

Gelatinization properties of white maize starch from three varieties of corn subject to oxidized and acetylated-oxidized modification

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Abstract: Maize-starch in conventional form is limited in use because of its physical properties, e.g. highly retrogradation properties, syneresis pasta, and low stability of pasta at high temperature and low pH. This research aims to modify three variety of white cornstarch (Local *Canggal*, *Srikandi*, *Pulut*) through oxidation and acetylation-oxidation, in order to improve its gelatinization properties. Modification of oxidation process is carried out using sodium hypochlorite. Acetylation-oxidation is a process of oxidation followed by acetylation using acetic anhydride at slightly alkaline conditions. Furthermore, conventional-maize-starch is used to compare the results of these treatments. The results show that *Pulut* white cornstarch has lower gelatinization temperature than *Srikandi* and local *Canggal* varieties. Oxidized and acetylated-oxidized starches have: (1) gelatinization temperature, (2) peak viscosity and (3) retrogradation lower than conventional-maize-starch. Low retrogradation is caused by stabilizer effect that retard syneresis (freeze thaw stability). Oxidized and acetylated-oxidized of maize-starches produce gel that more hardness than conventional-maize-starch, even in waxy and non-waxy starches.

Keywords: white maize-starch, oxidation, acetylation-oxidation, gelatinization

Introduction

Starch has many diverse applications in food production. However, physical properties of native starches are limiting their application. Typically, chemical modification is prepared before starch phase to extend the range of specific physical properties available for different uses. Applications of starch in food industries are primarily governing (limited) by functional properties of this starch. Chemically-modified-starches have markedly altered its functional properties compared to their parent starches (Adebowale and Lawal 2003). Oxidized starch is used in a number of products in the food industry, especially for products that require low viscosity and neutral taste.

Oxidation as a form of chemical modification, involve the introduction of carboxyl and carbonyl functional groups, by means of sub-sequent depolymerisation of the starch. Such starches have established to be whiter in color, and have restricted retrogradation (Kuakpetoon and Wang, 2001).

Acetylation of starches is an important substitution method. This method has been applied to starches that impart the thickening needed in food application.

Acetylated starch is a granular starch ester with the CH_3CO group introduced at low temperature. Acetylated starch has improved properties over its native form and has been used for its stability and resistance to retrogradation (Wurzburg, 1989). Acetylated starches are used in fruit pies, gravies, salad dressings and filled cakes. Acetylated starches are produced with acetic anhydride in the presence of an alkaline agent, such as sodium hydroxide. The acetylation of starches depends upon certain factors, such as starch source, reactant concentration, reaction time and pH.

An acetylated-oxidized starch is starch with double modification. In this case, oxidized starch is also subject of acetylation by acetate-anhydride in less alkali condition (Apeldoorn et al. 2000). Oxidized starches that experience acetylating, tend to have better properties like gummy and purified jelly. Those properties have great advantages in food industry (for example in confectionery). Principally, modified starch properties are influenced by ratio of amylose-amylopectin.

Wang and Wang (2002) announce that oxidation of non-waxy cornstarch will produce carboxyl group higher than oxidation of waxy-cornstarch. The same

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affect will influence carbonyl group. Both amylose and amylopectin will oxidized and degraded during oxidation, but amylose more sensitive to oxidation. Both of carboxyl and carbonyl group in amylose chain are the main factor to avoid retrogradation.

This study presents how oxidation and acetylation-oxidation affects the functional properties of white cornstarches. The sample used in this work is isolated from three local varieties of white corns.

Materials and Methods

In this research, we use three variety of maize-starch (*Pulut*, Local *Canggal*, *Srikandi*). *Pulut* variety is derived from Gorontalo (*Celebes*, *Indonesia*). Varieties of Local *Canggal* and *Srikandi* are taken from Temanggung (Central Java, *Indonesia*). Corn varieties Local *Canggal* and *Srikandi* are non-waxy maize, while *Pulut* is waxy maize.

