Rheological properties of native and modified corn starches in the presence of hydrocolloids

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Abstract

Starch and hydrocolloids were often used together in food industry to modify the rheological properties with the aim to enhance the starch tolerance to processing conditions. As such, the rheological properties of xanthan gum (XG), carrageenan, high (HMP) and low methoxyl pectin (LMP), with native corn starch (NCS) and modified corn starch (MCS) at different temperature were evaluated in this study. The flow behavior index (n) of corn starch-hydrocolloid mixtures were observed in the range from 0.160 to 0.604 where indicated the shear thinning behavior. The addition of hydrocolloids increased the apparent viscosity of the starch system. NCS mixtures showed consistency index (K) and apparent viscosities (n_a,100) decreased with increase in the temperature. The addition of XG and carrageenan increased the storage (G’) and loss (G”) moduli. Among the hydrocolloids, the XG addition to the NCS exhibited superior viscoelastic properties as evidenced by the highest G’ and lowest tan δ values. XG was observed capable to increase while pectin reduced the solid-like starch system. This result provides pragmatic data for food engineer in process design and food product development by minimizing the cost of trial and error.

Keywords

Rheological
Hydrocolloids
Corn starch
Xanthan gum
Carrageenan
Pectin

Introduction

Due to the massive global production volume of corn starch (Sheldrake, 2010; Kumar and Prabhasankar, 2014) and its characteristics of thickening and gelling (Eliasson and Gudmundsson, 2006) it has been widely used as food additive in the food industries. Modified corn starches (MCS) were used as substitutes for noodle (Yousif et al., 2012), gluten-free dough and bread (Witczak et al., 2012), and even in wheat-based food processing with the aim to reduce the glycemic index (Kumar and Prabhasankar, 2014). A more specific study was found where the corn starch modified by dry-heat in the presence of octenyl succinic acid has been attempted to apply in fat-reduced muffin (Chung et al., 2010). Recently, the pursuance of green materials with intention to reduce the environment impact, has further intensified studies of corn starch to be used as ingredient in production of biodegradable nanocomposite films for food packaging (Heydari et al., 2013; Xie et al., 2013; Katerinopoulou et al., 2014).

The wide varieties of applications of corn starches have provoked the emergence of physical and chemical modifications to alter the functional properties of the native corn starch (NCS) to overcome its characteristics of granule swelling, breakdown, and retrogradation during processing (Ashogbon and Akintayo, 2013). The physical modification includes the mechanical attrition to change the physical size of starch (Ashogbon and Akintayo, 2013), such as hydrothermal process (Malumba et al., 2010; Bahrani et al., 2013), tribomechanical micronization and activation (Herceg et al., 2010), and ultrasound (Jambrak et al., 2010). The chemical modification involves of starch structural changes by inducing chemical to hydrolyze the starch into smaller molecules (Sweedmn et al., 2013), such as the enzymatic (Ribotta et al., 2012; Yussof et al., 2013), alkali (Dokić et al., 2010), and acid (Lin et al., 2012).

Despite these two modification techniques, the incorporation of hydrocolloids into starches is still remained popular and this has been highlighted in a review by BeMiller (2011). Hydrocolloids are used in food formulation as thickeners and gelling agents due to their ability to alter the rheological properties of the solvent in which they are dissolved. Therefore, corn starch-hydrocolloid combinations have been used in processed foods not only to improve the texture and
their tolerance when exposed to heat, shear and acidic processing conditions (BeMiller, 2011) but to provide the stability in cold storage and freeze-thaw such as white sauces (Arocas et al., 2009), Chinese shrimp dumplings wrappers (Seetapan et al., 2013), and to control water mobility during processing (BeMiller, 2011). However, there are limited published reports on rheological behavior of starch-hydrocolloids mixtures.

The functional roles of food hydrocolloids are thickening and gelling which involved entanglement of conformationally disordered chains and inter-chain association (Saha and Bhattacharya, 2010). Different hydrocolloids incorporated into starches would have different effects on rheological properties for a starch-hydrocolloid system because they are diverse in terms of molecular chain structure, ionic charge, and degree of polymerization. This has been evidenced in a previous work by Heyman et al. (2014) where they discovered that xanthan gum (XG) has the ability to inhibit granule disruption of native waxy corn starch by preserving their structure, while guar gum did not show this property.

