



SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF CATIONIC POLYMERIC SURFACTANT FROM *Dioscorea pyrifolia* STARCH

(Sintesis dan Pencirian Fizikokimia Surfaktan Polimer Kationik daripada Kanji *Dioscorea pyrifolia*)

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Abstract

Cationic starch-based polymeric surfactant, 2-hydroxy-3-(N,N,N-trimethylammonium)propyloxy starch (S-ETAC) from *Dioscorea pyrifolia* tubers, was synthesized by etherification using 2,3-epoxytrimethylammonium chloride (ETAC) in the mass ratio of ETAC/starch (St) of 0.15:1, 0.25:1, 0.5:1, 1:1, 2:1 g/g and sodium hydroxide as a catalyst in aqueous medium. The degree of substitution (DS) and reaction efficiency (RE) were calculated using the percentage of nitrogen derived from the elemental analysis. The study found that the more the ETAC used, the higher the DS (0.11 ± 0.00 to 0.76 ± 0.00), but the RE decreased ($68.87 \pm 1.62\%$ to $35.35 \pm 0.54\%$). This S-ETAC was characterized by using the solubility and swelling power tests as well as attenuated total reflectance - Fourier transform infra-red (ATR - FTIR) spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) to prove the reaction occurs at the starch structure.

Keywords: cationic starch, etherification, *Dioscorea pyrifolia*

Abstrak

Surfaktan polimer berasaskan kanji kationik, kanji 2-hidroksi-3-(N, N, N-trimetilammonium) propiloksi (S-ETAC) dari ubi *Dioscorea pyrifolia*, telah disintesis melalui tindak balas pengeteran menggunakan 2,3-epoksi trimetilammonium klorida (ETAC) dalam nisbah jisim ETAC / kanji (St) 0.15: 1, 0.25: 1, 0.5: 1, 1: 1, 2: 1 g/g dan natrium hidroksida sebagai pemangkin dalam medium akueus. Darjah penukargantian (DS) dan kecekapan tindak balas (RE) telah dikira menggunakan peratusan nitrogen yang diperolehi daripada penganalisis unsur. Kajian ini mendapati bahawa lebih banyak ETAC yang digunakan, semakin tinggi DS (0.11 ± 0.00 kepada 0.76 ± 0.00), tetapi RE menurun ($68.87 \pm 1.62\%$ kepada $35.35 \pm 0.54\%$). S-ETAC dicirikan dengan menggunakan kelarutan dan ujian kuasa pembengkakkan serta spektroskopi transformasi Fourier infra merah - jumlah pantulan teratenuat (FTIR - ATR), kalorimetri pengimbas pembezaan (DSC) dan pembelauan sinar-X (XRD) untuk membuktikan bahawa tindak balas berlaku pada struktur kanji.

Kata kunci: kanji kationik, pengeteran, *Dioscorea pyrifolia*

Introduction

Starch modification is an alternative industry nowadays to meet the growing demand, reduce the cost of raw materials and reduce environmental pollution. The usage of native starch is usually limited due to its physicochemical properties that are not water-soluble and tend to form a non-stable emulsion. Thus, starch modification via physical, chemical or biological is used to increase the functionality that able to expand into to industrial use and has better features in terms of functional group and solubility [1]. Chemically modified starch

typically involves esterification, etherification or oxidation of hydroxyl groups on the α -D-glucopyranosyl of the starch structure. Most of the commercialized starches produced by adding reactants and organic solvents to the starch solution at control pH 7-9 for esterification [2] and pH 11-12 for etherification at temperatures above 60 °C [2, 3].

