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ABSTRACT

Esterification of citric acid (CA) with locust bean gum (LBG) was prepared by hydrochloric acid (HCl) as a catalyst and UV irradiation (254 nm) as esterification energy. This study aims to determine the best conditions of esterification. Other than that, it is to know the effect of amount HCl and UV irradiation time for the esterification process of CA with LBG. The amounts of HCl are 0.18 and 0.30 M, while the variations of UV irradiation time are 75 and 100 minutes. Polyester (CA-LBG) were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffractometer (XRD), esterification degree, and viscosity. Parameters for determining the best conditions for esterification are esterification degree and viscosity. The best conditions of esterification were obtained by using 0.30 M mL HCl and 100 minutes of UV irradiation time resulted in CA-LBG having a value of esterification degree 9.69 % and viscosity 7.46 cPs. HCl accelerates protonation on the O atoms and the formation of positive C atoms of carbonyl groups of citric acid. The time of UV irradiation gives the longer energy for the bond formation between the positive C atoms of the carbonyl group and the O atoms of the hydroxyl group at C-6 atoms of mannose and galactose.

1. Introduction

Locust bean gum (LBG) is derived from the endosperm of galactomannans, the family of Leguminosae. Monomer chains of LBG consist of mannose and galactose (4:1) [1]. The advantages of LBG compared to synthetic polymers are inert, safe, non-toxic, biocompatible, biodegradable, available in nature, and it can be a matrix for pharmaceutical products. The C-6 atoms of the monomer chain molecules potentially react with acids or base [2, 3, 4]. Several studies have been conducted on the LBG modification such as carboxymethylation of locust bean gum and acrylamide grafted locust bean gum [5, 6, 7].

Citric acid (CA) is one of the acid agents that can react with LBG. In CA, the O atoms of the carbonyl group can be protonated and form a positively C atoms. The carboxylate group of CA has the potency to replace OH in C-6 atoms from mannose and galactose [2]. One study of the use of CA for polymer modification which has been conducted is irradiation-induced acrylamide/citric acid hydrogel and their swelling behavior [8, 9].

Hydrochloric acid (HCl) is widely used as catalysts. In the carboxylate group, HCl can induce the O atoms of the carbonyl group to be protonated and form a positive C atom. Also, HCl may also induce hydroxyl release of C-6 atoms from LBG [10, 11]. The UV iradiation is the source of bond energy between the positive C atoms of the carboxylic group with the O at C-6 LBG. The low wavelength of UV irradiation (200–400 nm) produces a significant amount of energy [12, 13, 14, 15].

The novelties of this study know the best conditions of esterification to produce CA-LBG. Also, over cross design can help to know the effect of HCl as a catalyst and UV irradiation time as the energy source of bond for the esterification process of CA with LBG resulted in low viscosity CA-LBG but have the highest value of esterification degree. The advantage of this method is simple, economical, and easy to do.

2. Material and method

2.1. Materials

The materials used in this study were locust bean gum food grade (Viscogum) (*Cargill*, France), citric acid monohydrate pro analysis (Merk KgaA, Darmstadt, Germany), hydrochloride acid pro analysis (Sigma-Aldrich Chemie, GmbH, USA), sodium hydroxide pro analysis (Merk KGaA Darmstadt Germany), distilled water (Sterilized Water For Injection) (PT. Otsuka Indonesia) and aceton technical grade (Cawan

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Anugerah Chemika, Indonesia).

2.2. Preparation of esterification CA with LBG

LBG (7.10 10^{-6} Molar) was swollen in 50 mL of warm distilled water (55–60 °C) in a glass bowl. In the LBG swollen were added CA (0.42 Molar) and some amount of HCl. The mass of CA-LBG was stirred (10 minute) and irradiated by UV 254 nm (Shortwave 8 watt CH-4132 Muttenz, Camag, Switzerland) (Table 1). The mass of CA-LBG was precipitated with acetone, flushed with acetone-distilled water (1:1), and dried at ambient temperature [16]. The chemical structure of the material and the esterification mechanism is shown in Fig. 1.

LBG and CA-LBG were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffractometer (XRD), differential scanning calorimetry (DSC), esterification degree, and viscosity.

2.3. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was performed to characterize the functional group and structure in LBG and CA-LBG by using UATR Perkin Elmer Spectrum Version 10.4.3. The spectra data were collected over the wave number range of 4000–450 $cm^{-1.}$

Table 1
The various condition of esterification between CA with LBG.

Condition	LBG 10^{-6} (Molar)	CA (Molar)	HCl (Molar)	UV irradiation time (minute)
1	7.10	0.42	0.18	100
2	7.10	0.42	0.30	100
3	7.10	0.42	0.18	75
4	7.10	0.42	0.30	75

2.4. Nuclear magnetic resonance

Liquid state ^{13}C NMR spectroscopy JEOL RESONANCE ECZ 500R spectrophotometer (Japan) operated at 500 MHz was used to analyze the ^{13}C NMR analysis of LBG and CA-LBG. Approximately 7–20 mg of sample was inserted NMR glass tube.

2.5. Scanning electron microscope

LBG and CA-LBG surface morphology was examined using SEM system (JSM-6510LA, JEOL, Tokyo). The powder was coated with platinum to increase the conductivity of the electron beam. The acceleration voltage of 10 kV and the distance of observation 10 mm.

2.6. X-ray diffraction

XRD analysis of LBG and CA-LBG were recorded using X-ray diffractometer (Lab X XRD 6000, Shimadzu, Japan). The X-ray source was Cu, with the wavelength of 1.54060 A detector employed. The diffractometer was operated at a scanning speed of 4°/min, slit DS: 1°; SS: 1°; RS: 0.30 mm, and the scan range between 3.0200° and 80.0000° (θ-2θ).

