

The effect of water and citric acid on sago starch bio-plastics

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Abstract: Starch is a biodegradable polymer produced in abundance from many renewable resources. This study examined the influence of citric acid (0-40% w/wt%) and water (0-40% w/wt%) as secondary additive and glycerol as plasticizer on the mechanical properties of bio-plastic starch (BPS) from Malaysian sago. The CA content varies from 0 to 40 w/wt% while water was also varied from 0 to 40 w/wt%. FT-IR spectroscopy showed that citric acid improves the properties of BPS and water gives negative effects to the carbon hydrogen-bond. It is obvious that the addition of the CA at 30 wt/wt% improves the mechanical property of BPS more than 40% compared to the addition of water.

Keywords: Component, sago, starch, melt processing, citric acid

Introduction

Particular attention has been given in the recent years for the development of biodegradable polymers from renewable resources, especially for packaging and disposable applications to maintain sustainable development of economically and ecologically attractive technology, towards greener environment (Schlemmer *et al.*, 2010; Fischer *et al.*, 2011). Among these biopolymer, starch is one of the promising materials because of its large availability, low cost, renewable resources and inherent biodegradability (Shi *et al.*, 2007).

Native starch is the major source of polysaccharide in plants. Previously many researchers have focused on starches from corn, wheat and potato and very few reports are available on sago starch. Sago starch is produced from sago palm (*Metroxylon* spp.), which is also known as rumbia. Sago is initially present in South East Asia and can be found especially in Sarawak, Malaysia. Sago starch is commonly used as functional ingredient (e.g. thickener, stabilizer, gelling agent) in the food industry (Mohamed *et al.*, 2008). In order to adjust the properties of these starch-based materials for non-edible applications, it requires combination with other polymers that may need for starch modifications such as esterification, grafting and reactive or melting extrusion of thermoplastic starch (TPS), which is also known as bioplastic starch (BPS) (Carvalho, 2008).

BPS is an amorphous or semi-crystalline polymeric material composed of gelatinized or deconstructed

starch containing one or a mixture of plasticizer (Liu *et al.*, 2009). Various plasticizer and additives have been evaluated for the gelatinization of starch during thermal processing. Among the plasticizers, water is the most commonly used in the thermal processing of starch based polymers. BPS containing only water alone however, results in poor mechanical properties such as the brittleness due to the fast retrogradation (recrystallization). Therefore, other non-volatile plasticizers are investigated to improve the processing ability and product properties of the BPS such as, glycerol, glycol and sorbitol, sugars, urea, formamide, acetamide, ethylenebisformamide, ethanolamine and citric acid.

This study was carried out to investigate the potential of sago starch as natural sources for the production of BPS and to optimize the process condition of the starch plasticized with glycerol, and the effect of water and citric acid as co-plasticizer on the mechanical and thermal properties of the BPS. Further, morphological structure of the samples was observed by using scanning electron microscope (SEM).

Materials and methods

Materials

Sago starch powder (25% amylose) was purchased from Hup Seng Heng Sdn Bhd, Malaysia, glycerol (95% purity) with density of about 1.261 g/cm³ and citric acid were supplied by Merck.

Fabrication process

In this experiment there were two compositions prepared. First is a mixture of starch and glycerol.

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Secondly, a blend of starch powder, glycerol and citric acid. Basically, sago starch (25% amylose) was used in the experiment. The starch was plasticized with glycerol (95% purity) while citric acid and water were used as a co-plasticizer. Tables 1, 2 and 3 shows the material ratios and glycerol-mono-stearate was added as a lubricant.

