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Effect of single step oxidation-esterification process on the physicochemical properties of modified cassava starch

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Abstract

The oxidation and esterification are examples of starch modification processes which is often carried out. The conventional combination of the oxidation-esterification process has many defects due to its wasting of time, energy-consuming and quality-damping. This research focuses on combining chemical modification processes to produce modified cassava starch by developing a single-step process of oxidation-esterification and a drying process using a rotary UV dryer. The oxidized-esterified cassava starch is characterized by Fourier-transformed insfrared (FTIR) spectroscopy, X-ray diffraction, scanning electron microscope (SEM) and physicochemical properties. The results revealed that the oxidized-esterified cassava starch (COAEC 14) meets the SNI requirements for several parameters such as water content of 13.10±0.141%, ash content of 0.0042±0.0002%, and crude fiber content of 0.6677±0.0424%. In addition, the single-step oxidation-esterification process also improved the quality of swelling power and starch amylose content. Meanwhile, in SEM analysis, the single-step oxidation-esterification process did not change the surface morphology but changed the crystal system and size of starch using XRD analysis.

1. Introduction

Cassava starch is an odorless, white, complex carbohydrate with the molecular formula (C6H10O5)x (Veeramanipriya and Umayal Sundari, 2021) with a low amylose content of about 16–25% and a high amylopectin content of 75–84% (Ojogbo *et al*., 2020). Starch such as cassava starch is an important raw material in the food industry, as it can be used as a thickener, coagulant, or gelling agent, among others. These properties of starch are obtained when the starch is pre-stabilized (Grgić *et al*., 2019). Improving or stabilizing the properties or characteristics of starch is achieved by modifying starch (Thirumdas *et al*., 2017). Starch modification is a functional derivative with the aim of creating a competitive advantage in new products, improving product aesthetics, lowering recipe/production costs, improving the overall product, ensuring product consistency and extending shelf life while clearly making starch relevant at all stages of the food product production cycle (Kaur *et al*., 2012). Modification of cassava starch has been carried out, among others, chemical, physical, enzymatic and genetic (Sumardiono, Jos, Pudjihastuti *et al*., 2022).

The main chemical modification methods of starch include hydrolysis, esterification, oxidation, and etherification, among which the esterification method has been widely used (Zuo *et al*., 2017). The main reason starch is chemically treated before commercially use is to split the long glucose chains of the polymer molecule to increase and obtain the maximum possible amounts of starch in technical applications (Dias *et al*., 2011). Dual or combination modifications can assist in obtaining specific properties of starch that are impossible with a single method. Combination modification allows modifying the native starch in more ways from a single source to suit different industrial applications. In dual modification, either two physical methods or two chemical methods or a physical method and a chemical method can be combined (Khurshida *et al*., 2021). Oxidation and esterification are types of chemical modification that can be combined to obtain better characteristics of cassava starch (Puspita Dewi *et al*., 2018).

The oxidation process is a modification process where the hydroxyl groups in the starch molecule are substituted with carbonyl and carboxyl groups. The reaction also caused degradation of starch molecules resulting in modified starch with low viscosity (Sangseethong *et al*., 2010). Esterification is the reaction between carboxylic acid groups and alcohol groups with

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the removal of water molecules (Egharevba, 2020). Citric acid, lactic acid and acetic acids have been used for starch esterification (Shaikh *et al*., 2019). In the research of Ker *et al*. (2017), it is known that the starch modification process with oxidation-esterification treatment can be combined by developing a pseudo single-step process. The use of sodium hypochlorite as an oxidizer and acetic anhydride as an esterification reagent provided the latest characteristics of cassava starch to be used as raw material for noodles.

The focus of this research is to develop a modified single-step oxidation-esterification process using hydrogen peroxide as an oxidizer and lactic acid and ester (lactic acid and ethanol) as esterification reagents with drying technology using a rotary UV dryer. As it is known, UV irradiation in the starch modification process can affect the characteristics of starch (Sumardiono, Cahyono, Jos *et al*., 2021) so that it can produce modified cassava starch that can be used as a substitute for wheat flour.