2.7. Differential scanning calorimetry

DSC thermograms of LBG and CA-LBG were obtained using DSC-60 Plus (Shimadzu, Japan). The samples 2.5–3.5 (10^{-3}) g were wetted with 5–10 μL of distilled water. The heating process was carried out from 50 °C to 250 °C underpure nitrogen condition by the flow rate of 50 mL/min, and the heating rate of 10 °C/min.

2.8. Potentiometric

The potentiometric analysis was performed to determine the amount of CA dissolved in acetone and acetone-distilled water. The titrant of this analysis used NaOH (0.2 N). The standardization of NaOH (0.2 N)

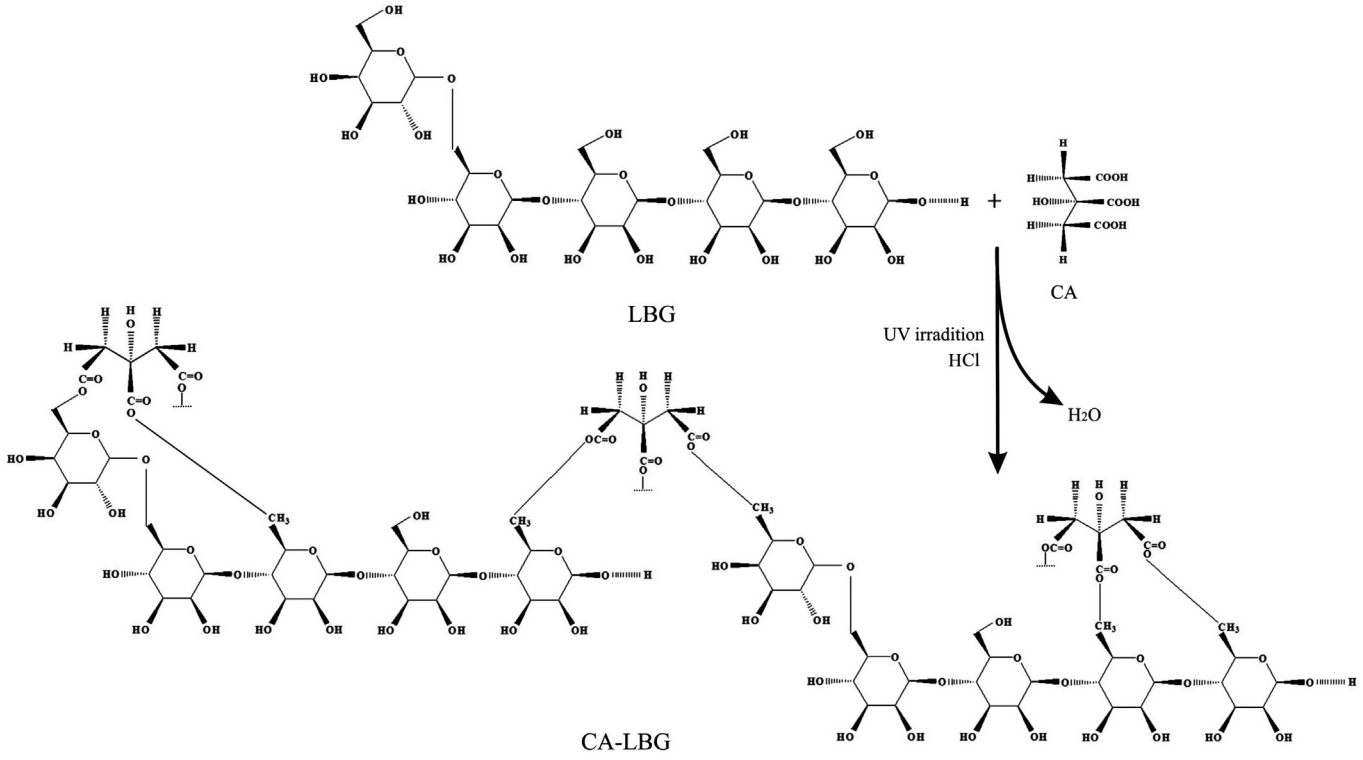

Fig. 1. Proposed mechanism esterification CA with LBG.

solution was conducted using oxalic acid. Total acid dissolved (meq) (CA dissolved and HCl dissolved) was determined from titrant volume were calculated with Eq. (1). The CA dissolved at mEq unit was converted to grams unit (W CA dissolved) and calculated CA reacts corresponding to Eq. (2). The weight of the carboxylic group in the CA reacts (gram) were calculated through the weight multiplication of the CA reacts with the ratio of the mass molecular relative (Mr) between the carboxylic group and CA. The weight of the carboxylic group in the CA reacts at gram unit converted to Molar unit. The percent of esterification degree were calculated with the ratio between the carboxylic group on the CA reacts at Molar unit and carboxylic group on the CA initial at Molar unit (Eq. (3)).

Dissolved CA (meq)

$$dissolved\ CA(meq) = dissolved\ total\ acid(meq) - dissolved\ HCl\ \ (meq) \quad (1)$$

Weight CA reacts (g)

$$W\ CA\ reacts\ = W\ initial\ CA - W\ dissolved\ CA \quad (2)$$

Percentage of esterification degree

$$Esterification\ degree\ (\%) = \frac{carboxylic\ group\ on\ the\ CA\ reacts\ (Molar\ )}{carboxylic\ group\ on\ the\ CA\ initial\ (Molar)} x\ 100\ \% \quad (3)$$

2.9. Viscosity study

The viscosity of LBG and CA-LBG (3% w/v) were determined by Brookfield Viscometer (Model LVDV-I Prime, AP6510416, Brookfield Engineering Labs, Inc., Middleboro, MA, USA). The samples were dissolved in 150 mL of distilled water at the temperature of 80 °C after the sample completely dissolved then distilled water was added, until the volume of the solution was 300 mL. The spindle (Spindle no. S61) was rotated at speed 100 rpm, and viscosities were recorded. Products that have low viscosity are one of the criteria for determining the best conditions for esterification.