Table 1. BPS with different glycerol content

| Sample | Starch (w/w%) | Glycerol (w/w%) |
|--------|---------------|-----------------|
| GA1 | 100 | 15 |
| GA2 | 100 | 20 |
| GA3 | 100 | 30 |
| GA4 | 100 | 40 |

Table 2. BPS with different water content

| Sample | Starch (w/w%) | Glycerol (w/w%) | Water (w/w%) |
|--------|---------------|-----------------|--------------|
| WA1 | 100 | 30 | 0 |
| WA2 | 100 | 30 | 10 |
| WA3 | 100 | 30 | 20 |
| WA4 | 100 | 30 | 30 |
| WA5 | 100 | 30 | 40 |

Table 3. BPS with the addition of citric acid

| Sample | Starch (w/w%) | Glycerol (w/w%) | Citric Acid (w/w%) |
|--------|---------------|-----------------|--------------------|
| CA1 | 100 | 30 | 10 |
| CA2 | 100 | 30 | 20 |
| CA3 | 100 | 30 | 30 |
| CA4 | 100 | 30 | 40 |

Bio-plastic starch (BPS) was produced mixing the materials and the resulting mixture was stored for 24 hrs in an air tight polyethylene bags at room temperature before being processed with a twin screw extruder (Thermo HAAKE Rheomix 600), to melt blending purposes at a temperature of 130°C and 100 rpm. The extrudate was granulated and stored under controlled conditions for 48 hours and the granulates were injection molded according to the parameter in Table 4.

Table 4. Injection moulding parameters

| | |
|--------------------|-----------------------|
| Injection Pressure | 1400 bar |
| Injection rate | 50 cm ³ /s |
| Holding pressure | 600 bar |
| Temperature Z1 | 110°C |
| Temperature Z2 | 115°C |
| Temperature Z3 | 120°C |
| Temperature Z4 | 125°C |
| Temperature Z5 | 150°C |

Fourier transform infrared spectroscopy (FTIR)

The IR spectra were measured with a Nicolet-210 spectrophotometer (Nicolet Co., USA). TPS was cut into small pieces, milled and diluted with KBr powder. The spectra were taken in 256 scans between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹.

Scanning electron microscope (SEM)

The morphology of sago starch granules and the extruded BPS were examined using the scanning electron microscope.

Tensile test

Tensile test was conducted in accordance to the ASTM D 412 by using the universal testing machine. The dumbbells were cut from the polymer sheets (1.5 x 160 x 160 mm) that had been prepared by injection molding.

Results and Discussion

Tensile strength

The effect of adding glycerol on the tensile strength of BPS is shown in the Table 5. BPS with less than 20 w/w% glycerol content had low tensile strength (Table 5) and I increasing the concentration up to 30 w/w% resulted in a maximum tensile strength value and also provides flexible product. The tensile strength decreased as the glycerol increased up to 40%. Thus, 30% glycerol provided the maximum tensile strength and was used for subsequent studies. Ma *et al.* (2009) reported that at low concentrations of glycerol (<15w/w %), there is not enough plasticising effect and the starch molecules become brittle. On the contrary, at concentrations above 30 w/w%, the plasticising effect is too pronounced and makes the starch molecules move easily. Thus, in this study the optimum amount of glycerol added was 30 w/w% as it generate high tensile strength of 23.06 MPa.

Table 5. Tensile strength for bps at different glycerol content

| Sample | Glycerol (w/w %) | Tensile Strength (MPa) |
|--------|------------------|------------------------|
| GA1 | 15 | 13.330 |
| GA2 | 20 | 15.300 |
| GA3 | 30 | 23.060 |
| GA4 | 40 | 5.099 |

Table 6. Tensile strength for bps at different water content

| Sample | Water (w/w %) | Tensile Strength (MPa) |
|--------|---------------|------------------------|
| WA1 | 0 | 3.29 |
| WA2 | 10 | 2.97 |
| WA3 | 20 | 2.89 |
| WA4 | 30 | 2.79 |
| WA5 | 40 | 2.69 |

The effect of adding water on the tensile strength of BPS is shown in the Table 6. It was observed that, all BPS-water blends exhibited a typical brittle characteristic, with lower tensile strength ranging from 2.65-3.89 MPa. The strength of the blends decreased with the addition of water, which gives the impression that the existence of water in BPS had a significant negative effect on the tensile properties of BPS (Table 6). The negative effect in strength can be ascribed to the hydrophobic nature of the glycerol which contributed to poor dispersion and compatibility of glycerol with sago starch due to the existence of water.

