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Acetylation of xanthan gum in densified carbon dioxide (CO₂)

Henky Muljana^{a,b*}, Asaf Kleopas Sugih^a, Anastasia Prima Kristijarti^{a,b}, Rifandi Karlus^a,
Ricky Kurnia^a, Crist Evan^a, Francesco Picchioni^b

^aDepartment of Chemical Engineering, Parahyangan Catholic University, Ciumbuleuit 94, Bandung 40141, West Java Indonesia

^bDepartment of Chemical Engineering, ENTEG, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

Abstract

Xanthan Gum (XG), known as a microbial polysaccharide, is potential renewable resources in the biodegradable plastics synthesis. However, native xanthan gum needs to be chemically modified in order to improve its properties required for further application as thermoplastics material. We here report our preliminary studies on the acetylation of xanthan gum in densified carbon dioxide (CO₂) as the 'green' solvent. Within the experimental conditions, xanthan acetates with a broad range of degree of substitution (DS) values (1.27 – 7.08) were obtained. In addition, the products give a higher thermal stability and an altered morphology compared with their native counterparts.

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Keywords: Xanthan gum; acetylation; densified CO₂

1. Introduction

Bio based and circular based economies are two important terms which become a platform for researcher in various research areas, not only in social economic aspects but also in the technological aspect. In the latter, a lot of research has been done to access and to gain insight on the technology to transform biomass into energy and chemicals including the development of bio based polymer product [1,2]. The aim of the bio based polymer synthesis is to reduce the use of non-biodegradable petroleum based polymers in our daily life [2].

* Corresponding author. Tel.: +62-22-2032655 ; fax: +62-22-2032700

E-mail address: henky@unpar.ac.id or hmuljana@gmail.com

Amongst biomass resources, polysaccharide such as starch have been successfully modified, both physically and chemically, resulting with thermoplastics material [3-5]. The modification of the starch, and also the other polysaccharide are essential in order to improve its properties and to meet the requirement as biodegradable plastics. Most of natural polysaccharides are hydrophilic in nature and exhibit poor mechanical properties due to its brittleness [6]. Example of physical modification of starch involves an extrusion process with plasticizer such as glycerol with a variation in temperature and throughput of the material [4]. The resulting product is called thermoplastics starch (TPS). Chemical modification of starch, in other hand, involves an esterification reaction with various reagents such as acetic anhydride, vinyl acetate, and various fatty acid esters [5-7]. The products, starch esters, are potential to be applied as thermoplastics material as well.

Instead of starch, a lot of researches have already been done in order to explore the esterification of different polysaccharides such as cellulose, and chitin/chitosan to produce biodegradable plastics [8-10]. However, to the best of our knowledge, only limited information on the esterification of XG for biodegradable plastic application is reported in literature. XG, produced by fermentation process using bacterium *Xanthomonas Campestris*, is widely used in food (gelling agent and thickener), pharmaceutical (controlled drug release), medical application and oil recovery [11]. For instance, the published work from Hamcerencu et al. describes the esterification of XG with acryloyl chloride, maleic anhydride and acrylic acid to result with xanthan ester product that show a potential application in the controlled water soluble drug delivery system [11]. Only recent work from Endo et al. shows a potential application of acetylated xanthan gum (with relatively degree of acetylation, 50.3%) as new green bio-based and plasticized materials. In their work, xanthan gum is acetylated with acetic anhydride in ionic liquid [12].

We here report our preliminary studies on the acetylation of xanthan gum in densified CO₂ as the solvent. The novelty of our work is the application of densified CO₂ as the solvent in the reaction. The densified CO₂ is used due to its green properties (inert, non-toxic), and an easy separation of the solvent from the reaction by simply depressurization. In addition, the hybrid properties of CO₂ (gas like diffusivity and liquid like density) at the supercritical state and the plasticizing effect of CO₂ on the biopolymer are considered as beneficial from the processing aspect [13].

In this study, the role of densified CO₂ in the reaction was explored at different pressures (8 MPa – 12 MPa) and temperatures (80°C – 120°C). The effects of important process parameters such as different salt base catalysts (potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), and sodium acetate (NaOAc)) and catalyst intake (0.1 – 0.5 mol/mol XG repeating unit (XGU)) on the reactivity (quantify by the degree of substitution (DS) values from the product) were also studied. Relevant product properties were characterized with Fourier Transform Infra-Red (FT-IR), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC).