2.10. Disintegration studies on tablets

The tablets were prepared using CA-LBG (2 mg) as a disintegration agent, polyvinylpyrrolidone K-30 (PVP K-30) (2 mg) as a binder, and lactose monohydrate (196 mg) as fillers. Sodium Starch Glycolate (SSG) is used as a standard disintegrant agent for comparison. Standard tablets are prepared using SSG (2 mg), PVP K-30 (2 mg) and lactose monohydrate (196 mg). The composition above is intended to produce conventional tablets by wet granulation, tablet weight of 200 mg, and tablet hardness of 10–13 kgf.

Evaluation of tablet disintegration was done by randomly selecting (six tablets) and put into a basket on a disintegrantion tester (Erweka ZT 3, Germany). The media used is distilled water (900 mL; 37 ± 2 °C) [29]. Tests are carried out until no part of the tablet is left in each gauze basket.

2.11. Dissolution studies on tablets

Tablets were prepared using CA-LBG (1 mg) and lactose monohydrate (99 mg) while standard tablets contained LBG (1 mg) and lactose monohydrate (99 mg). Excipient granules were produced using the wet granulation method. The mixture of excipient granules and ketoprofen as the active ingredient model (100 mg) was compressed with a tablet weight of 200 mg, and tablet hardness of 9–12 kgf.

The ketoprofen released from the tablet was analyzed by dissolution of the USP II apparatus tester (Electrolab TDT-08L, India). The dissolution medium used was of phosphate buffer pH 6.8 (900 mL; 37 ± 0.5 °C; 50 rpm; 60 minutes) [29]. Sampling at 5, 10, 20, 30, 45 and 60 minutes.

3. Result and discussion

3.1. Esterification of CA with LBG

Modification of LBG was conducted by esterification of between of CA with LBG. HCl was used to create acid conditions. It could be induced the O atoms of the carbonyl group to be protonated and form positive C atom. The proposed reaction scheme is shown in Fig. 1. In this mechanism, The citric acid carbonyl group was protonated and reacts the hydroxyl (OH) group at C-6 atoms of mannose and galactose, produces tetrahedral cation. Oxygen in OH was protonated ($^{+}OH_2$) to convert the OH loose, H_2O loss and produce the ester (CA-LBG) [17, 18]. Based on the spectra of Fourier transform infrared (Fig. 2), esterification can produce CA-LBG. The hydroxyl group (OH) appear about 3300 cm^{-1} derived from mannose and galactose in LBG, the C-H appear about 2950 cm^{-1} from CA, the C-C appear about 1643 cm^{-1} originating from mannose and galactose in LBG and CA. The carbonyl ester group (C = O) appear to be about 1735 cm^{-1} which is an additional peak and specific in CA-LBG that was not previously seen in LBG. The energy UV irradiation has used the formation of bonds between the positive C atoms of the carboxylic group with oxygen in the position at C-6 LBG, thus shortening the esterification time. The details of the experimental conditions are shown in Table 1.

3.2. Fourier transform infrared spectroscopy

The fourier transform infrared spectra (UATR mode) of LBG and CA-LBG are shown in Fig. 2. An extensive stretching peak of around 3300 cm^{-1} is a hydroxyl (OH) group bound to C atoms in mannose and galactose. The OH group that appears is the OH group does not react with CA. The sharp peak of about 2900 cm^{-1} shows symmetrical C-H originating from CA. The peak and vibration around 1600 cm^{-1} [19] are C-C from the bond between C atoms of manonose and galactose in the LBG. In addition, C-C from the bond between C atoms of CA. The carbonyl ester group (C = O) around 1735 cm^{-1} is an additional characteristic that does not appear in pure LBG. This group is the specific group of esterification CA on LBG. This group formed from the bond between a positive C atom from a carboxylic group with O on C-6 LBG. Spectra showed that CA-LBG from esterification conditions of 0.30 M HCl and 100 minutes of UV radiation has the sharpest peaks because they has the most carbonyl ester groups and were in accordance with the esterification degree (Table 2). In this condition, HCl quickly protonates the O atom and forms a positive C atom from the CA carbonyl group. Long time UV irradiation provides more opportunities for the formation of bonds between positive C atoms of carbonyl groups and O atoms of hydroxyl groups on C-6 atoms of mannose and galactose.

The amount of HCl 0.18–0.30 M and the time of 75–100 minutes of UV irradiation produced a good and clear CA-LBG spectra in all esterification conditions. CA-LBG results of this esterification were confirmed further by the ^{13}C NMR liquid state study.

3.3. Nuclear magnetic resonance

The ^{13}C NMR spectra of CA and CA-LBG are shown in Fig. 3. In the ^{13}C NMR spectra of CA (Fig. 3a), intense absorptions peaks at δ = 176.828 ppm and δ = 173.449 ppm relates to the carboxylic acid groups (COOH), δ = 73.306 ppm relates to the central carbon of the molecule, δ = 43.310 ppm relates to two methylene carbons (CH). The previous study reported that two methylene carbons (CH) appear at δ = 44 - 43 ppm, the central carbon of the molecule appear at δ = 80 - 70 ppm, and the carboxylic acid groups appear at δ = 180 - 170 ppm [20, 21, 22, 23].