Cationic starches from sources such as corn, tapioca, wheat and potato have been widely used in the production of paper, textiles, cosmetics and treatment of waste water because they can improve the properties of viscosity, surface, retention performance and change the properties of colloids [2]. Cationic starches commonly used in most products which contained 0.1 – 0.4% nitrogen (< 0.05 DS) [2]. In previous studies, modified corn starch used quaternary ammonium group and dioxane-water-THF as the medium to produce cationic starch with DS 1.37 [3]. Reaction of corn starch with quaternary ammonium in the ionic liquid produced cationic starch with DS of 0.99 [1]. Homogenous reaction conditions using medium DMSO can increase the DS compared to heterogeneous reaction condition in ethanol/water medium [4]. Although there are several ways of obtaining cationic starches with high DS, the use of harmful solvents, difficult in purification process and high cost of solvents limits the production of the cationic starches. Conventional methods which use a lot of organic solvents are not only reduce the DS but also increase pollution to the environment [1].

Dioscorea pyrifolia is a monocot plants possess edible tubers, grown and sold in markets at east coast states of Malaysia [5]. The tubers are called “Ubi Itik” among the people in these states. Although cationic starches from sources as corn, tapioca, wheat and potato is an important product in the industry [2], the preparation and properties of cationic starch from *Dioscorea pyrifolia* tubers are not been reported yet. The information on the modified starch from this plant is still limited to the industry. In this study, a cationic starch-based surfactant from *Dioscorea pyrifolia* tubers is synthesized through etherification of ETAC and aqueous NaOH as a catalyst (Figure 1) using semi-dry method. The effect of the increasing ETAC in the NaOH/water medium was investigated with the calculation of the degree of substitution (DS) and reaction efficiency (RE) using percentage of nitrogen obtained from elemental analyzer. Then, the S-ETAC is characterized to ensure that the reaction occurs in the structure of the starch.

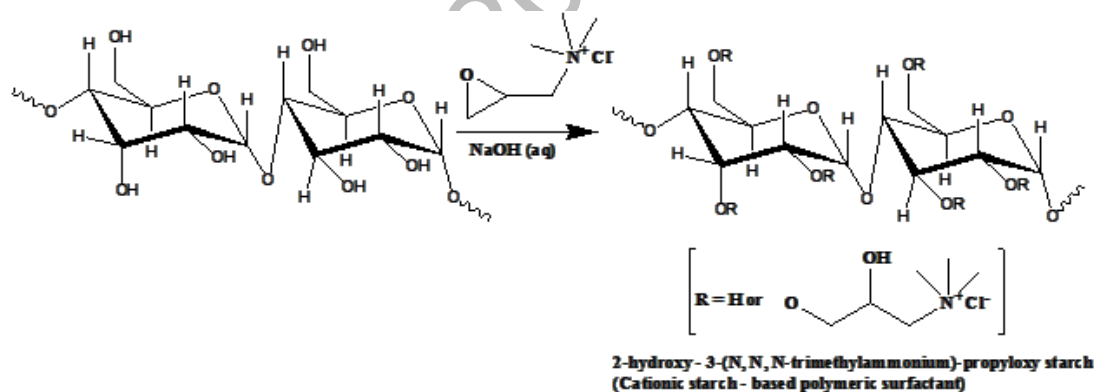


Figure 1. Synthesis of cationic starch-based polymeric surfactant

Materials and Methods

Materials

Starch was extracted from *Dioscorea pyrifolia* tubers taken in Kelantan, Malaysia. Chemicals used in this study are 2,3-epoxytrimethylammonium chloride (Sigma-Aldrich, >90%, technical grade), sodium hydroxide (R & M Chemical, 95%), ethanol (R & M Chemical, 95%, analytical grade) and acetone (EMSURE, 99.5%, analytical grade). Sodium hydroxide solution was prepared using deionized water.