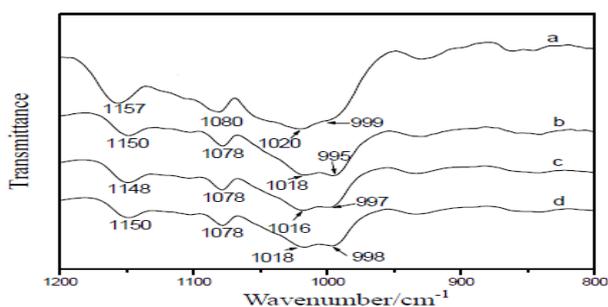
Table 7. Tensile strength for bps at different citric acid content

| Sample | Citric Acid (w/w%) | Tensile Strength (MPa) |
|--------|--------------------|------------------------|
| CA1 | 10 | 13.24 |
| CA2 | 20 | 15.97 |
| CA3 | 30 | 24.76 |
| CA4 | 40 | 21.88 |

The addition of citric acid to the mixture improved the tensile strength compared to the water. Concentration of citric acid less than 20 w/w% provide relatively low improvement while concentration at 30 w/w% gives high molecular weight of the starch, leading to better tensile strength compared to mixing starch with glycerol alone. Hence, addition of 30 w/w% citric acid into BPS gave an optimum value of tensile strength of 24.76 MPa (Table 7).

Fourier transform infrared spectroscopy (FT-IR) analysis

The analysis of Fourier transform infrared spectroscopy (FT-IR) spectra of the blends enabled the hydrogen bond interaction to be identified. Lower wave number results in stronger interaction of hydrogen bond (Wang *et al.*, 2009). Figure 1 shows that the characteristic peaks 1080 cm^{-1} and 1157 cm^{-1} indicate the C-O bond stretching of C-O-H group in the GA blends.

**Figure 1.** FT-IR spectra of BPS with different glycerol content

The peak 1080 cm^{-1} was shifted to 1078 cm^{-1} and from 1150 cm^{-1} to 1148 cm^{-1} which means that the OH group of starch was involved in the hydrogen bond formation. Another two peaks at 999 cm^{-1} and 1020 cm^{-1} are attributed to C-O bond stretching of C-O-C group (Santos *et al.*, 2009). The peaks were shifted from 998 cm^{-1} to 995 cm^{-1} and 1018 cm^{-1} to 1016 cm^{-1} respectively. This lead us to conclude that the FT-IR test for composition 1 showed that glycerol could form a more stable hydrogen bond. The interaction of polymer blends could be identified with FT-IR spectra. If two polymers formed completely

immiscible blends, there were no appreciable changes in the FT-IR spectra of the blends with the respect of co-addition of each component (Corradini *et al.*, 2007). However, if two polymers were compatible, a distinct interaction (a hydrogen bonding or dipolar interaction) existed between the chains of one polymer and those of others, causing FT-IR spectrum blends to change by band shifting and broadening. As a result, FT-IR could identify segment interaction and provide information about the phase behavior of polymer blends (Tomasik *et al.*, 1995). Figure 2 showed the FTIR spectra of BPS with the addition of water blends in specific stretching regions, respectively. The addition of water has shifted the peak to a lower wave number in the range of 1050-950 cm^{-1} .

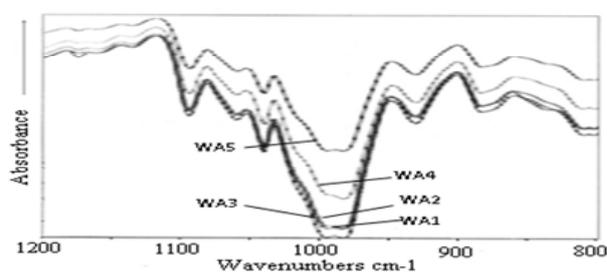
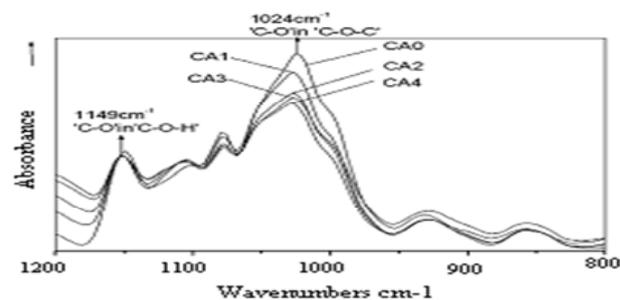
**Figure 2.** FT-IR spectra of BPS with different water content**Figure 3.** FT-IR spectra of BPS with different citric acid content