2. Materials and methods

2.1 Materials

The samples of cassava starch in powder form were obtained from the local commercial market. The oxidizing agent used was H_2O_2 (30% hydrogen peroxide), while the reagents used for the esterification process were lactic acid (90%), ethanol (90%), NaOH, HCL and distilled water. All reagents were of analytic and food grade.

2.2 Single-step oxidation-esterification process of cassava starch

This was conducted with a research design using a factorial design involving four factors, each at two different levels, were selected and experimental trials were performed using all possible combinations. The concentration of hydrogen peroxide (3.6% and 7.2%), the use of lactic acid and ethyl lactate as esterification reagents, esterification time (1.5 and 3 hrs), and drying time (30 and 60 mins) were selected as independent variables, while the water content, ash, crude fiber, amylose and swelling power were selected as dependent variables.

Native starch (200 g) was dispersed in distillate water and hydrogen peroxide acid at ambient temperature (25°C), according to experimental design concentration. Then, it was continuously stirred in a thermostatic water bath (30°C) for 60 mins of the oxidation process After 60 mins the dispersion was added with an esterification reagent for 1.5 and 3 hrs, according to the experimental design. After the esterification process was completed, the starch was further neutralized using HCl, then filtered, rinsed, and dried for a certain drying time, according to the experimental design. From the results obtained, the selected sample of oxidized-esterified cassava starch (COAEC) was characterized by physicochemical and functional properties.

2.3 Moisture content

Typically, the moisture content is determined via a thermogravimetric approach, i.e., by loss on drying, in which the sample is heated and the weight loss due to evaporation of moisture is recorded. In this study, the moisture content was evaluated using the Sartorius MA150 moisture analyzer. The oxidized-esterified cassava starch (COAEC) (2 g) was placed in a moisture analyzer which was previously set at 130°C. At a certain time, the moisture analyzer showed the water content contained in the sample.

2.4 Ash content

The ash content of the starches was evaluated according to SNI for the commercial cassava starch (Badan Standardisasi Nasional, 2011). The crucible was heated in the furnace at 550°C for 1 hr and put in a desiccator, then weighed with an analytical balance (W_0). Then, COAEC weighing 5 g was placed in a crucible and then weighed (W_1). The crucible was put into the furnace at a temperature of 550°C until white ash was formed. Then, put it in a desiccator so that the temperature reach room temperature and then weighed (W_2). It was repeated until the weight was stable.

$$\text{Ash content} = \left(\frac{W_2 - W_0}{W_1 - W_0}\right) \times 100\%$$

When W_0 = empty crucible weight (g), W_1 = weight of crucible containing COAEC before incinerated (g) and W_2 = weight of crucible containing COAEC after incinerated (g)

2.5 Crude fiber content

The crude fiber content of the sample was determined by Labconco Fibertech (Lab-conco Corporation, Kansas City, MO, USA) as described in AOAC (2005) method No.978-10. Briefly, 1 g of moisture and the fat-free sample was taken in a 1000 mL beaker, and 200 mL of diluted (1.25%) sulphuric acid was added. Samples were digested by boiling for 30 mins. It was filtered (via suction apparatus), and residues were washed with hot water at least three times until they became acid-free. This method was repeated thrice until samples became alkali-free. Residues were transferred into a pre-weighed crucible and dried in an oven at 70–80°C until a constant weight was attained. Finally,

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residues were charred on a burner and ignited in a muffle furnace at 550°C for 5–6 hrs and cooled in a desiccator, then weighed. The loss in weight during incineration represented the weight of crude fiber in the sample (Arshad *et al*., 2021).

$$\text{Crude fiber (\%)} = \left(\frac{\text{Loss of weight of CAOEC during ashing (g)}}{\text{Weight of native starch (g)}}\right) \times 100$$

2.6 Amylose content

For the determination of amylose content, starches samples were defatted with 85 mL/100 mL methanol in reflux with a Soxhlet extractor for 12 hrs. Amylose content was measured according to method ISO-6647 (Santos *et al*., 2021).