The ^{13}C NMR spectra of CA-LBG (Fig. 3b), the presence of peaks at δ = 176.886 ppm, δ = 173.488 ppm, δ = 73.325 ppm, and 43.329 ppm relate to CA. The presence of peaks at δ = 100.154 ppm, δ = 99.971 ppm, δ = 96.458 ppm, δ = 76.560 ppm, δ = 75.034 ppm, δ = 71.415 ppm, δ = 71.310 ppm, δ = 69.937 ppm, δ = 69.294 ppm, δ = 60.521 ppm indicate CH and CH_2 on mannose and galactose. Several previous studies reported

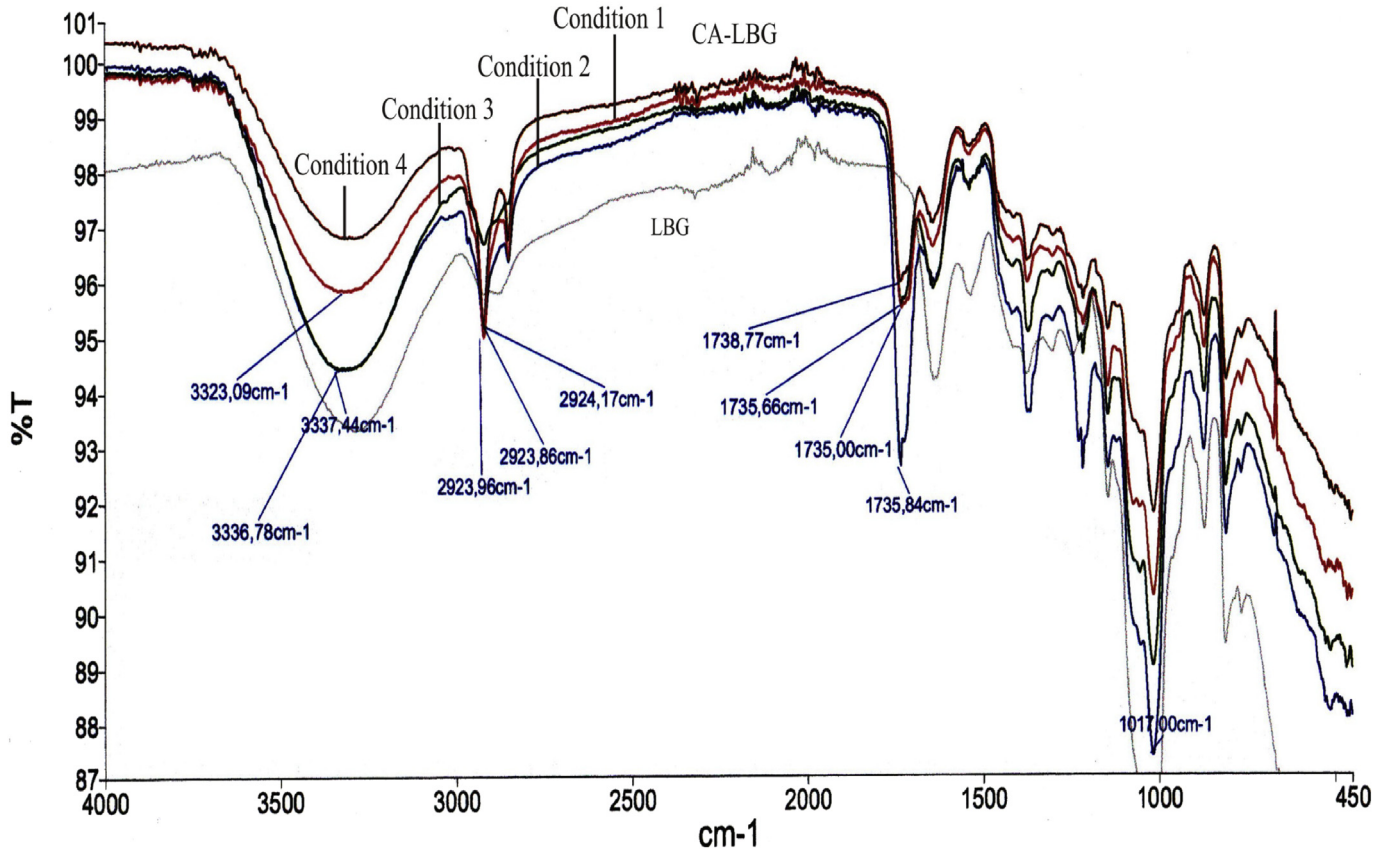

Fig. 2. FTIR spectrum of LBG and CA-LBG of various condition of esterification.

that the absorptions peaks of mannose and galactose appear at δ = 105-60 ppm [24, 25, 26, 27]. The presences of slight change of CH_2 peaks at δ = 176.828 ppm to δ = 176.886 ppm, δ = 173.449 ppm to δ = 173.488 ppm, δ = 73.306 to δ = 73.325 ppm, and δ = 2.817 ppm to δ = 43.310 ppm indicates the occurrence of CA bonded on LBG.

The concentration of esterified CA with LBG will affect changes in peak shift in CA-LBG for each esterification condition. This will affect the length of the chain and the molecule complex bonds formed in CA-LBG. The concentration of esterified CA with LBG can be confirmed by the degree of esterification.

3.4. Scanning electron microscopy

The SEM CA, LBG and CA-LBG images are shown in Fig. 4. CA (Fig. 4a) has a coral shape and rough surface. LBG (Fig. 4b) has a wavy and fibrous surface. Morphologically, CA-LBG (Fig. 4c) has a more complex and irregular surface than LBG. Morphology looks complex because of its existence like a sheet attached to a wavy surface. Complex morphology is the result of interaction between LBG and CA.

3.5. Differential scanning calorimetry

The addition of 5–10 μL distilled water in the preparation of the DSC analysis aims to determine the effect of temperature on CA-LBG in wetted or swollen conditions so that it can be used in pharmaceutical formulations. DSC thermograms of LBG and CA-LBG are shown in Fig. 5. Analysis of thermogram is CA-LBG which expands due to being dampened by distilled water experiencing evaporation and loss of moisture. The dry CA-LBG is then melt.