Figure 3 illustrates the FT-IR result for the effect of acid citric content. The peak height referred to are at the stretching vibration peak of 'C-O' in 'C-O-H' group at 1149 cm^{-1} . The peak's height increased as the citric acid content increased. These results of the FT-IR suggest that the esterification happened during melt blending, and the esterification increased as the CA percentage increased. The esterified citric acids which were bound to the starch chains are capable of disrupting the inter- and intra-molecular hydrogen bonds (Yang *et al.*, 2006). Moreover, it also increased solubility of starch. Thus, the citric acid reacted with starch can be considered as the internal or co-plasticizer.

Scanning electron microscopy (SEM)

The morphology structure of polymer blends was a very important characteristic to understand many properties of polymer blends, especially the

mechanical properties (Wilemse *et al.*, 2006). The morphology of sago starch granules and the extruded BPS are shown in Figures 4(a)– 4(f). Figure 4(a) illustrates that the sago starch has an amorphous homogeneous matrix surrounds with predominant granular domains. BPS plasticized by 20% of glycerol result in a less coarse granules compared to native sago starch, possibly due to starch granule fusing into homogeneous phase as revealed in Figure 4(b), which led to some empty space in the BPS. Furthermore, plasticized BPS with glycerol had a clear and smooth surface as seen in Figure 4(c) for the compositions of 30 w/w%, and vice versa for 40 w/w% plasticization. It is noted that, as plasticizer content increases, melt viscosity decreases which made the plasticization of starch difficult, due to the reduction in shear during processing (Da Roz *et al.*, 2006).

Compared to the smooth structure with the addition of just glycerol, the BPS which blend with water had a typical two phase polymer blend structure as in Figures 4(c)-(f), especially with the addition of 40 wt/wt% water (Figure 4(f)). The sample surface was obviously rugged. At the same time many starch granules were noticed not too plasticized and some of them were removed from the sample surface and creating cavities in the surface, which could be ascribed to the high interfacial tension between hydrophilic sago and water and hydrophobic glycerol. In this situation, glycerol became less effective plasticizer than it should be and the permeation effect of sago starch chain was poor which limited the mobility and orientation of polysaccharide during processing.

Conclusion

Fourier Transform Infrared Spectroscopy (FTIR) analysis showed that glycerol could form a stable hydrogen bond while the addition of citric acid could disrupt inter and intra molecular hydrogen bond effectively. The additions of water, however give some negative effect on the effective bonding of carbon hydrogen in BPS. Scanning Electron Microscopy (SEM) proved that thermoplastic starch (BPS) plasticized with 30% glycerol result in fined granule compared to native starch. The addition of water has given poor starch chain and produced samples with cavities. Optimum tensile strength for composition with starch and glycerol was 23.06 MPa while for composition starch-glycerol and citric acid was 24.766 MPa. The addition of water in starch glycerol resulted in the optimum tensile strength of 3.29 MPa.

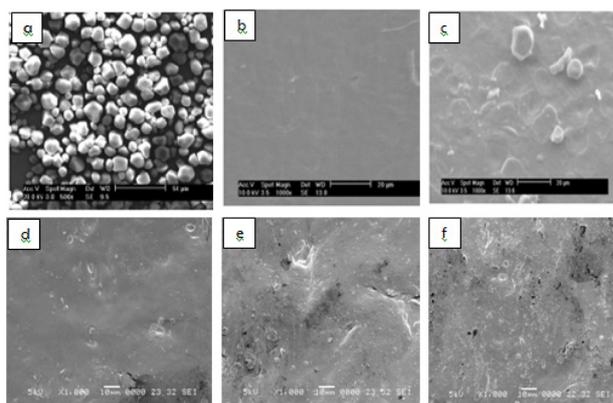


Figure 4. The SEM photographs of (a) pure sago starch (native state) (b) 30 wt/wt% glycerol (c) 20% wt/wt% acid citric (d) 10 wt/wt% water (e) 20 wt/wt% water (f) 30 wt/wt% water

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