2.7 Swelling power

The COAEC (0.5 g) (dry basis) was mixed with distilled water to obtain a 1% (w/w) starch slurry in a centrifugal tube. The suspensions were heated at 95°C for 30 mins. The cooked samples were then cooled to room temperature and centrifuged at 3500 rpm for 20 mins. The swelling power was calculated as the weight ratio of the wet sediment to the initial dry matter without water-soluble starch. Three replications were measured for the experiment (Sumardiono, Cahyono, Jos *et al*., 2021).

2.8 Scanning electron microscopy

The scanning electron microscopy (SEM) micrographs were taken with instrument JSM-6510 accel volt 10 under a magnification of 500× and 1000×.

2.9 X-ray diffraction

The X-ray diffractograms of powdered SWA samples were analyzed using the Shimadzu LabX XRD-600 at 30 mA and 40 kV (Cu foil filtered). The scanning region was collected from 2 to 50 diffraction angles (2Θ) at 0.02 step size and 1.20 s count time.

2.10 Fourier- transform infrared spectroscopy

The functional group of the oxidized-esterified cassava starch (COAEC) was observed using a Fourier Transform infraRed (FTIR) Shimadzu (type IRprestige 21, Shi-madzu Corporation, Kyoto, Japan).

2.11 Statistical analysis

The results were presented as the mean ± standard deviation of two replicates. The analysis procedure used Minitab version 19.0 statistical software was used for analyzing factorial design, the Analysis of Variance (ANOVA) and Tukey with significant differences were reported at a 95% confidence level.

3. Results and discussion

3.1 Moisture content

Moisture content is an important parameter of starch, as moisture levels greater than 13% are considered undesirable, as it makes the starch susceptible to microbial spoilage (Liu *et al*., 2019). Meanwhile, the standard moisture content in commercial cassava starch according to SNI 3541-2011 is a maximum of 14%. The moisture content of starch varies with the inclusion of hydrophilic or hydrophobic groups during modification and the degree of drying achieved during modification (Wang *et al*., 2022). Table 1 shows that the moisture content of COAEC in this study ranged from 13.10±0.141% to 27.41±0.742%. COAEC 14 can be used as a substitute for wheat flour in terms of moisture content, because it has a moisture content of 13.01±0.141% which complied with SNI 01-3751-2018 for commercial wheat flour. The single-step oxidation-esterification process significantly affects the moisture content of cassava starch, where the most significant factor in this process is drying time and the interaction between the type of reagent used and drying time.

Samples with a drying time of 60 mins (COAEC 9, COAEC 14 and COAEC 16) have a lower moisture content than samples with a drying time of 30 mins (COAEC 3, COAEC 6 and COAEC 7). This can be explained by the fact that the longer the drying time, the more water or liquid in the starch will evaporate. The interaction between the type of reagent for the esterification process and drying time also affects the moisture content of modified cassava starch, where modified starch using lactic acid and ethanol with a drying time of 30 mins (COAEC 6) has a higher

Table 1. The chemical properties of COAEC.

Sample	Moisture Content (%)	Ash Content (%)	Crude Fiber Content (%)
COAEC 3	26.24±0.891[a]	0.0028±0.0007	0.851±0.1317[b]
COAEC 6	27.41±0.742[a]	0.0023±0.0014	1.5154±0.0543[b]
COAEC 7	24.72±0.191[a]	0.0025±0.0002	2.2478±0.0004[b]
COAEC 9	13.41±0.233[b]	0.0027±0.0005	8.1214±0.066[a]
COAEC 14	13.10±0.141[b]	0.0042±0.0002	0.6677±0.0424[b]
COAEC 16	15.50±0.276[b]	0.0015±0.0017	3.2949±0.0731[a]

Values are presented as mean±SD. Values with different superscripts within the same column are statistically significantly different ($p<0.05$).