2. Materials and Methods

2.1. Materials

Xanthan Gum (XG) from *Xanthomonas Campestris* was purchased from Sigma (Singapore). The water content of XG was 13.9 % wt as determined with a gravimetric method. Analytical grade acetic anhydride (AAH), ethanol, potassium hydroxide (KOH) and salt catalysts (potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), sodium acetate (NaOAc)) were purchased from Merck (Singapore). All chemicals were used as received without further purification. High purity CO₂ (> 98% volume) and N₂ (> 98% volume) were purchased from Sangkuriang (Indonesia).

2.2. Methods

2.2.1. Acetylation of Xanthan Gum (XG) using Acetic Anhydride (AAH)

XG (4 g, dry basis), AAH (5 mol/mol XGU), and salt catalysts (0.1 – 0.5 mol/mol XGU) were charged into the high pressure reactor. The autoclave was then closed and flushed with N₂ for five minutes to remove traces of air. Afterwards, CO₂ with initial pressure of 5 MPa was inserted to the autoclave and followed by the heating of the reactor to the required temperature. Additional CO₂ was inserted to the reactor with the high pressure centrifugal

pump till reach the desired pressure. After reaction (3 h), the reactor was depressurized and cooled with circulated air to room temperature. The solid product, xanthan acetates (XA) was filtrated from the unreacted liquid AAH and washed with water in several washing and filtrating steps to ensure the purity of the products (free from unreacted AAH). XA was dried in a vacuum oven at 70°C until constant weight.

2.2.2. Determination of Degree of Substitution (DS) of the Product

The DS values were determined using a hydrolysis method according to a published procedure for acetylated starch product [14]. The solid product (XA, 0.5 g) and 30 ml of ethanol (75%wt) were placed in a 250 ml Erlenmeyer. Subsequently, the Erlenmeyer was heated in a water bath ($T = 75^{\circ}\text{C}$, 30 minutes) follow by additional of 30 ml KOH (0.5N) into the XA suspension. The mixture was stirred in a room temperature for 3 h. Afterwards, a few drops of phenolphthalein was added and the excess of alkali in the suspension was titrated with HCl (0.25 N) till the pink colored of phenolphthalein disappeared. The degree of substitution (DS) was calculated based on the following formulas [14] with slight modification for XG:

$$\%A = \frac{[V_{\text{HCl},o} - V_{\text{HCl},\text{sample}}] \times N_{\text{HCl}} \times 43}{1000 \times m_{\text{sample}}} \times 100 \quad (1)$$

$$DS = \frac{833 \times \%A}{4300 - (42 \times \%A)} \times 100 \quad (2)$$

where $V_{\text{HCl},o}$ is the volume of HCl used to titrate blank, $V_{\text{HCl},\text{sample}}$ is the volume of HCl used to titrate sample, N_{HCl} is the normality of HCl, m_{sample} is the mass of the xanthan acetates sample (g), 833 and 43 are the molecular weight of XG repeating unit (XGU) and acetates as substituent on the xanthan gum backbone, respectively.

2.2.3. Analytical Equipment

Fourier Transform Infrared (FT-IR) spectra were performed on a FTIR Prestige 21 Shimadzu. X-ray Diffraction (XRD) analyses were acquired in a diffractometer type PW1710 BASED with Anode Cu. TGA and DSC measurements were performed simultaneously using a Linseis STA Platinum Series. The samples were heated to 500 °C in an inert atmosphere (N_2 , flow rate 1.6 – 4 l/h) at a heating rate of $10^{\circ}\text{C min}^{-1}$. The morphology of xanthan gum and its modified products were done in a Scanning Electron Microscope type JEOL T330A.

3. Results and Discussion

3.1. Proof of principle

Figure 1 shows the FT-IR spectra from native XG and its derivative. In the spectra of native XG (Fig. 1 a), the strong absorption bands of -OH stretching at $3400 - 3500 \text{ cm}^{-1}$, -OH bending at $1500 - 1600 \text{ cm}^{-1}$, -CH stretching at $2950 - 3000 \text{ cm}^{-1}$, -CH bending at $1420 - 1450 \text{ cm}^{-1}$, and highly coupled C-O and C-C vibrational modes at $900 - 1300 \text{ cm}^{-1}$ are clearly shown [15]. These strong bands are the typical absorption bands occurred in native polysaccharides. Moreover, an additional of small peak (shoulder) at 1750 cm^{-1} (Fig 1a) is clearly visible. This indicates the presence of C=O (carbonyl) of acetate group in the native XG.

