Production and physicochemical characterization of modified tapioca

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Abstract. Tapioca can be modified by using chemicals or other additives. One of the opportunities to alter and improve starch hydrophobicity quality is by adding acetic acid and coconut oil. This research activity aims to change cassava starch or tapioca and carry out the resulting product's physicochemical characterization. The production method is carried out using physical mixing techniques combined with drying technology with an oven. Modification process is performed by using acetic acid, coconut oil, and virgin coconut oil. The physicochemical characteristics analyzed include proximate levels, viscosity profile with RVA, crystallinity profile with XRD, and microstructure analyzed using SEM. Based on the results obtained, chemical elements for the modified tapioca proximate composition with the addition of coconut oil have a higher fat content of 4.44% compared to other treatments. The highest peak viscosity of starch added with coconut oil has the highest value of 3982 cP. The treatments resulted in different crystalline and amorphous phases by the XRD results. The microstructure in the SEM analysis results showed agglomeration and did not show any damage to the granular starch.

1. Introduction
Tapioca can be modified by using chemicals or other additives. Tapioca modification technology is diverse depending on the purpose and alternative use to avoid limited natural application of starch for food and non-food products [1]. Starch properties can be modified through physical or chemical treatment or a combination of the two accordingly to increase the added value [2]. Such types of starch have physicochemical properties that differ significantly from the parent starch, thus widening their usefulness in many applications in food manufacturing and other industrial processes [3]. Modification of cassava starch has been carried out, especially for the chemical, physical, enzymatic and genetic [4].

Physical modification of starch can be conducted in several ways. Among them are drying, extruding, spray drying, heating, cooling, cooking and other physical treatments [5]. The starch modification process can also be carried out chemically by cross-linking, substitution or a combination of both methods using chemicals as reaction aids during the processing process.

One of the commercially modified starch products is starch ester [6]. Starch esters have been widely used for food, paper coating, biodegradable plastics or other products [7]. Chemical modification by esterification, which changes the functional group of starch from highly hydrophilic...
hydroxyl groups to more hydrophobic ester groups, can produce more hydrophobic materials, depending on the ester group's nature and the DS [8,9]. Esterification is a modification that can impart hydrophobicity to starch products by substituting a free hydroxyl group. [10] This process has been carried out by a variety of pathways [11]. Esterification of starch using long-chain fatty acids will produce thermoplastic starch, which can be further utilized to fulfill the demand of the pharmaceutical and plastics industries [12].

One of the opportunities to make modifications and improve starch hydrophobic quality is adding acetic acid and coconut oil. Herawati et al. [7] compared the use of acetic acid and succinic acid and compared the use of different methods between conventional methods and shortwave combinations. This research aims to modify cassava starch or tapioca and characterize the physicochemical of product.

2. Materials and Methods
Starch esters' processing is performed by modifying tapioca using coconut oil, virgin coconut oil (VCO) from "Herba Bagoes Indonesia" (No. PIRT. 2073573011864-21) and PA acetic acid. The coconut oil is handmade, started with crushing the coconut, extorting and obtaining thick coconut milk. Water was then added to the grated coconut. The coconut milk was then stirred until it had a smooth texture and cooked until the oil is cleared and no water in the mixture. The VCO composition used consists of 14% total fat content and 80 kcal energy. The composition of fat in the form of saturated fat is 43%. Acetic acid used is glacial acetic acid PA Merck.

The starch used is commercial tapioca or cassava starch. 5 kg of starch is then added with the solution containing 300 ml of additives and 900 ml of water. Tapioca and solution are mixed evenly. Starch blended evenly with additives in the mixing tank unit and repeatedly rotated until it is evenly mixed. The results obtained were then dried at 75 °C for 8 hours and stored.

The modified starch obtained was then analyzed, including the proximate, RVA, XRD, and SEM.

3. Results and Discussion
The modification of the starch is achieved by using three types of additives, include coconut oil extract, commercial VCO and glacial acetic acid.

3.1. Proximate analysis results
The composition of starch esters was compared with controls based on the proximate analysis results as listed in Table 1 below. Proximate analysis results consist of water content, ash, fat, protein, and carbohydrate (by difference). Based on the results of the proximate analysis, the energy produced can be analyzed.

| Sample            | Moisture Content (%) | Ash Content (%) | Fat Content (%) | Protein Content (%) | Carbohydrate Content (%) | Energy (kcal) |
|-------------------|----------------------|----------------|----------------|---------------------|-------------------------|-------------|
| Esterified Starch 1 (ES1) | 7.73               | 0.13           | 4.44           | 0.37                | 87.33                   | 357.44      |
| Esterified Starch 2 (ES2) | 8.55               | 0.15           | 3.72           | 0.34                | 87.24                   | 383.76      |
| Esterified Starch (ES3) | 8.74               | 0.18           | 0.49           | 0.22                | 90.33                   | 366.80      |
| Control           | 8.47               | 0.02           | 0.13           | 1.04                | 90.34                   | 366.69      |
The moisture content of cassava or control tapioca starch and esters ranges from 7.73 to 8.74%. Fat content is quite varied. Esterified Starch 1 and 2 using modified ingredients such as coconut oil and VCO have higher fat content than starch esters 3 and control. The highest fat content, namely ester 1 starch, is 4.44%. The use of additives for the modification of starch esters affects the number of starch esters produced.

3.2. RVA analysis results
Rapid Visco Analyzer (RVA) can determine the starch viscosity profile due to the modification process. Any changes found in the addition of water treatment combined with heat treatment can be observed in the results of pasting properties and gradual viscosity changes. Figure 1 shows the RVA analysis of the control starch compared with the starch ester.