First, isolated cornstarch is prepared by method of Yang et al. (2005). Second, oxidation is conducted using method proposed by Parovouri et al. (1995). In this case we use 100 g of maize-starch. This sample is dissolved to 200g of distilled water. Subsequently the sample was oxidized using 10 g of NaOCl at 30°C and pH 9.5 (pH settings performed using 0.5M NaOH). Oxidation process carried out for 30 minutes. Then the sample was neutralized using H₂SO₄ up to pH 7 and wait for 10 minutes. After that, the sample centrifuged to separate the starch and liquid using centrifuge at a speed of 2000 rpm for 30 minutes. Finally, the starch is washed by distilled water (repeated 3 times), then it is dried by cabinet dryer (30 ± 2°C) during 48 hours.

Three, acetylation-oxidation is prepared by combining two methods: (1) method proposed by Chen (2003) and (2) method proposed by Parovouri et al. (1995). In this treatment: 100 g of maize-starch is diluted into 200 ml of distilled water, then is oxidized using 10 g of NaOCl at 30°C, and pH 9.5 using NaOH 0.5 M for 30 minutes. After 10 minutes then the sample is neutralized using H₂SO₄ up to pH 7. After that, it is washed by distilled water (1:2). Furthermore, acetylating process is prepared by addition of acetate anhydride 10.1 g at 30°C, and pH = 8 (adjusted with NaOH 0.5 M) during 60 minutes. Then, it is adjusted to pH 4.5 using HCl 0.5 N and it is waited for 10 minutes. Finally, it is centrifuged at 2000 rpm for 3 minutes. Four, starch is washed using distilled water (repeated 4 times), and then it is dried using cabinet dryer at 50°C (± 2°C) for 48 hour.

Gelatinization properties is analyzed using Brabender amilograph to find out gelatinization

temperature, peak viscosity, hot viscosity, cold viscosity, setback viscosity and breakdown viscosity (AACC 2000).

Results and Discussion

Based on research that has been done, we get the result of research as can be seen in Figure 1 to 6.

Gelatinization temperature

The presence of excessive water will increase the temperature of the suspended starch granules compared gelatinization temperature. Starch granules lose birefringence properties and crystalline as a result of concurrent swelling. This change is irreversible and called "gelatinization". Gelatinization is the swelling process of granule, followed by disruption of granule structures. In this case, the loss of crystalline order can be observed in the form of disappearance of the X-ray diffraction.

Some components of starch (mainly amylose) leaching from the granule before granule rupture. This occurs when there is an increase in temperature. Viscosity began to increase when the achievement of gelatinization temperature. This phenomenon (increased viscosity) is caused by irreversible swelling of starch in the water. These phenomena start when molecular energy of water is stronger than starch energy in the granule.

Starting temperature of white maize starch gelatinization ranged from 62-74°C (Fig. 1). *Pulut* varieties have a gelatinization temperature of 71°C, lower than the two other varieties. The reason is because *Pulut* variety has lower amylose content than two others, so the starch granules absorb more water, since a result of the development of starch granules at low temperatures. Sodhi and Singh (2004) observed that waxy starches reach gelatinization at lower temperature.

This is in contrast with the results of Wang and Wang (2002) replacing the carboxyl group and carbonyl condition leads to hydration and development of starch gelatinization temperature increased but the enthalpy remains. In addition, the presence of fat and protein affect the development of granule, which in turn will affect the gelatinization temperature difference.

Modified starches have lower gelatinization temperature than conventional-starch. Oxidized-acetylated starch has lower gelatinization temperature than oxidized-starch. Reduction of pasting temperatures, following oxidation and acetylating is a consequence of structural weakening and disintegration during the modification process.