Synthesis of cationic starch-based surfactant

The cationic starch-based polymeric surfactant was prepared by semi-dry process in a series of mass ratio ETAC:St starting with 0.15:1, and varying the masses of ETAC to 0.25, 0.5, 1 and 2 in 4 mL of 0.1 g/mL NaOH solution. The process was initiated by putting 1.5 g ETAC in a beaker containing the NaOH solution and stirred for 5 minutes. Then 10 g of starch incorporated into the solution and stirred, resulting in dough. It was heated in a water bath at 80 °C for 2 hours, and 4 mL water was added into the beaker to stop the reaction. Ethanol (5 mL) was added to the beaker and stirred to wash away the unreacted reagents. Next, acetone (10 mL) was added into the beaker so that the S-ETAC precipitates. The S-ETAC was rinsed three times with ethanol before dried in an oven at 50 °C. This S-ETAC was pulverized and sieved (600 µm pore size). This method has been reported by Lin et al. [6] with slight modifications.

Degree of substitution and reaction efficiency

The DS value is important to know the average number of ETAC replacement into the anhydrous glucose unit (AGU) of the starch structure. The actual and theoretical DS and RE (%) of the reaction were calculated by the percentage of nitrogen derived from the elemental analysis (Thermo-Finnigan, EA 1112 CHNS Analyzer series, Italy) using equations (1), (2), and (3), respectively:

$$\text{Actual DS} = \frac{(162.15 \times N)}{(1401 - 151.64 \times N)} \quad (1)$$

$$\text{Theoretical DS} = \frac{W1/151.64}{W2/162.15} \quad (2)$$

$$\text{RE (\%)} = \frac{\text{Actual DS}}{\text{Theoretical DS}} \times 100 \quad (3)$$

where N is the percentage of the nitrogen determined by elemental analysis, the 162.15 is the molar mass of anhydrous glucose units (AGU) in the starch, the molar mass of 151.64 is hydroxypropyltrimethylammonium chloride, 1401 is 100 times the mass of the nitrogen atom, W1 and W2 are the masses of ETAC and starch used [6, 7].

Solubility and swelling power

Native starch and S-ETAC incorporated into the different vials contained distilled water (1% w/v) and stirred for 30 minutes at room temperature before being cooled/heated at different temperatures (25, 35, 45, 55, 65, 75, 85 and 95 °C) for 1 hour. The starch slurry was cooled to room temperature, poured in a centrifuge tube and centrifuged at 3000 rpm for 15 minutes. The supernatant was gently put into a vial and dried in an oven at 110 °C. Wet starch in the centrifuge tube was weighed before dried. Different starch slurry was used for each different temperature and analysis carried out in triplicate [8]. Solubility and swelling power were calculated using equations (4) and (5), respectively.

$$\text{Solubility (\%)} = \frac{\text{mass of dry supernatant}}{\text{mass of dry starch}} \times 100 \quad (4)$$

$$\text{Swelling power (g/g)} = \frac{\text{mass of wet starch}}{\text{mass of dry starch} - \text{mass of dry supernatant}} \quad (5)$$

Fourier transform infrared analysis

S-ETAC and native starch (30 mg) were determined using a Fourier Transform Infra-Red – Attenuated Total Reflectance (FTIR-ATR Spectra 2000 Perkin Elmer) at 4000 to 650 cm⁻¹ at spectral resolution of 4 cm⁻¹ [6].

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC 822 Mettler Toledo) was used to measure the gelatinization temperatures and enthalpies of the native starch and S-ETAC. DSC was calibrated with indium and empty aluminum pan was used as blank. Slurry of starch and water in a mass ratio of 1: 3 was placed in aluminum pan, sealed and let for 1

hour. Then the aluminum pan containing the sample was heated from 25 to 100 °C at a heating rate of 10 °C/min [9].

X-ray diffraction

The degree of crystallinity of starch and S-ETAC can be determined using X-ray diffraction (Bruker D8 Advance). The samples were put in special containers and diffraction patterns recorded in a reflection 5 – 80° (2 θ) at room temperature, operating at 40 kV and 40 mA with Cu K α radiation, $k = 0.5406$ nm [1, 10].