The concentration of esterified CA affects the chain length and bonding of the CA-LBG molecular complex. This can affect the process of wetting and dissolving CA-LBG particles. The CA-LBG thermograph shape (condition 1), the peak seems to be going back when the rising temperature. This indicates the presence of dissolved CA-LBG particles so that the evaporation process increases. The concentration of esterified CA with LBG can be confirmed by esterification degree.

Thermogram of LBG shows the endothermic peak at 137.73 °C with the ΔH of 6.70 kJ/g. Based on Fig. 5, it can be seen that CA-LBG shows a distinct feature from LBG. The CA-LBG has the endothermic peak varies from 108 °C up to 145 °C (Table 2). This variation is due to the different amount of HCl used during the esterification. The the endothermic peak of CA-LBG is lower than LBG. The value of the endothermic peak is an indicator of thermostable. The higher the the endothermic peak indicates that the macromolecule is more stable thermodynamically [28]. The endothermic peak are also influenced by the amount of HCl, the higher the amount of HCl used, the lower the endothermic peak. The UV

Table 2
Detail thermodynamic parameters, crystallinity degree, esterification degree, viscosity of LBG and CA-LBG of various condition of esterification.

Batch code	Condition	Endothermic peak (°C)	Enthalpy ΔH(kJ/g)	Transition glass temperature Tg (°C)	Crystallinity degree (%)	Esterification degree (%)	Viscosity 3% (cP)
LBG		138	6.70	122	2.61	-	386.7 ± 0.70
CA-LBG	1	141	4.13	128	1.44	8.35	11.37 ± 0.15
	2	122	3.56	103	6.19	9.69	7.46 ± 0.09
	3	146	4.22	129	3.00	8.64	8.78 ± 0.12
	4	109	2.84	99	3.74	8.49	7.82 ± 0.09

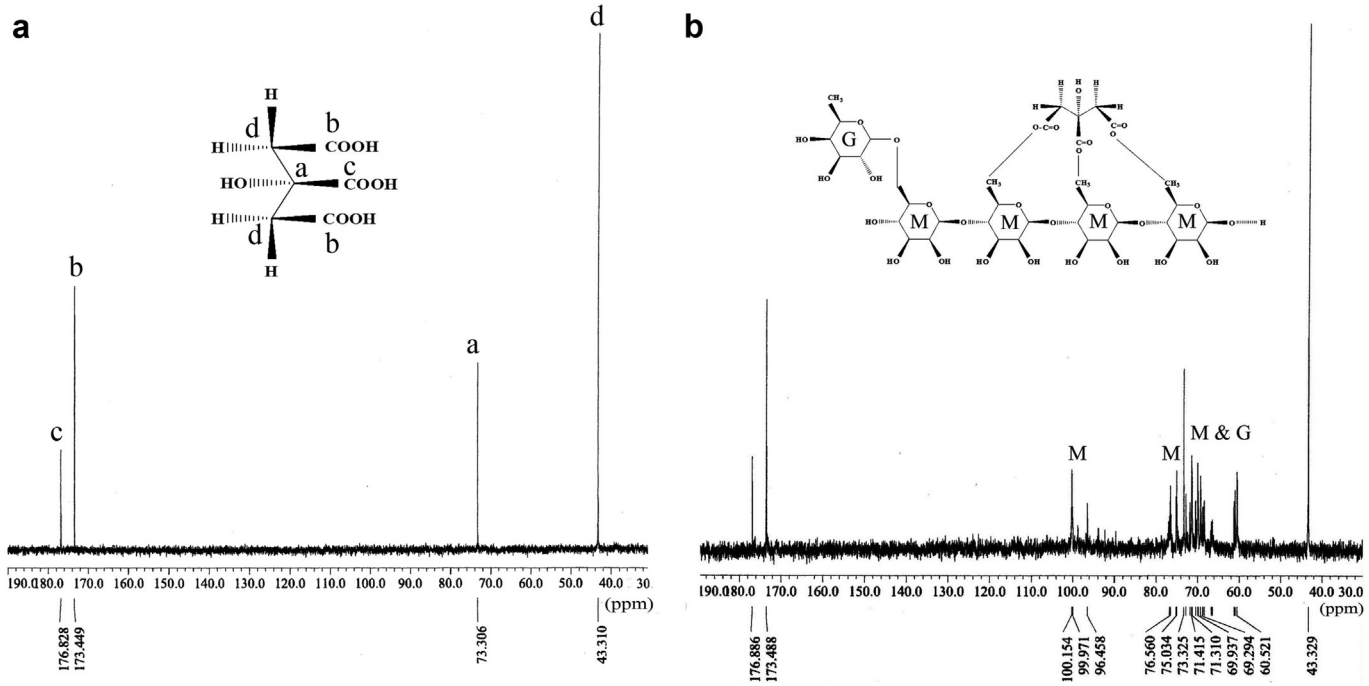

Fig. 3. a. ^{13}C NMR spectrum of CA. b. ^{13}C NMR spectrum of CA-LBG representative of various condition (condition 2).