Native and modified corn starches are widely used as food ingredients in product formulation, and starch and hydrocolloids was used together to enhance the starch tolerance to processing conditions. Hydrocolloids will give different effect on starch gels due to the difference in molecular characteristics. Therefore, it is important to understand the rheological parameters of starches with hydrocolloid, which are very critical to the functionalities of food products. For this reason, the present study is conducted to evaluate the steady shear and dynamic flow of NCS and MCS incorporated with hydrocolloids of XG, carrageenan, high (HMP) and low methoxyl pectin (LMP). This study will help in minimizing the trial work error of food product developer during the food product formulation for controlling the texture of the products and also help the food engineering during the process design calculations.

Materials and Methods

Sample mixtures preparation

NCS, MCS, carrageenan, XG, HMP and LMP were purchased from Cargill (Selangor, Malaysia). A total of 14 samples were prepared to evaluate the rheological properties of corn starches, corn starch-hydrocolloid mixtures, and hydrocolloids. NCS and MCS (5% w/w) without addition of hydrocolloids were dispersed in distilled water as control. The corn starch-hydrocolloid mixtures were prepared by mixing corn starch (4.5% w/w) with the same weight basis (0.5% w/w) of hydrocolloids (XG, carrageenan, HMP and LMP) to obtain a final weight of 5% w/w before dispersed in distilled water. Sample pastes of only hydrocolloids (0.5% w/w) dispersed with distilled water were also prepared and evaluated. The mixture was mixed in a beaker using a magnetic stirrer with moderate stirring for 1 hour at room temperature (25 ± 2°C) to completely dissolve the mixtures, and heated to 95°C in a water bath for 30 minutes until the mixtures gelatinized (Choi and Yoo, 2009; Kim and Yoo, 2011). At the end of the heating period, the hot sample mixture was immediately transferred to the rheometer plate for rheological properties measurement at temperature of 25°C, 40°C, 50°C, and 60°C.

Rheological properties determination

The steady and dynamic shear rheological data of starch-hydrocolloid mixtures were determined using a stress rheometer (AR-2, TA Instruments, Crawley, England) attached with a parallel plate system (3 cm diameter) at 500 μm gap. The sample was transferred to the rheometer plate at the defined temperature and the excess material was wiped off with a spatula.

Steady flow measurement

Steady shear measurement (shear stress and shear rate) data were obtained over the shear rate range of 1.0–1000 s⁻¹ (Choi and Yoo, 2009) at temperatures of 25°C, 40°C, 50°C, and 60°C. These data were fitted into power law model to describe the rheological properties of samples under steady shear for non-Newtonian flow using Equation 1.

\[
\tau = K \gamma^n
\]

(1)

Where \(\tau\) is the shear stress (Pa), \(\gamma\) is the shear rate (s⁻¹), \(K\) is the consistency index (Pa sⁿ), and \(n\) is the flow behaviour index (dimensionless) (Achayuthakan and Suphantharika, 2008; Choi and Yoo, 2009). The effects of hydrocolloids and temperatures on apparent viscosity (\(\eta_{app}\)) at 100 s⁻¹ were evaluated by calculated from the values of \(K\) and \(n\). The rheological measurements in steady shear were performed in triplicates.

Viscoelastic properties

Dynamic shear data were obtained from frequency sweeps test in range of 0.63–63 rad/s at 1% strain which in the linear viscoelastic region. Dynamic controlled stress rheometer was used to obtain the experimental data and to calculate the storage modulus (\(G'\)), loss modulus (\(G''\)), and loss factor (tan δ = \(G''/G'\)). The rheological measurements
in dynamic shear were performed in triplicates at temperature of 25°C. The frequency dependence of both $G'$ and $G''$ can be described by the following power law relationship (Choi and Yoo, 2009; Kim and Yoo, 2006; Wang et al., 2009).

$$G' = K'\omega^{n'}$$  \hspace{1cm} (2)

$$G'' = K''\omega^{n''}$$  \hspace{1cm} (3)

Where $K'$ and $K''$ are constant and $n'$ and $n''$ may be referred to as the frequency exponents, and $\omega$ is the angular frequency.