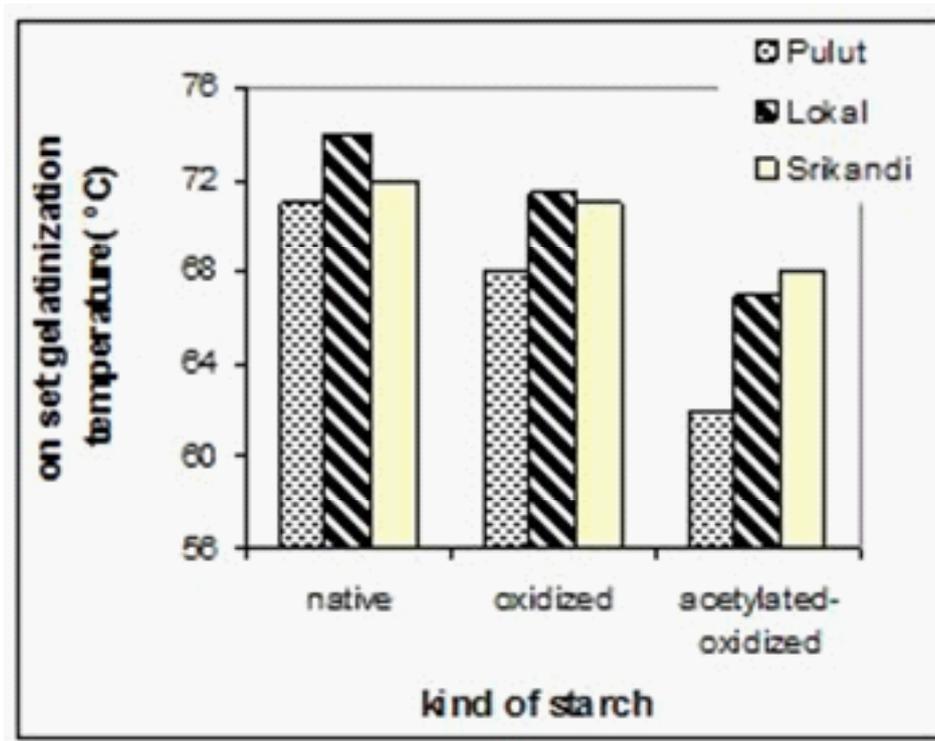


Fig 1. Effect of corn variety and modification of starch to gelatinization temperature of white cornstarch

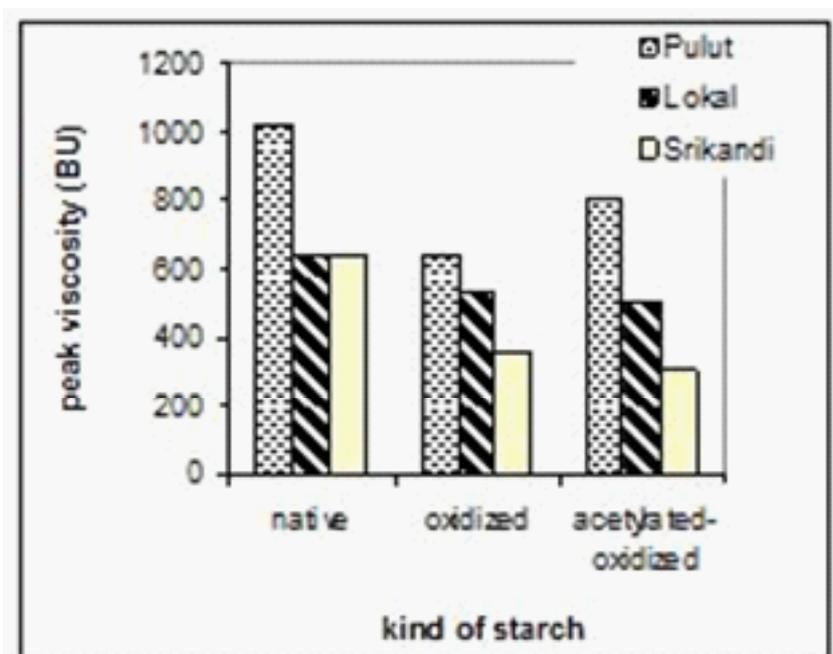


Fig 2. Effect of variety and starch modification to peak viscosity of white cornstarch