Results and Discussion

Degree of substitution and reaction efficiency

The actual DS (0.11, 0.16, 0.30, 0.48 and 0.76) in this study was increased as the mass ratio of ETAC:St increases (0.15:1, 0.25:1, 0.5:1, 1:1, 2:1), compared with theoretical DS (0.16, 0.27, 0.53, 1.07 and 2.14) (Figure 2 (a)). The percentage of RE decreases with the increasing amounts of ETAC by, 69, 59, 56, 45 and 35 % (Figure 2 (b)). The results show that the more the amounts ETAC added, the lower the RE (%) of the reactions. Kavaliauskaite et al. [11] produced a cationic starch having a DS of 0.2 to 0.85 using different ratios of reactant and different conditions at a temperature of 45°C for 24 to 48 hours. Wang et al. [3] also produced cationic starches with DS 0.27 to 1.37 using dioxane-tetrahydrofuran-water as the reaction medium at 60 °C for 4 – 8 hours. Wang and Xie [1] produced a cationic starch having a DS 0.19 to 0.99 using ionic liquid as the reaction medium at 70 °C for 24-72 hours. Lin et al. [6] also produced cationic starches with DS between 0.13 and 0.26 at 80 °C for 2 hours from waxy maize starch. All of the above studies using different starches, ETAC, NaOH ratios and different solvents. The findings of this study will give information about the reaction to produce a cationic starch using faster and more environmentally friendly method because it does not use organic solvents as well as the yield is easily purified.

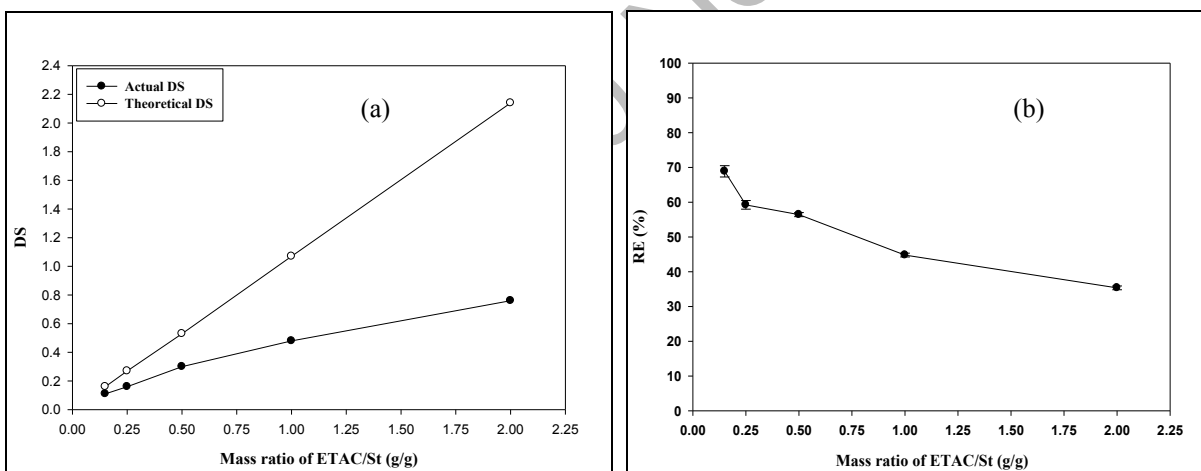


Figure 2. (a) Actual and theoretical DS and (b) RE (%) of S-ETAC at difference mass ratio of ETAC/St (g/g)