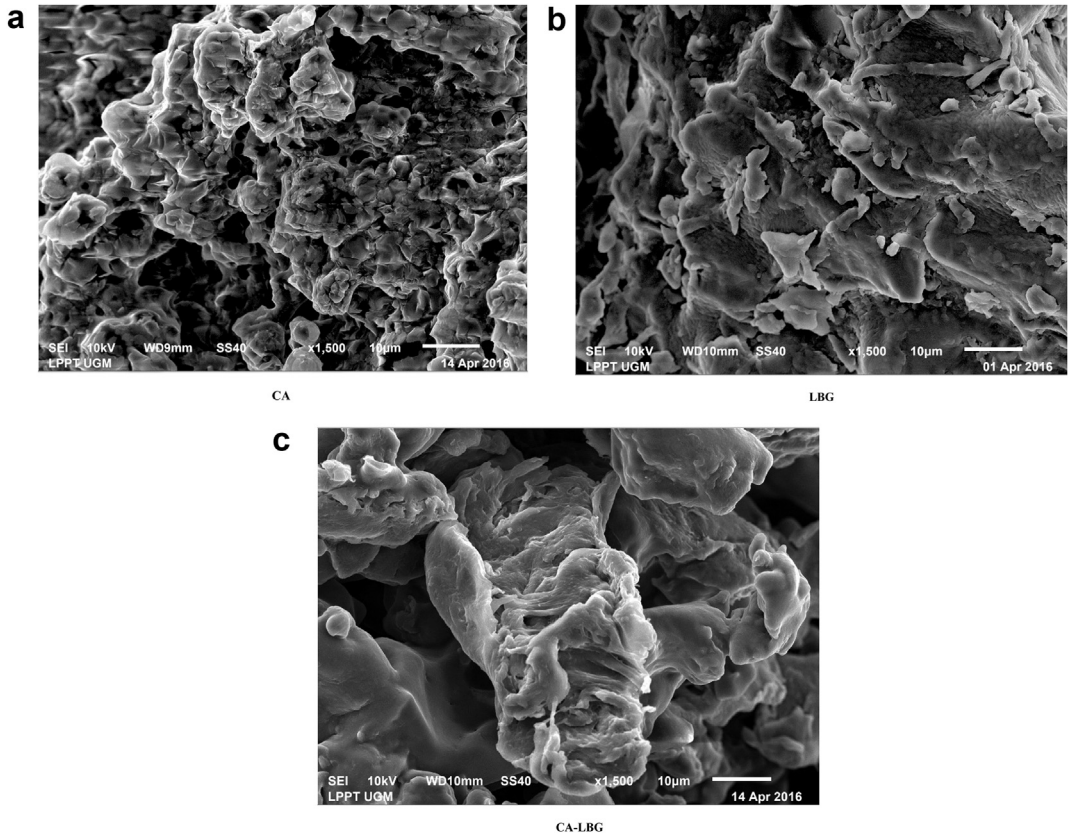

Fig. 4. a. SEM images of CA. b. SEM images of LBG. c. SEM images of CA-LBG representative of various condition (condition 3).

irradiation also gave the same effect as HCl in endothermic peak.

The CA-LBG has transition glass temperatures (Tg) vary from 98 °C to 128 °C (Table 2). The variation of transition glass temperature is due to the different amount of HCl. In the case of Tg variation, the higher the amount of HCl the value of Tg decreases. A similar trend was also observed for UV irradiation, the value of Tg decreased with the increased

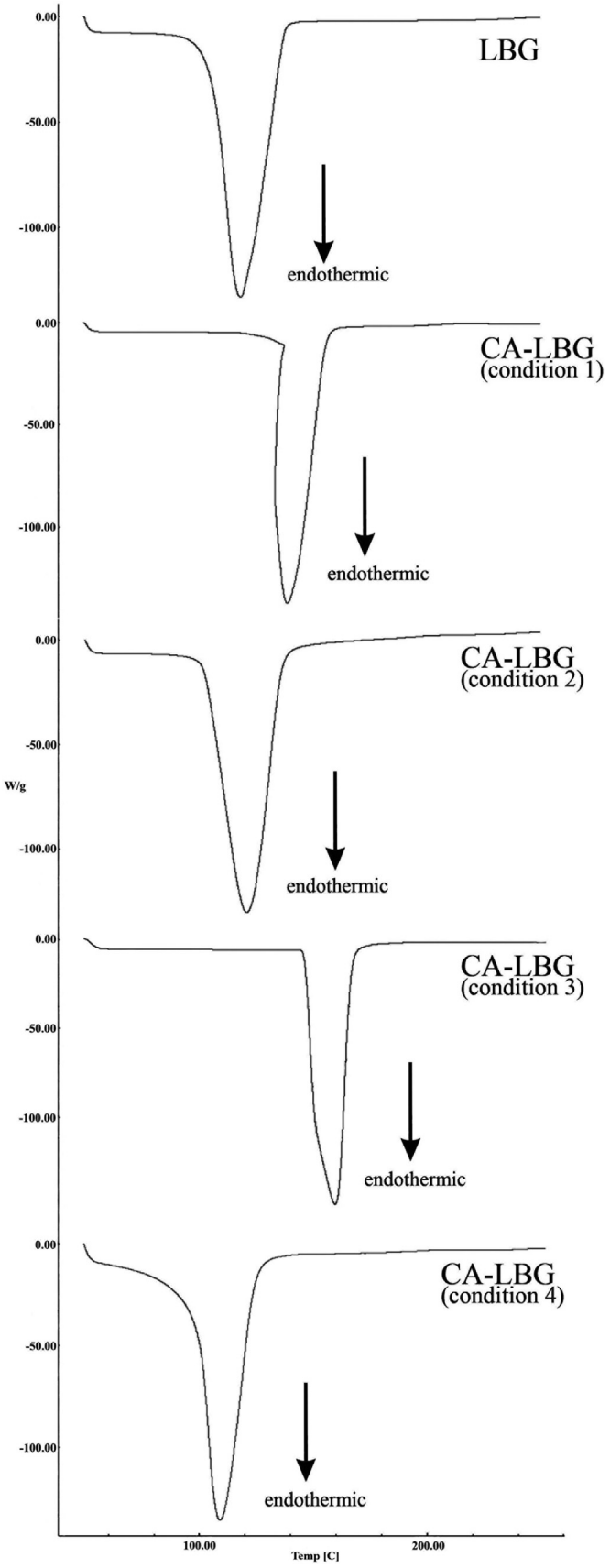

Fig. 5. DSC thermogram of LBG and CA-LBG of various condition of esterification.

of UV irradiation.