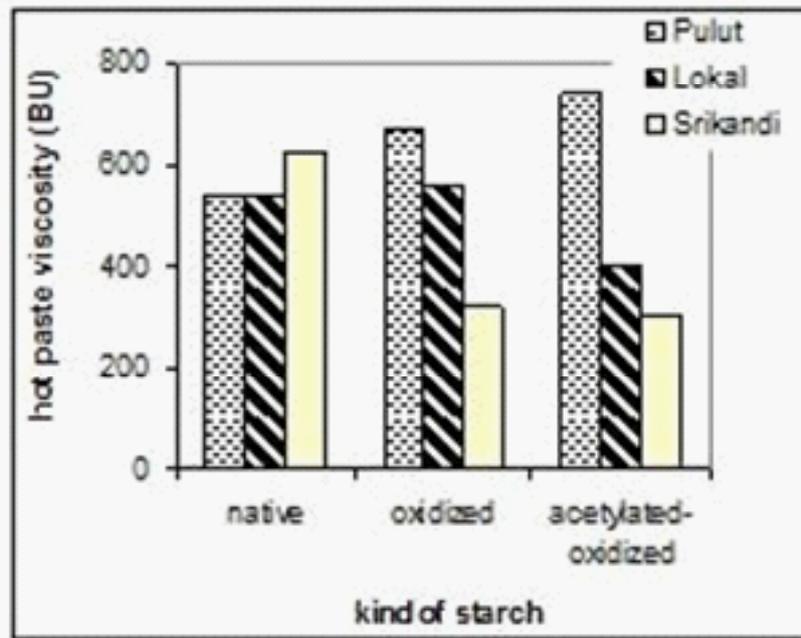


Fig. 3. Effect of variety and starch modification to hot paste viscosity of white cornstarch

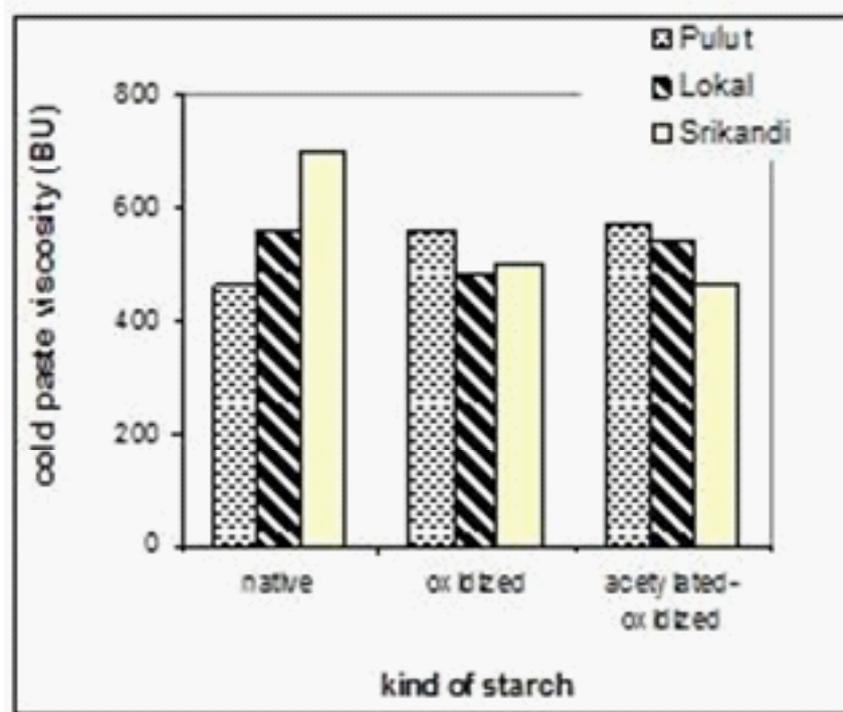


Fig. 4. Effect of variety and starch modification to cold paste viscosity of white cornstarch