The peak viscosity of starch esters is time-shifted, showing that the starch is more viscous compared to the control starch. The esterified starch 3 experienced a significant decrease in peak viscosity compared to control, the esterified starch 1, and esterified starch 2. This is possibly because the modification process affecting the pastiness ability on esterified starch 3. Table 2 shows the detailed RVA profile analysis.

The highest peak viscosity was obtained by the control starch, which was 4302 cP. The modification process can affect rheology, especially the peak viscosity capacity of the tapioca. The presence of additional materials used may affect the physical characteristics of the resulting ester starch. Likewise, the highest capacity of cold paste was also found in the control starch. This shows that the control starch’s peak viscosity capacity and cold paste viscosity higher than that of the modified starch ester. The addition of ester molecules into starch molecules caused the bonds between starches molecules to weaken, and the value of swelling power increased. The higher ester concentration will replace more hydroxyl groups in starch structure [13].
Table 2. Viscosity profiles of esterified starch (ES1, ES2, ES3) and control.

| Parameter Analysis                                | Esterified Starch 1 | Esterified Starch 2 | Esterified Starch 3 | Control |
|---------------------------------------------------|---------------------|---------------------|---------------------|---------|
| PT: temperature (°C) at 20cp                      | 73.9                | 73.6                | 73.3                | 73.1    |
| Pt: time (s) at 20cP                              | 178                 | 177                 | 176                 | 174     |
| Peak viscosity (cP) PV                            | 3982                | 3929                | 2716                | 4302    |
| Temp. at peak viscosity (°C) PVT                  | 88.3                | 87.9                | 87.2                | 82.7    |
| time at peak viscosity (s) PVT                    | 250                 | 248                 | 244                 | 222     |
| Hot paste peak viscosity (cP) HPV                  | 1634                | 1515                | 715                 | 1538    |
| Temp HPV (°C) HPVT                                | 88.1                | 89.3                | 81.7                | 93.1    |
| Cold paste viscosity (cP) CPV                     | 2523                | 2441                | 1210                | 2905    |
| Cooking ability (s) CA                            | 72                  | 72                  | 68                  | 48      |
| Viscosity beginning plateau (cP) VBP              | 3250                | 3100                | 2071                | 2774    |
| Viscosity end plateau (cP) VEP                    | 1717                | 1579                | 799                 | 1569    |
| breakdown (cP) BD                                 | 2348                | 2414                | 2001                | 2765    |
| Setback (cP) SB                                   | -1459               | -1488               | -1506               | -1397   |
| Consistency(cP) CS                                | 890                 | 926                 | 495                 | 1368    |

3.3. XRD analysis results

The XRD results show starch's physical characteristics. Based on the results, it can be observed that there was a change in the angles of 2 theta, which shows the profile of starch or modification of the resulting starch. Figure 2 shows the 2-theta profile of the control and the modified starch ester.

![XRD profile of esterified starch (ES1, ES2, ES3) and control](image)

Figure 2. XRD profile of esterified starch (ES1, ES2, ES3) and control.

Starch can be classified into three types (A, B and C) based on their X-ray diffraction patterns. Type "A" starch presented more substantial diffraction peaks at around 15°, 17°, 18° and 23°, which were mainly of cereal starches; type "B" starch usually displays the peaks at around 5.6°, 17°, 22° and 24°; the mixture of "A" and "B" patterns is type "C" starch [14,15].
The XRD analysis shows the amorphous and crystalline phase composition of the control starch compared to the starch ester. The XRD analysis on the amorphous and crystalline phase found that the control starch compositions and ester starch are displayed in Table 3.

Table 3. Composition of amylose and amyllopectin levels from esterified starch and control.

| Sample           | Crystalline (%) | Amorphous (%) |
|------------------|-----------------|---------------|
| Esterified Starch 1 | 32.1            | 67.9          |
| Esterified Starch 2 | 31.8            | 68.2          |
| Esterified Starch 3 | 29.4            | 70.6          |
| Control           | 37.9            | 62.1          |

Amorphous phase composition of the tapioca starch increases with the modification. The highest crystalline phase was in control at 37.9%. This is possibly because the change affects the increase in the formation of amorphous phases of the modified starch. In the control starch, the crystalline structure is more dominant because there is no starch modification process.

3.4. SEM analysis results

Figure 3 shows that the tapioca modification techniques produces microstructures. Some starch granules clustered with one another, both in the ester and control starch. Starch granules are intact, not gelatinized and do not break apart or join one another.

![Figure 3. SEM of esterified starch analysis results (1,2,3) and control (magnification of 100x and 500x).](image)

Figure 3 shows that the modification process does not damage the starch granules. Tapioca granules are semi-round with one end conical with a size of 5-35 μm [16]. This shows that chemical modification that does not involve the process of increasing temperature above the gelatinization temperature can maintain the shape and size of tapioca granules. Sumardiono et al. [13] stated that based on the Surface morphology of cassava starch that was observed using Scanning Electron Micrograph (SEM), the cassava starch before and after modification has unchanged shape and size since the modifications performed under the gelatinization temperature. Both structures are round and have irregular pieces at the ends. The size of both types of particles varies [13].
4. Conclusions
The Esterified Starch 1 with coconut oil addition and Esterified Starch 2 with VCO addition have higher fat content than control. The peak viscosity and cold paste viscosity of starch esters were smaller compared to control. The esterification process increases the amorphous phase of the starch ester. The starch ester modification process did not damage the starch granules.

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