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moisture content than using lactic acid for 60 mins (COAEC 14), whose values are 27.41±0.742% and 13.10±0.141%, respectively. This is according to previous studies that stated that the increase in moisture content associated with the percentage of acetylation can be attributed to the hydrophilic groups incorporated in the native starch (Mbougueng *et al*., 2012).

3.2 Ash content

Ash content indicates the mineral composition present in starch (Agbemafle, 2019). In general, cassava contains few minerals, and the single-step oxidation-esterification process with the process variables specified in the study did not have a significant effect on the ash content of oxidized-esterified cassava starch (COAEC). Table 1 presents the ash content of COAEC ranging from 0.0015±0.0017% to 0.0042±0.0002%. With a maximum value of 0.7% for commercial wheat flour, the results obtained by COAEC are acceptable for SNI 01-3751-2018. The data shows that COAEC can be used well in the food industry, especially its use as a substitute for wheat flour when viewed from the value of the resulting ash content. The amount of ash content affects the final product such as product color and dough stability. The lower the ash content, the better the product quality.

3.3 Crude fiber content

Crude fiber measurements indicate 80% hemicellulose content, 50–90% lignin content, and 20–50% cellulose content, which lead to increased satiety after eating (Rajapaksha *et al*., 2017). Table 1 presents the crude fiber content of COAEC, ranging from 0.6677±0.0424% to 8.1214±0.066%. The type of reagent used, between ester (lactic acid + ethanol) and lactic acid, and the interaction with the length of esterification time are significant factors in the single-step modified oxidation-esterification process. COAEC using lactic acid as reagent in the esterification process for 1.5 hrs (COAEC 1) had a fiber content of 8.1214±0.066%, this value was higher than COAEC using ester (lactic acid + ethanol) with an esterification time of 1.5 hrs (COAEC 3) of 0.851±0.1317%.

The samples using lactic acid with 3 hrs esterification time (COEC 6 and 14) had lower crude fiber values compared to the samples that used ester with 3 hrs esterification time. The data also indicated that there was a decrease and increase in crude fiber of natural starch by 2.7133%. Where the acid reacts through the substitution of its acyl group with the free hydroxyl moiety of the available glucose monomer resulting in a modified starch substrate (Otache *et al*., 2021). The degradation of cellulose that makes up the cell wall of cassava starch will cause the starch to become free (Sumardiono, Budiyono, Kusumayanti *et al*., 2021; Sumardiono, Jos, Antoni *et al*., 2022). Low fiber will make the viscosity of cassava starch low so that it has soft characteristics and small grain size.

3.4 Amylose content

The amylose content of COAEC ranged from 21.451±0.0459% to 28.708±0.0456%, as can be seen in Table 2. The interaction of the type of esterification reagent used with esterification time became a significant influencing factor. Starch using lactic acid with an esterification time of 1.5 hrs and drying for 60 mins (COAEC 9) had the highest amylose content of 28.708±0.0456%. While the starch with ester treatment (lactic acid + ethanol), esterification for 1.5 hrs and drying time for 30 mins (COAEC 3) had the lowest amylose content of 21.451±0.0459%.

Table 2. The functional properties of COAEC.

Sample	Amylose Content (%)	Swelling Power (g/g)
COAEC 3	21.451±0.0459^{b}	3.646±0.0679^{a}
COAEC 6	23.174±0.1840^{b}	4.245±0.0552^{a}
COAEC 7	23.367±0.0455^{b}	2.826±0.2090^{b}
COAEC 9	28.708±0.0456^{a}	3.424±0.4440^{a}
COAEC 14	27.230±0.0453^{a}	2.296±0.1245^{b}
COAEC 16	27.134±0.0891^{a}	2.416±0.0170^{b}

Values are presented as mean±SD. Values with different superscripts within the same column are statistically significantly different ($p<0.05$).