Solubility and swelling power

Solubility and swelling power of starch and S-ETAC are shown in Figure 3. Solubility of native starch and S-ETAC increased as temperature increased (Figure 3 (a)) but solubility S-ETAC increased dramatically at temperatures above 75 °C. This means that the reaction of starch and ETAC molecules produced will increase solubility of S-ETAC in water from 43.5 to 109.7% compared to the native starch. Modification of the structure of starch causes steric hindrance and repulsion between starch molecules, thereby facilitating the absorption of water in the crystalline regions in the starch granules [6]. Swelling power of native starch and S-ETAC also increase as the temperature increases (Figure 3 (b)). Swelling power increases because of the repulsion of the starch molecules cause water to penetrate into the S-ETAC molecules thus increased the swelling power between 124 and 548% compared to the native starch. Lin et al. [6] produces the cationic starch (using dry methods) that have higher

swelling power than the native starch but the solubility index is lower than the native starch. In this study, solubility and swelling power of the cationic starch are higher than the native starch. This may be caused by the gelatinization occurs during the reaction (using a semi-dry method) which causes the cationic starch produced is more soluble than the native starch.

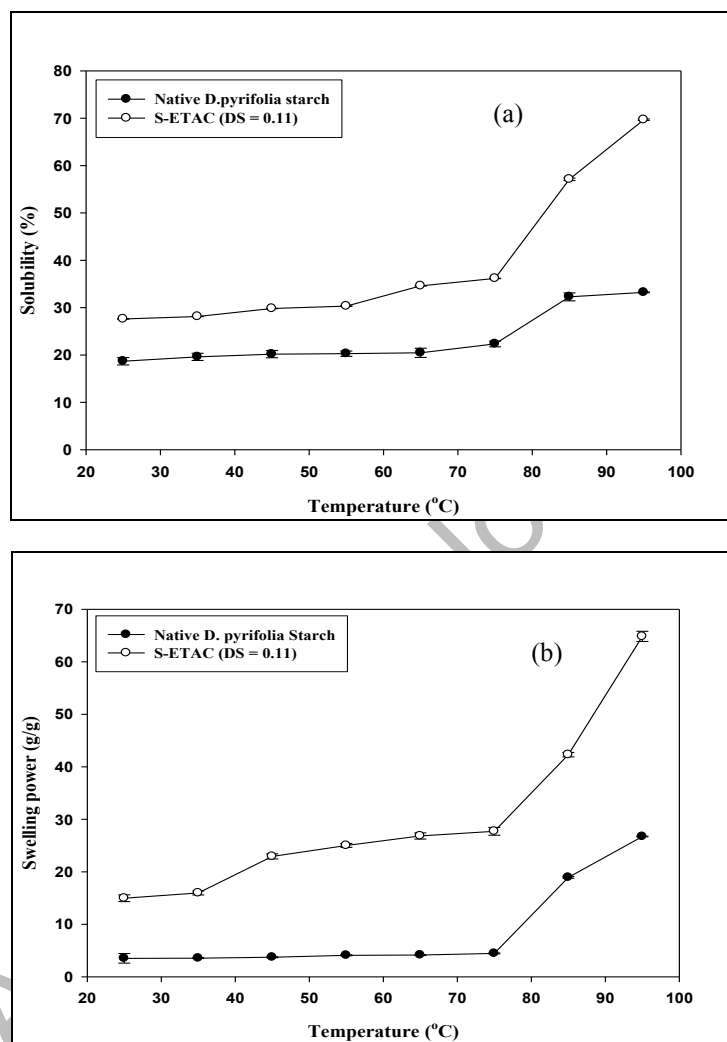


Figure 3. (a) Solubility (%) and (b) swelling power (g/g) of native starch and S-ETAC

Fourier transform infrared analysis (FTIR)

Figure 4 shows FTIR spectra of the native starch and S-ETAC. Infrared profile shows not much difference between the two spectra. Starch backbone shows at 3294 (-OH stretching), 2928 (-CH stretching), 1149, 1078, 996 (C-O stretching), 1363 (C-H deformation) and 1642 cm^{-1} (major peak of starch). The highlight of the S-ETAC at 855 cm^{-1} (-CN deformation) and 1483 cm^{-1} (C-N stretching) proved that the ETAC structure is bonded on the structure of starch. This finding is similar to findings reported by Wang and Xie [1], Wang et al. [3], and Lin et al. [6].