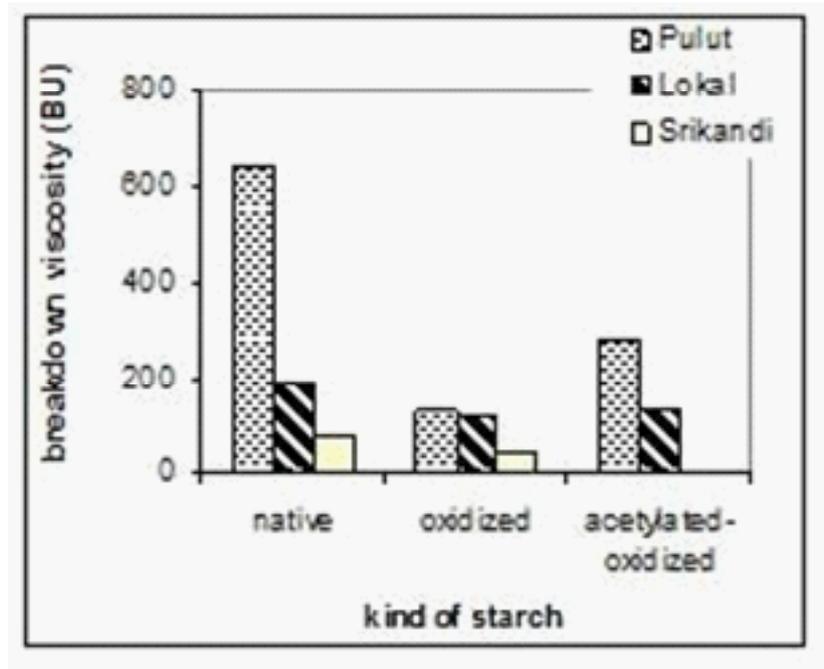


Fig 5. Effect of variety and starch modification to breakdown viscosity of white cornstarch

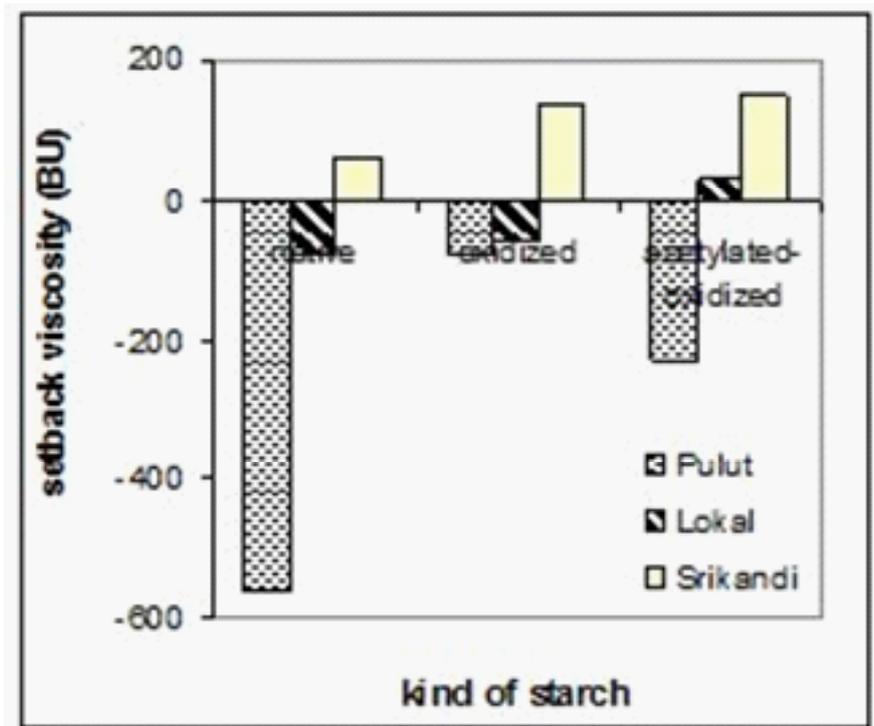


Fig. 6. Effect of variety and starch modification to setback viscosity of white cornstarch

Heating the starch granule in excess water leads to further granule swelling, additional leaching of soluble components and total disruption of granules.