According to Li *et al*. (2020), reaction time is an important factor affecting the degree of reaction in chemical reactions. Too long or short a reaction time has an adverse effect on the esterification reaction, and the optimal esterification time is 2.5 hrs. In this study, the esterification time of 1.5 hrs resulted in different amylose levels; therefore, in the interaction between reagents and esterification time, the most influential factor is the type of reagent used. The use of lactic acid produces high amylose levels compared to ester (lactic acid + ethanol); this is according to research conducted by Martins *et al*. (2018), which reported that esterification modification with acids causes an increase in ester groups, which strengthens amylose and amylopectin bonds, increases stability between iodine/amylose complexes and reduces molecular depolymerization. In addition, Sumardiono, Putri, Jos *et al*. (2019) reported that the amylose content of natural starch decreased after modification using the esterification method (lactic acid and ethanol). Amylose reduction is caused by the partial depolymerization of amylose by esters and sunlight irradiation. Depolymerization of amylose causes the formation of a starch network structure that affects the expandability. Lower amylose content leads to better starch expansion

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properties.

Drying time is also a factor that significantly affects the single-step oxidation-esterification process that gives variations in the amylose content of COAEC. The drying process will cause the breaking of bonds on the amylopectin branches that make up the granules into straight chains (amylose), causing the amylose ratio to increase (Syafutri *et al*., 2020). The results of this study are similar to research conducted by Mbougeng *et al*. (2012), who reported that the increase in amylose content in acetylation is due to the interference of acetyl groups with amylose and amylopectin functions.

3.5 Swelling power

The swelling power of COAEC ranged from 2.296±0.1245 g/g to 4.245±0.0552 g/g, as shown in Table 2. COAEC with lactic acid treatment and an esterification time of 3 hrs and drying for 60 mins (COAEC 14) had the lowest swelling power value of 2.296±0.1245 g/g. Meanwhile, starch treated with lactic acid treatment, with an esterification time of 3 hrs and a drying time of 30 mins (COAEC 6), had the highest swelling power value of 4.245±0.0552 g/g.

The esterification time is a factor that affects the swelling power value, according to Li *et al.* (2020) reaction time is an important factor affecting the degree of reaction in chemical reactions. Too long or short a reaction time has an adverse effect on the esterification reaction, and the optimal esterification time is 2.5 hrs. While in this study the esterification time occurred for 3 hrs, resulting in different swelling power values, other process variables played a role in determining the swelling power value. Swelling power is strongly influenced by the network bond between starch molecules (Sumardiono, Jos, Pudjihastuti *et al*., 2022). The interaction of the use of esterification reagents and drying time is a determining factor for the swelling power value. According to Khurshida *et al*. (2021), the low swelling power value can be due to the attachment of hydrophobic groups of acids to starch molecules that do not allow water molecules to bond with starch molecules, resulting in a low swelling power.

3.6 Morphology

The surface morphology of COAEC was observed using SEM (Scanning Electron Micrograph) with 1000 times magnification (Figure 1). The samples used in SEM analysis were native cassava starch and modified cassava starch (COAEC 14), which had crude fiber content (0.6677±0.0424%), moisture content (13.10±0.141%), and ash content (0.0042±0.0002%), which were compliant with the SNI of commercial cassava and wheat starch. This study is in agreement with Sumardiono, Riska, Jos *et al*. (2019), who reported that the esterification process does not change the morphology of starch because it is carried out at gelatinization temperature. Cassava starch after and before modification both have a round structure and have irregular pieces at the ends. The results of SEM morphological analysis in this study are also in agreement with the research conducted by Khurshida *et al*. (2021), who carried out esterification modification of cassava starch using acetate, reporting that cassava starch granules are oval and irregular and no significant differences were observed after modification with acetic acid.