Results and Discussion

Steady flow properties

It is important to evaluate the effect of temperature on starch-hydrocolloid mixture because heating is a process that cannot be avoided in food industry. Hydrocolloids are added into starches to produce food products which have consistency in texture. The flow curves of NCS and NCS with hydrocolloids additions (Figure 1) were influenced more by the temperature changes compared to the MCS (Figure 2). This graph indicated that MCS is more heat stable compared to NCS. However, with the additions of 0.5% (w/w) of XG and carrageenan into NCS, both hydrocolloids showed their capability in narrowing down the temperature effect (Figure 1). This implied that the stability of NCS could be improved by incorporating with XG and carrageenan. The rheogram of NCS and MCS with addition of XG and carrageenan were observed having shear thinning behavior. The flow curves of MCS at different temperature and addition of hydrocolloids are illustrated in Figure 2. All the curves showed shear thinning behaviors, except for the LMP addition where it showed a tendency towards Newtonian. This might due to the low molecular weight of the LMP and interaction between polymer chain when pectin are dissolved or dispersed (Yaseen et al., 2005).

Comparing among the hydrocolloids at 25°C, XG has been observed having the lowest $n$ value of 0.209 which showed it has highly shear-thinning behavior, while carrageenan, HMP and LMP showed lower shear-thinning behavior with high $n$ values of 0.806, 0.920, and 0.848, respectively (Table 1). The $n$ value of XG found in this study was almost similar with the previous study done by Sikora et al. (2008) where they reported value of 0.194. Although both XG and carrageenan addition into both NCS and MCS decreased the $n$ values, the XG has been observed to have more marked effect due to the unique rigid, rod-like conformation and high molecular weight of xanthan gum (Urlacher and Noble, 1997). This might explain by XG which having the lowest $n$ value among the hydrocolloids attributed to this pronounced effect. The incorporation of XG into starches resulted decreased of $n$ value has been evidenced in previous works. Achayuthakan and Suphantharika (2008) observed that the $n$ values of waxy corn starch mixtures decreased to 0.40, 0.36, and 0.37 as the percent of XG additions increased from 0.35%, 0.70%, and 1.00%, respectively. Besides corn starch, XG was evidenced its capability in decreasing the $n$
values from 1.011 to 0.299 when mixed with potato starch from 0% to 90% (Sikora et al., 2008).

The addition of XG has been observed more pronounced in decreasing the $n$ value when incorporated into NCS than MCS of 65% and 38%, respectively. However, Heyman et al. (2013) have a contradict observation where they reported that NCS with addition of 0.2% unheated XG decreased the $n$ value by 34% while MCS decreased by 39%. This difference in observation was because the starches and XG in Heyman et al. (2013) were prepared by dispersing in salt solution (0.1M NaCl), instead of distilled water in this study. This is because, the presence of salts helps to maintain the rigid ordered conformation of XG, which in turn causes a relative insensitivity of the viscosity to additional salt and elevated temperature (Wüstenberg, 2014).

The addition of HMP and LMP into the NCS and MCS increased the $n$ values, indicating pectin could decrease the shear thinning behavior of the mixtures. The pectin solutions are Newtonian but after diluted at certain moderate concentration, they exhibit the non-Newtonian, pseudoplastic behavior characteristics. From these results, it was found that the rheological behaviors of corn starch–pectin mixtures were apparently dependent on the concentration of pectin.

The consistency index ($K$) obtained from the power law model increased with the addition of hydrocolloids (Table 1). There were marked increased of $K$ values in XG addition into both NCS and MCS. Similar results were reported that XG play a determinant role on the increase of $K$ due to its effect of thickening (Wang et al., 2009). Since the viscosity of starch-hydrocolloid systems are influenced predominantly from the physical entanglement of conformational disordered chains of individual hydrocolloid (Saha and Bhattacharya, 2010), therefore, the incorporation of different types of hydrocolloid into starches result in varying viscosity (Table 1). All the hydrocolloids investigated in this study were observed increased the viscosity when incorporated into NCS and MCS.

Due to the difference of starch and hydrocolloid nature, their influences on viscosity were varied in the order of NCS: HMP>XG>carrageenan>LMP, while MCS: carrageenan>XG>HMP>LMP. Among the hydrocolloids, XG incorporation into both NCS and MCS were observed to have minimal influence on viscosity in increasing temperature up to 60°C. The viscosity of NCS/XG mixture was decreased.

Figure 2. Effects of hydrocolloids addition ((□) xanthan gum, (○) carrageenan, (×) high methoxyl pectin, (+) low methoxyl pectin) on MCS flow curves, at different temperature levels. (-) indicates pure MCS without hydrocolloid.
by 3.1%, while the viscosity of MCS/XG mixture increased by 6.55% when exposed to temperature 25°C to 60°C. This is good evidence that XG can be used to stabilize NCS in competence to MCS.