The DSC study (Table 2), it was found that the enthalpy (ΔH) for all the CA-LBG was lower than LBG. The lower value of ΔH was found in CA-LBG which has lower viscosity. This phenomenon was caused by the damage to the structure of mannose and galactose because of influence ΔH and lead to network failure to hold water.

Esterification with small amounts HCl produces CA-LBG that has molecules stable thermodynamically. The stable molecules have limited movement of space. Therefore, they need high heat energy to move freely. The longer of UV irradiation time is increasing the thermodynamic parameters CA-LBG. Because it gives more opportunity for forming bonds between the positive C atoms of the carbonyl group of atoms with the O atoms of the C-6 mannose and galactose hydroxyl groups. The CA-LBG structures formed are rigid. Therefore, they decrease the space move between molecules in CA-LBG.

3.6. X-ray diffraction

Diffractograms of XRD analysis of LBG and CA-LBG are shown in Fig. 6. The XRD analysis of CA was carried out as a control that CA-LBG of all esterification conditions showed no effect of pure CA which did not react to esterification. The diffractogram of all conditions have a peak that is not sharp and different from a pure CA diffactogram. This shows that various esterification conditions produce CA-LBG which is amorphous. This characteristic is caused by the low concentration of CA that can be esterified with LBG. Parameters of degree of crystallinity can be used to confirm an esterified CA with LBG. The diffractogram CA-LBG peak intensity in all esterification conditions increased compared to LBG. This is due to the presence of an esterified CA with LBG. The CA-LBG (condition 1 and 2) gave a higher peak than LBG. The CA-LBG (condition 3 and 4) gave a lower than LBG.

The CA-LBG (condition 2) gave a higher crystallinity degree than LBG (Table 2). This phenomenon suggested that LBG is more amorphous than CA-LBG (condition 2). CA-LBG (condition1,3 and 4) gave a lower crystallinity degree than LBG. This phenomenon suggested that CA-LBG (condition 1,3 and 4) is more amorphous than LBG. Esterification by the more amounts HCl and the longer of UV irradiation time increased the crystallinity degree. The CA esterified and thermodynamic parameters influence regular of structure molecules in CA-LBG.

3.7. Potentiometric

Esterification by the more amounts HCl increased the acidity of the esterification condition, thus accelerating the protonation of the O atoms to form positive C atoms of the carbonyl group. The UV irradiation time gives longer energy for the formation of the bond between the positive C atoms of the carbonyl group and the O atoms of the hydroxyl group. Esterification by higher amounts HCl and the longer of UV irradiation time produce CA-LBG that has high esterification degree (Table 2).

3.8. Viscosity study

Esterification by the more amounts of HCl decreases viscosity (Table 2) because it potentially damages the structure of mannose and galactose. Therefore CA-LBG can not withstand distilled water. The longer UV irradiation time (Table 2) increases the viscosity CA-LBG because it gives more opportunity for forming bonds between the positive C atoms of the carbonyl group of atoms and the O atoms of the C-6 mannose and galactose hydroxyl groups. The structures CA-LBG formed are rigid. Therefore, it can withstand distilled water and increase the viscosity.

3.9. Disintegration studies on tablets

The purpose of this experiment was to determine the ability of CA-LBG as disintegrant on conventional tablets. The disintegration time of