The spectra of the xanthan acetates at different DS are shown in Fig. 1 b and 1c. In comparison with the spectra of native XG (Fig. 1 a), it is obvious that the intensity from the -OH peaks (at $3400 - 3500 \text{ cm}^{-1}$ and at $1500 - 1600 \text{ cm}^{-1}$) of the products is lower compared with the one of the native XG. The decrease of the OH peaks is most likely due to the substitution of this -OH group by the acetate group after the esterification reaction. This is also confirmed by an increase of the absorption band of the acetate group (at $1750 - 1755 \text{ cm}^{-1}$) of the products [15]. These findings imply that the acetylation reaction in densified CO_2 is successful.

Fig. 1. FT-IR spectra of the (a) native xanthan gum; (b) xanthan acetate with DS of 2.38; (c) and xanthan acetate with DS of 7.08.

The morphology of the native XG and the esterified products were obtained by Scanning Electron Microscope (SEM). The SEM pictures are given in Figure 2. Native XG is a fibrous material as clearly seen in the larger magnification (Fig 2a and 2b) [16]. The change of the product morphology is clearly shown especially at the higher DS (Fig 2d). Compared with the native XG, the particle of xanthan acetates at DS of 7.08 tends to agglomerate and formed a larger particle. The agglomeration of the XG particle after the reaction can be related to an increase of the hydrophobic (van der Waals) interaction of the acetate group in the xanthan gum backbone especially at higher DS. The similar morphological changes also reported elsewhere for starch acetate product [13]. Moreover, in line with the FT-IR results (see above), the changes in the product morphology also confirms the successful of the reaction [13].

Fig. 2. The morphology of the (a)XG (magnification,150 x); (b) XG (magnification 1000x); (c) xanthan acetate with DS of 2.38; (d) and xanthan acetate with DS of 7.08.

3.2. The effect of process variable on the DS value

The acetylation of XG in densified CO₂ is influenced by the change of pressure as shown in Fig 3. As the pressure increases from 8 MPa to 10 MPa, DS value increases as well and this happens in all catalyst type. However, the opposite effect occurs, the DS value decreases when the pressure increases to 12 MPa. The opposite positive and negative effect on the reactivity may be related to the plasticizing and the compressive effect of pressure on XG upon reaction. When pressure increases from 8 to 10 MPa, the plasticizing effect occurs and increases the segmental mobility of XG matrices, induces swelling and increase the diffusion rate of the reagent, in this case acetic anhydride, inside the XG particles [13]. This will increase the overall reaction rate (higher DS). In other hands, at higher pressure (12 MPa), the compressive effect is dominating, and when this happens, the free volume inside the XG particles decreases and hinders the diffusion of the reagent inside the XG particles and reduces the reactivity (lower DS).

Fig. 3. DS values at various pressures and different type of catalyst. All experiments were done at temperature of 100°C and catalyst intake of 0.1 mol/mol XGU.

Not only influenced by the change of pressure, the different type of catalyst also gives a significant change on the DS values. It is clear that K₂CO₃ always gives the highest DS values and the lowest DS is obtained when using NaOAc as catalyst. Similar result is also reported for the acetylation reaction of potato starch. The role of the catalyst on the reaction is strongly related with the basicity (pK_b) value of the catalyst (Table 1). Although the detailed reaction mechanism of XG and acetic anhydride in densified CO₂ is not yet clear, however it is reasonable to assume that the catalyst plays role in the deprotonated of the XG-OH by the base to form XG alkoxide (XG-O⁻) [13]. This intermediate XG alkoxide will react further with acetic anhydride to form the desired xanthan acetates. Therefore, it is obvious that the strongest base (K₂CO₃) will result with highest reactivity and eventually results with the highest DS value. In addition, the different cation (K⁺ and Na⁺) may influence the reactivity as well.