Peak viscosity

Viscosity of starch, as a food component, is a crucial factor to be considered in the food system application. Peak viscosity is the peak viscosity of dough during heating process. Viscosity of dough can be used as an indicator of cooking performance. High viscosity of dough indicates that the dough is cookable, contrary to low viscosity of dough.

Peak viscosity indicates the dough strength performed by gelatinization during food processing (food application). As the suspended starch is heated, the granules (which are developed since temperature gelatinization occurs) will continue to expand. During gelatinization process, amylose tends to leach from starch granules. Furthermore, amylose and amylopectin are more hydrated. Consequently, the suspended-starch becomes clearer and the viscosity increased until reach the peak. Finally, granules have a maximum hydration at peak viscosity.

Experiment show that *Pulut* (waxy starch) has peak viscosity higher than non-waxy starch (Local *Cangal* and *Srikandi*) (Fig 2).

This result is similar to Collado and Corke (1997). They stated that peak viscosity have negative correlation compared to amylose content.

Peak viscosity of white cornstarch varied between 310 BU to 1020 BU. Modified starches have peak viscosity lower than native starches (Fig 2). The decrease in viscosity after oxidation is caused by partial cleavage of the glycoside linkages upon oxidation. This will propagate decrease in molecular weight of starch molecules.

Result shows that peak viscosity of modified starch tend to decrease. This decrease is caused by *shear*. Starch granules are tends to degrade as a respon to shear, which in turn decrease the peak viscosity. This phenomenon is confirmed by Kuakpetoon and Wang (2001). They stated that these degraded granules can not maintain its integrity and reduce the network strength. Degraded networks are not resistant to shear and therefore produce a lower viscosity. Decrease in peak viscosity after oxidation and acetylation has been reported by Lawal (2004). Jyothi et al. (2005), also declare that degradation of starch granule with oxidation use sodium hypochlorite, responsible to decrease viscosity.

Acetylating can influence the interactions between the starch chains through three possible mechanisms; 1) by simple steric hindrance preventing close association of chains to allow formation of hydrogen bonds, 2) by altering the hydrophilic of the starch

and thus affecting bonding with water molecules, or 3) by participation of the acetyl groups in improved hydrogen bonding with other starch chains. The observed effects of acetylating are consistent with an overall reduction in bonding between starch chains and a consequent increase in the ease of hydration of the starch granule. Gelatinization can thus commence at a lower temperature and greater swelling of the granule will lead to an increased peak viscosity.

Agitation during modification process affects the viscosity because it inhibits the development of starch granules. Mormann and Higari (2004) stated that mechanical stirring reduce viscosity of the hot pasta.

Starches that usually having high swelling performance can easily be broken by to agitation and therefore decreases the viscosity. Agitation also affects the interaction of amylose and amylopectin. Amylose and amylopectin are difficult to interact because the existence of energy that breaks the hydrogen-bonding. This resulted in starch pastes flow more easily so the resulting starch paste viscosity is lower.

Hot viscosity

Hot paste viscosity was measuring when heating of starch paste reach 95°C, then hold for 15 minutes. Hot viscosity is an index reflecting the ease of cooking and weaknesses in the granule swells. Hot paste viscosity would not be expecting to show much change as starch-starch interactions are already reducing by thermal and shear force. Hot paste viscosity was influencing by the extent of amylose leaching, amylose-lipid complex formation, granule swelling, and competition between leached amylose and remaining granules. During gelatinization, amylose was leaching from granule starch that is swelling in water at 57-100°C.

Pulut cornstarch has high amylopectin content. The viscosity tends to increase when maintained at a temperature of 95°C for 15 minutes. Specifically, this phenomenon is appeared on *putul* starch modified by oxidation (Fig. 3).

Srikandi and Local *Cangal* modified by oxidation are not different from natural starch.