The oxidation process is also one of the influential factors; in the research of Tung *et al*. (2021), it was reported that the jackfruit seed starch granules oxidized using hydrogen peroxide still have the same shape as the original jackfruit seed starch. Ker *et al*. (2017) also reported that SEM micrographs showed that no macroscopic transformation involving granular size and shape occurred during treatment with a pseudo-single-step process on modified cassava starch oxidation using sodium hypochlorite and esterification using acetic anhydride.

3.7 X-ray diffraction

Starch can be classified into types A, B and C. The X -ray diffraction patterns of native cassava starch and COAEC 14 are presented in Figure 2. There are three strongest peaks with diffraction peaks of 17.28°, 18.20°, and 23.43° for native cassava starch, while COAEC 14 is 17.38°, 18.24°, and 23.49°, based on the X-ray diffraction patterns of cassava starch, and COAEC 14 shows a type A pattern (Mei *et al*., 2015). Such results

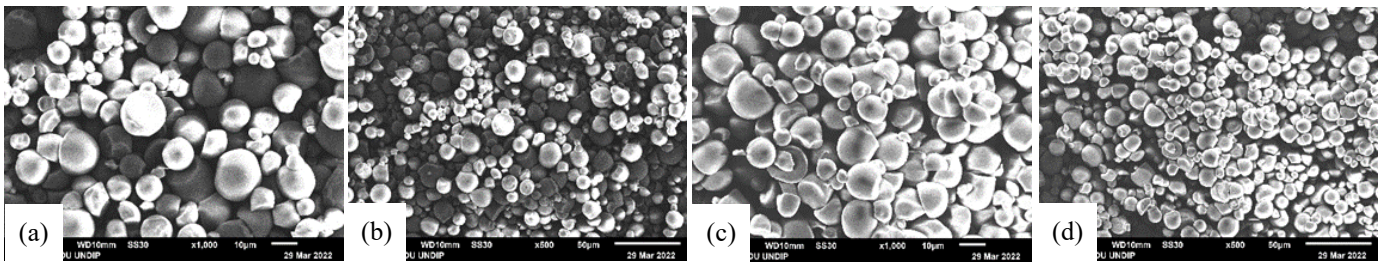

Figure 1. SEM micrograph starch granules of native starch (a) magnification of 1000× (b) magnification of 500× and COAEC 14 (c) magnification of 1000× (d) magnification of 500×.

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indicate that the reaction mainly occurs in the amorphous region of starch and therefore maintains the type A crystallinity of starch (Li *et al*., 2020).

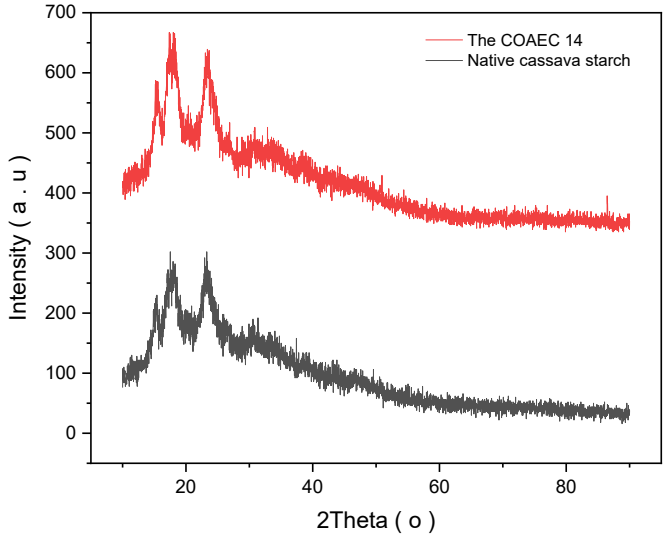

Figure 2. X-ray Diffraction pattern of native cassava starch and COAEC 14.