Table 1. Basicity of the catalyst [13].

	pK _b
K ₂ CO ₃	3.66
Na ₂ CO ₃	3.66
NaOAc	9.24

Figure 4 shows the effect of temperature and catalyst intake on the DS values. The strong and positive effect of temperature is clearly shown in Fig 4. The DS increases from 3.2 to 6.8 when temperature increases from 80 °C to 120°C at K₂CO₃ intake of 0.1 mol/mol XGU. Indeed, the same trend occurs for the other K₂CO₃ intake (0.3 and 0.5

mol/mol XGU) as well. As expected, the overall acetylation rate increases with temperature. However, one should realize that the overall reaction rate consists of complex interaction between reaction kinetics, mass transfer (diffusion rate) and phase behavior amongst the component involve in the reaction. Further studies are required to elucidate the complex interaction.

Fig. 4. DS values at various temperatures and different K_2CO_3 intakes. All experiments were done at pressure of 10 MPa.

In contrary with the strong influence of different catalyst, the catalyst intake, surprisingly, does not give any strong influence on the reactivity (Fig 4). As can be seen from Fig 4, the DS values are almost constant at different catalyst intake in the same temperature value except for temperature of 80°C. At 80°C, the DS value decreases from 3.1 to 2.6 when catalyst intake increases from 0.1 to 0.5 mol/mol XGU. The results may be related with the fact that there is side reaction occur in the acetylation reaction [13]. The AAH can be hydrolyzed with water to form acetic acid. Instead of the main acetylation reaction, K_2CO_3 may also catalyze the hydrolysis reaction. Additional experiment is required to investigate the role of K_2CO_3 in the hydrolysis of acetic anhydride to form acetic acid and this will be reported in our next publication.

3.6. Product properties

The change in the molecular structure of the product was analyzed with X-Ray Diffractometer (Fig 5). Native XG is amorphous in nature (Fig 5a) [16]. It is clear that no crystalline peak appears in the diffractogram of native XG (Fig 5.a).

Fig. 5. X-ray diffractogram of (a) native XG; (b) xanthan acetates with DS of 2.38; (c) DS of 3.68 (b) and DS of 7.08.

Moreover, there are no significant changes in the diffractograms of the xanthan acetate product compared with the one of native XG suggesting that the products are amorphous as well. It suggests that in the experimental window, the acetylation reaction does not change the molecular structure of the products. In line with XRD analysis, there are no melting and crystallization peaks in DSC thermogram of the native XG and the products (Fig 6) as well.

Fig. 6. DSC results of (a) native XG; (b) xanthan acetates with DS of 2.38; (c) DS of 7.08.

As shown in Fig 6, all thermograms (native XG and products) show endothermic peak at nearly 100 °C. This endothermic peaks are related with the evaporation of water from the material. Moreover, an exothermic peak appears around 284 °C for native XG, 307 °C and 309 °C for xanthan acetate with DS of 2.38 and DS of 7.08, respectively is related with the degradation temperature of the material. It is obvious that the degradation temperature of the products is higher compared with one of native XG. The degradation temperature increases with the DS values. This imply that the acetylated XG products have a better thermal stability compared with native XG. The acetate group seems to enhance the molecular interactions (van der Waals) of the XG chain and thus improve the thermal stability of the end products [6]. Furthermore, the higher degradation temperatures of the products compared with native XG are clearly visible from the TGA curves (Fig 7). In agreement with the DSC profile (Fig 6), this confirms the higher stability of the products.

Fig. 7. TGA thermograms of native XG, xanthan acetates with DS of 2.38 and DS of 7.08.

4. Conclusions

We here report our preliminary work on the acetylation of XG using AAH in densified CO₂. The successful of the reaction was confirmed by the FT-IR (enhance intensity of C=O, carbonyl group, at 1750-1755cm⁻¹) and SEM (the change in the product morphology). The reactivity of the reaction is clearly a strong function of temperature, and different type of catalyst, while the catalyst intake gives a limited influence on the DS value. In other hand, pressure gives an optimum DS value due to the interplay between plasticizing and compressive effect at higher pressure. Moreover, the product has a full amorphous structure and an enhanced thermal stability compared with native XG. This work shows some fundamental aspects on the process and product relationship and provides an outlook to use XG in the biodegradable plastics synthesis.

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