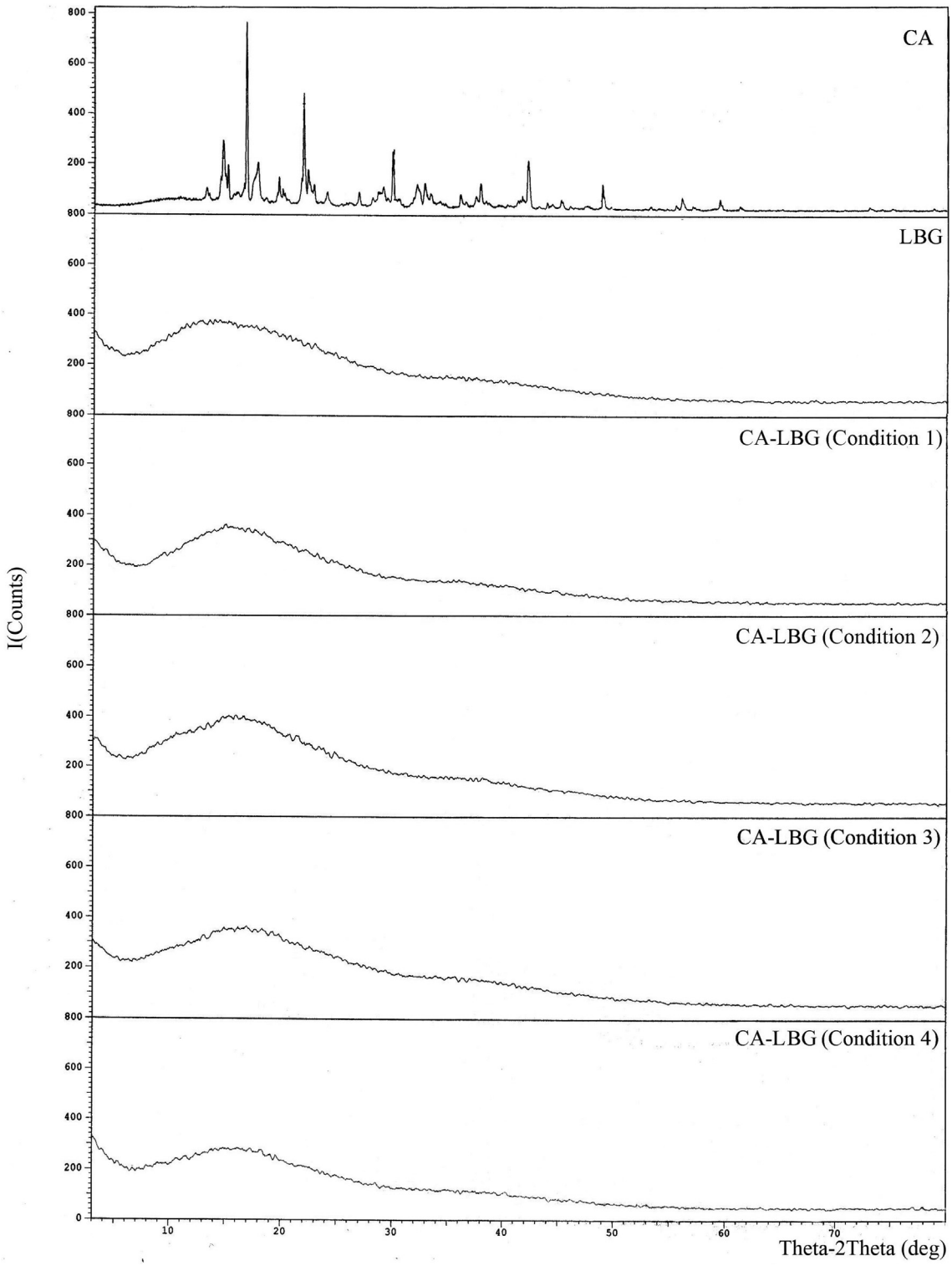

Fig. 6. XRD difractogram of CA, LBG and CA-LBG of various condition of esterification.

tablets containing CA-LBG is 5.58 minutes while tablets containing SSG is 11.62 minutes. The difference in time value of disintegration because both disintegration agents have different disintegration mechanisms. Although CA-LBG has a hardness of 10–13 kgf, but CA-LBG has low adesivity with other particles making up tablets. This condition causes CA-LBG particles to resist interacting with other particles when wetted by disintegrant media so that the tablet disintegrates. When wetting the media is disintegrated, SSG particles swell and push other particles around it so that the tablet disintegrates. The process of swelling SSG particles is influenced by the penetration speed of disintegrant media so that it also influences the time of tablet disintegration.

3.10. Dissolution studies on tablets

The tablet release profile containing CA-LBG and tablets containing LBG is shown in Fig. 7. The purpose of this study was to compare the effect of CA-LBG with LBG in tablets to drug release. Tablets containing CA-LBG have a slower drug release profile compared to tablets

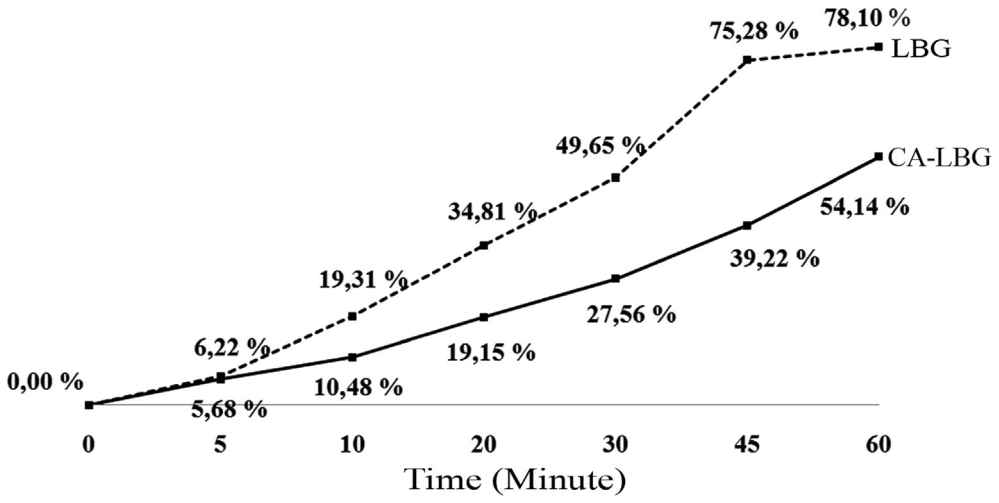

Fig. 7. In-vitro drug release profile from tablets.

containing LBG. The CA-LBG interaction with ketoprofen in tablets inhibits the wetting of ketoprofen and inhibits drug release from tablets. Although CA-LBG can give a time of rapid disintegration, tablets that disintegrate into granules are not easily dissolved. CA-LBG particles are located on the surface of the granule inhibits the penetration of dissolution media. The release of ketoprofen is influenced by the speed of granule wetting.

In tablet containing LBG, wetting and swelling starts from LBG on the surface of the tablet into the granule and inhibiting the dissolution of ketoprofen. The LBG swells and high viscosity (Table 2) when moistened by dissolution media. Wetting and swelling starts from LBG on the surface of the tablet and then gradually into the center of the tablet along with the speed of entry of the dissolution media. The release of ketoprofen starts from ketoprofen on the surface of the tablet and then depends on diffusion and swollen LBG erosion.

4. Conclusion

The CA-LBG was created from esterification between 7.10×10^{-6} Molar LBG and 0.42 Molar CA under conditions created using 0.30 M HCl and 100 minutes of UV irradiation time. The CA-LBG having value of esterification degree 9.69 % and viscosity 7.46 cPs. HCl accelerates protonation on the O atoms and the formation of positive C atoms of carbonyl groups of CA. The time of UV irradiation gives the longer energy for the formation of the bond between the positive C atoms of the carbonyl group and the O atoms of the hydroxyl group at C-6 atoms of mannose and galactose.

Declarations

Author contribution statement

Wuryanto Hadinugroho: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Suwaldi Martodihardjo, Achmad Fudholi, Sugeng Riyanto: Conceived and designed the experiments; Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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