### Dynamic shear properties

Figure 3 shows the variation of $G'$, $G''$, and tan δ as a function of angular frequency for selected mixtures at 25°C and strain amplitude of 1.0%. The magnitudes of storage ($G'$) and loss ($G''$) moduli increased with the increase in angular frequency, $\omega$ (rad/s). Figure 3 demonstrated that $G'$ is much greater than $G''$ at all values of $\omega$, which is indicated all the pastes in this study were a slightly frequency dependency. The addition of XG into both NCS and MCS increased the $G'$ and $G''$, and this suggest that XG dominate the elastic properties of the mixtures. The same was observed for wheat starch-xanthan mixtures aging (Mandala and Palogou, 2003). Similarly, Kim and Yoo (2006) reported that the $G'$ and $G''$ increased with the increase in XG concentration in rice starch. The XG addition into starch-sucrose paste was also observed increased the $G'$ and $G''$ moduli as in Krüger et al. (2003).

Among the hydrocolloids studied, the XG addition into NCS resulted in the highest $G'$ and lowest values of tan δ which indicated that XG was more superior to alter the NCS to be more structured and solid-like. The phenomenon of higher $G'$ and lower tan δ values attributed to more solid-like properties of a paste as evidenced in numerous studies. Wang et al. (2008) revealed that the addition of 0.5% XG into waxy maize starch gave higher $G'$ and lower tan δ values and they concluded that XG was the main determinant in contributing to the solid-like properties of a paste.
like properties. Achayuthakan and Suphantharika (2008) observed that the dynamic viscoelasticity measurements of waxy corn starch incorporated with XG exhibited slightly superior viscoelastic properties than the guar gum incorporated, as evidenced by their higher G’ and lower tan δ values. Despite corn starch, the ability of XG in giving more structured and elastic gel-like paste was also evidenced in sweet potato starch (Choi and Yoo, 2009). From these observations, we can conclude that the starch–xanthan mixtures showed more solid-like behavior than the starch alone, indicating that XG can reinforce the network structure of the starch. Therefore, the addition of XG appears to contribute synergistically to the rheological properties of starch–xanthan mixtures. Due to these properties, starch-XG has been used in improving rheological and sensory properties of dessert sauces as thickener (Sikora et al., 2007).

The values of K’, K”’, n’, and n”’ are tabulated and presented in Table 2. The addition of XG, carrageenan, HMP and LMP into both NCS and MCS obviously increased the n’ values. However, the n”’ values were observed influenced differently with hydrocolloid and starch. For NCS, the n”’ values increased with the addition of carrageenan, HMP and LMP into NCS except XG, while for MCS, the n”’ values decreased. From dynamic rheological data (Table 2), it was found that the corn starches–hydrocolloids mixtures displayed weak gel-like behavior because the slopes (n’ = 0.09–0.31; n”’ = 0.08–0.31) are positive. Obviously, the values of K’ and K”’ also increased with the addition of XG, carrageenan and HMP, but decreased with the addition of LMP. The mixture in the presence of 0.5% XG give the highest value of K’ followed by HMP and carrageenan. Alloncle and Doublier (1991) reported that this may be attributed to an increase in the viscoelasticity of the continuous phase in starch–XG composite systems due to the thickening properties of XG and also indicated that the modification of dynamic rheological properties in the starch–gum composite systems could be described to phase separation processes in relation to incompatibility phenomena between unlike polysaccharides. However, the mixture in the presence of 0.5% LMP had slightly lower K’ value than starch dispersion (0% hydrocolloids). This trend was also found from rice starch–galactomannans (Kulicke et al., 1996), corn starch–locust bean gum mixtures (Alloncle and Doublier, 1991) and rice starch with the addition of 0.2% XG (Kim and Yoo, 2006). From these observations, it was found that the dynamic rheological properties of corn starch–hydrocolloids mixtures were affected by the addition of hydrocolloids, and depend on the concentration of hydrocolloids.

**Conclusion**

This work showed presence of hydrocolloids significantly change the rheological properties of the corn starches. The data recommend that XG, carrageenan, HMP and LMP could be used to alter the texture, mouth feel and processing parameters in order to fulfill consumer demands on food products. The addition of XG and carrageenan both increased the G’ and G” particular in NCS which indicate the potential of these hydrocolloids to transform starch system to a more elastic form. However, the addition of LMP decreased the solid-like properties of the mixtures, while XG, carrageenan and HMP play the opposite role. For these reasons, this study was initiated in order to gain an insight into the properties of hydrocolloids and their effects on rheological properties of corn starches.

**References**


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