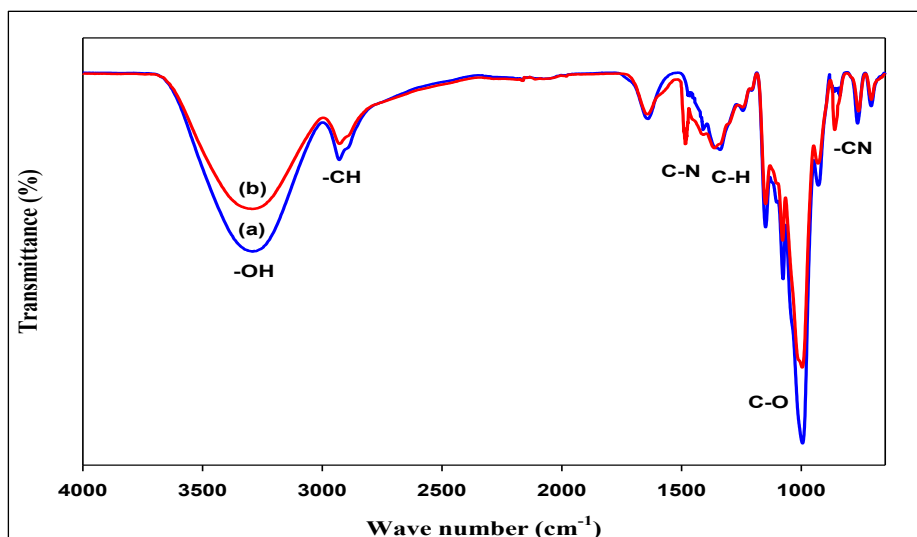


Figure 4. FTIR spectra of (a) native starch and (b) S-ETAC (DS = 0.11)

Differential scanning calorimetry (DSC)

Figure 5 shows the DSC thermogram for the native starch and S-ETAC. Gelatinization temperature of native starch was at 71 °C (onset temperature), 75 °C (peak temperature) and 78 °C (conclusion temperature) (Figure 5 (a)), while gelatinization endotherm was not detected in the S-ETAC (Figure 5 (b)). The reaction between the starch and ETAC makes the gelatinization temperature of S-ETAC cannot be determined. This finding is similar to that previous study reported in Zhang et al. [12] using cationic acetylcholine groups as reagent for etherification of potato starch. The interaction between starch and ETAC will loosen starch structure causing starch molecules more easily absorb water during heating. The starch heating at high temperature of 80 °C caused the water to enter the starch granules so hydrogen bonds within and outside of the starch molecules are disrupted and swell. At high temperature, starch crystallites become unstable and disordered due to thermal motion and swelling force. Next, water will fully enter into starch crystallites region and breaks up the order of starch crystallites. The order of starch crystallites will destroy and turned into amorphous form. Thus, gelatinization temperature disappeared. These results confirmed by the X-ray diffraction analysis.

X-ray diffraction (XRD)

X-Ray diffraction patterns of the native starch (a) and S-ETAC (b) shown in Figure 6 are used to determine the changes of crystalline structure. Native starch showed crystallization of type-C pattern, while the diffraction pattern of S-ETAC changed to single broad peak with reduced intensity. This is due to starch crystallites region partly destroyed and converted into amorphous form after etherification of native starch with ETAC molecules. The amorphous properties from XRD diffraction pattern have been previously discussed by Wang et al. [3] and Zhang et al. [12]. The loss of crystallites region is caused by alkaline environment and water during etherification of starch. Therefore, these cationic starches have potential as flocculants because the presence of amorphous and solubility properties are important in practical point of view to improve its ability to form a colloidal or solution in cold water especially in waste water treatment plant [3]. It also has potential as additive to increase the viscosity of colloidal emulsion.