The single-step oxidation-esterification process affected the starch crystal system; using Profex application software, it was found that the crystal system of COAEC 14 was hexagonal and the native cassava starch had an orthorhombic crystal system. Moreover, the crystal size can be calculated using the Debye-Scherrer equation with the wavelength, intensity, 2θ, and FWHM values generated from the XRD analysis. The Debye-Scherrer equation shows that the resulting crystal size value will be inversely proportional to the FWHM value, while the FWHM value is influenced by the intensity of each crystal field, where the higher the intensity, the smaller the FWHM value. In this study, the calculation of crystal size was carried out on the original cassava starch sample and COAEC 14, and the calculation results obtained an average crystal size of 80.26 nm for the original cassava starch sample and 48.13 nm for the COAEC 14.

3.8 Fourier transform infrared spectroscopy

The FTIR spectra of native starch and COAEC are shown in Figure 3. In both spectra, several peaks of functional groups that are characteristic of starch can be seen, including CO ranges with wave numbers of 1,000–1,260 cm^{-1}, CH bends between 1,290-1,430 cm^{-1}, C=C between 1,630-1,690 cm^{-1}, CH ranges between 2,800-2,950 cm^{-1}, and OH ranges of 3,300-3,400 cm^{-1} (Wardhani *et al.,* 2018; Wardhani *et al*., 2019; Sumardiono, Riska, Jos *et al*., 2019). Figure 3 shows the FTIR analysis for native cassava starch and COAEC 14, and the spectra showed similar profiles.

From the results of the absorption peak, there was a decrease in the OH (hydroxyl) group from 3,452.81 cm^{-1} to 3,271.05 cm^{-1}, The decrease in the OH group indicated that the single-step oxidation-esterification process disrupted the molecular structure of starch with the substitution of hydroxyl groups from starch molecules with functional groups such as carbonyl, which caused changes in the structure of modified starch (Sumardiono, Riska, Jos *et al*., 2019).

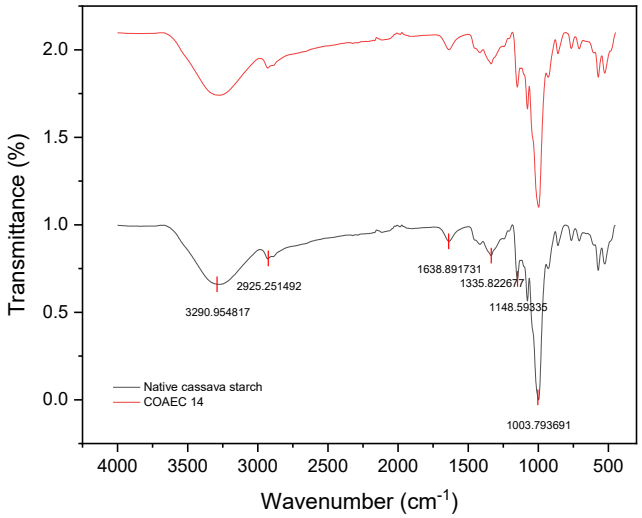

Figure 3. FT-IR spectra of native cassava starch and COAEC 14.

4. Conclusion

From this study, it can be concluded that the single-step oxidation-esterification process can be effectively used to improve the chemical properties of native cassava starch. The concentration of hydrogen peroxide did not have a real or significant effect in this study. The use of lactic acid as a reagent for esterification treatment and esterification times of 3 hrs followed by 60 mins of drying had a significant effect on the moisture content, amylose, crude fiber, and swelling power value of modified starch (COAEC). The single-step oxidation-esterification modification on COAEC 14 provided chemical and functional properties that can be used as a substitute for wheat flour. The results of instrumentation analysis in the form of SEM and XRD showed no change in cassava starch before and after modification. While the results of FTIR analysis showed a decrease in OH groups due to the single-step oxidation-esterification modification process.

Conflict of interest

The authors declare no conflict of interest.

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