Cold viscosity

Cold viscosity is the viscosity which is maintained at 50°C for 15 minutes. Viscosity of starch paste will increase during cooling. During cooling, reassociation of amylose molecules develop new gel structure and therefore increase viscosity. Cold paste viscosity is influenced by the relationship between chain amylose to form starch gel, in this

case process of acetylation will reduce the viscosity and gel strength. Singh et al. (2004) also states that the tendency of amylose to retrogradation during cooling will affect the cold viscosity of pasta. This will increase the viscosity of paste.

Modified starches, have been subject to conformational re-ordering and re-arranging and are less prone to such re-association. Introduction of functional groups to replace the hydroxyl groups limits formation of such binding forces. This accounts for reduction in cold paste viscosity of oxidized and acetylated-oxidized white cornstarch compared with the unmodified starch (Fig 4).

Carboxyl groups in starch molecule will interfere with pasta stability of oxidized starches. If there are more carboxyl groups than replaced hydroxyl in amylose, it will agitate amylose to associate and retrograde.

In acetylated-oxidized starch, modification by acetylation cannot prevent the increase of viscosity at cooling stage. Acetylation only restrains change of viscosity sharply, which make more stabilized of starch paste than native.

Paste Stability

During storage, starch pastes may become cloudy and eventually deposit an insoluble white precipitate. This is caused by the recrystallization of starch molecules; initially the amylose forms double helical chain segments followed by helix-helix aggregation. This phenomenon is termed "retrogradation". Retrogradation is the term that describes the changes that occur in gelatinized starch from an initially amorphous or disordered state to a more ordered or crystalline state. It is the tendency of a starch gel to thicken and form stiff gels.

The development of turbidity, opacity and syneresis of water from the paste occurs during retrogradation and it depends on the source of the starch, starch concentration, storage time and temperature (Adebowale and Lawal, 2003). Amylose is a major cause retrogradation in a short time because the solubility of amylose molecules tend to occur in parallel form.

Phenomenon of retrogradation can be observed from breakdown value. The breakdown value of a starch paste, defined as the difference between the peak viscosity and the viscosity after holding for 15 min at 95°C.

Oxidation and acetylation-oxidation tends to decrease the degree of retrogradation. This observed on all varieties of starch, which can be seen from the values of breakdown viscosity (BU) (Figure 5).

Breakdown viscosity of modified starch is lower

than native starch. Furthermore, Srikandi cornstarch modified by acetylation-oxidation have no breakdown value, this indicate that Srikandi starch has good stability. Lawal (2004) state that oxidation and acetylation will reduces breakdown viscosity value. In addition, Jyothi et al. (2005) states that sodium hypochlorite as an oxidizing compound will reduce the viscosity of the peak, so the breakdown was also decreased.

Setback viscosity is the increase in viscosity when the starch paste is cooled. The augmentation of viscosity during cooling determines the re-associates starch granules. This indicates the tendency of starch products to be retrograded. Setback viscosity indicate retrogradation index of starch paste.

Modification of starch by oxidation and acetylation-oxidation reduce viscosity and setback viscosity, except in varieties of Srikandi (Fig 6). This conformed to Lawal (2004) results. Lawal (2004) stated that the range of setback viscosity decreased after oxidation and acetylation. Oxidized starches prepared using 1000 ppm of active chlorine at pH 10.5 produces a stable viscosity.

Chen (2003) state that retrogradation depends on the origin of starch, starch concentration, storage temperature, pH, temperature procedure and the composition of the starch paste. Retrogradation is generally stimulated by a high starch concentration, low storage temperature and pH values between 5 and 7. The salts of monovalen anions and cations can retard retrogradation.

Conclusion

Based on the results, we have several conclusions. Firstly, Oxidation and acetylating-oxidation processes propagate different characteristics in waxy and non-waxy of white cornstarches. In this case, *Pulut* variety has lower LGC and gelatinization temperature than *Srikandi* and Local variety. Secondly, Oxidized and acetylated-oxidized starches have lower: gelatinization temperature, peak viscosity and retrogradation than native starch because of stabilizer effect. This influence is beneficial because it can inhibit syneresis (freeze thaw stability).

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