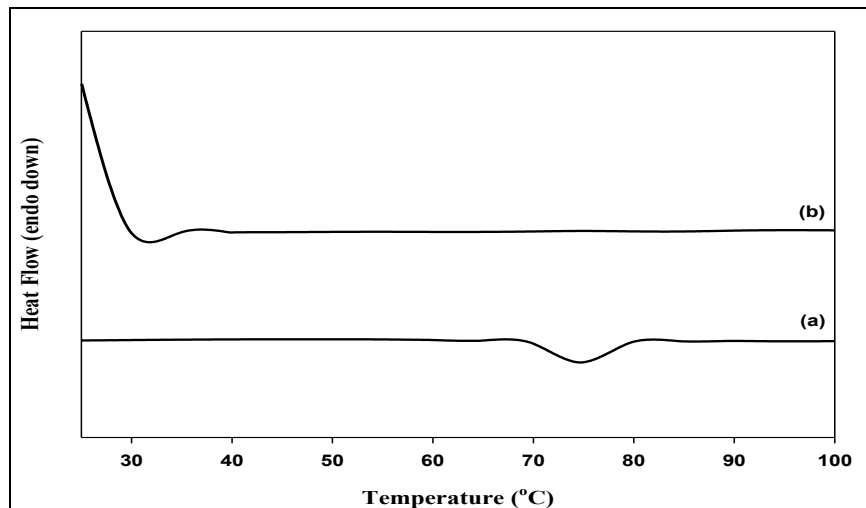


Figure 5. DSC thermogram of (a) native starch and (b) S-ETAC (DS = 0.11)

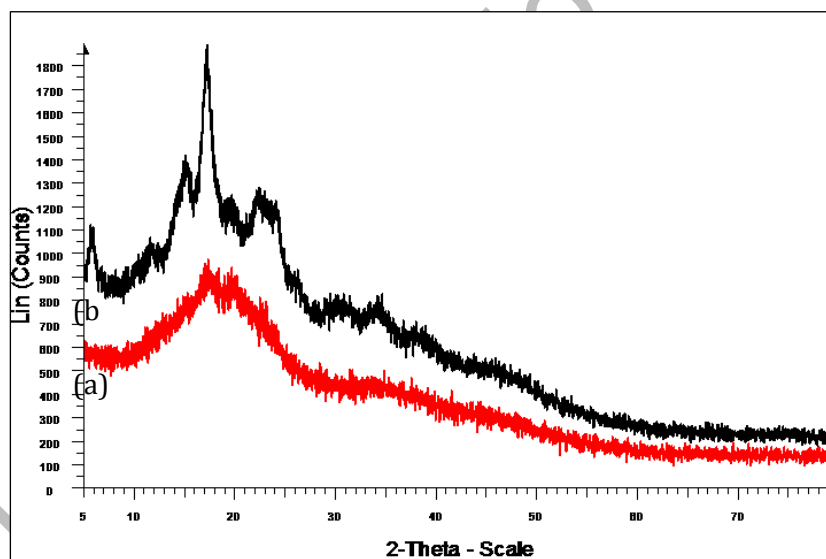


Figure 6. XRD patterns of (a) native starch and (b) S-ETAC (DS = 0.11).

Conclusion

Cationic starch-based polymeric surfactant (S-ETAC) from *Dioscorea pyrifolia* starch tubers has been successfully synthesized in a series of mass ratio ETAC:St at a temperature of 80 °C for 2 hours and the optimum reaction is in ratio of 0.15:1, which has a DS 0.11 and RE 68%. S-ETAC was characterized using the solubility and swelling power tests as well as analyses of FTIR, DSC and XRD. The results showed that the S-ETAC produced has a solubility and swelling power better than the native starch. The S-ETAC was high in solubility and swelling power in water. Preparation of S-ETAC is also more environmentally friendly, inexpensive and can be produced on a large scale. Further study is to characterize surface properties of S-ETAC to replace petroleum-based surfactant of similar character.

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