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The Effects of Citric Acid on Thermal and Mechanical Properties of Crosslinked Starch Film

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Plastic waste from film packaging is one of the major threats to environmental sustainability. The problem can be reduced by using a biodegradable raw material such as starch to replace the non-biodegradable petroleum-based plastic. However, starch is highly hydrophilic and brittle, which needs to be modified to improve these drawbacks. In this research, a mixture of tapioca starch (S) and glycerol (G) was crosslinked with citric acid (CA) at different ratios (0, 0.4, 0.6, 0.8, 1.0 wt% of dry basis). Effects of CA contents on the degree of crosslinking, thermal stability, and tensile properties were investigated. The sample that contained 0.6 wt% CA showed the highest degree of crosslinking (i.e. 56 %), good thermal stability, high modulus (10 MPa) and tensile strength (0.16 MPa), and low elongation at break (161 %) when compared with other samples. Samples that have higher CA contents (i.e. 0.8 wt% and 1.0 wt%) experienced the acid hydrolysis on the crosslinking site, reducing the degree of crosslinking, thermal stabilities, and tensile properties.

1. Introduction

Excessive wastes from plastics packaging have become one of the major threats to the environment (Geyer et al., 2017). The awareness of the negative impacts brought by the non-biodegradable plastics packaging has urged the development of biodegradable-based plastics from polysaccharides such as starch, glycogen and cellulose. Starch is one of the most used polysaccharides to produce biodegradable plastics since it is renewable, abundance and low cost. However, native starch is known for its hydrophilicity and poor mechanical properties which consequently, restricts its usage as the packaging (Ghanbarzadeh et al., 2011). Some modifications are essentials to improve the properties.

Many methods have been proposed to overcome these limitations such as blending the starch with the commercial plastics for examples polyvinyl alcohol (Sreedhar et al., 2006), polyester (Olivato et al., 2012) or polyurethane (Rusman et al., 2017). Crosslinking is one of the options where the crosslinking agent is introduced to substitute the hydroxyl group (-OH) of starch and forming a new chemical bond between the molecular starch structure (Chen et al., 2015). However, some of the crosslinkers such as glutaraldehyde (Yoon et al., 2006) and epichlorohydrin (Sreedhar et al., 2006) display toxicity that limits their usage in biomaterials and food-contact materials. In search for a non-toxic crosslinker, citric acid (CA) has been reported numerously as an effective material to improve the properties of native starch (Owi et al., 2017). Besides, CA possesses tri-functional carboxylic acid that can interact with the OH of starch to form ester (Shi et al., 2007) and also establishing stronger hydrogen bonding (Reddy and Yang, 2010).

The crosslinked starch films can be prepared in several ways. Reddy and Yang (2010) used sodium hypophosphite as a catalyst to promote crosslinking in starch/glycerol/CA. The film was thermally cured at 150 °C. Menzel et al. (2013) and Olsson et al. (2013) prepared the crosslinked starch films without any catalyst but the curing temperatures were varied at 105 °C and 150 °C. Later, an amount of CA was added after the gelatinisation of starch/glycerol. They found that at higher curing temperature, the film experienced severe hydrolysis. Seligra et al. (2016) used a simple method where a mixture of starch, glycerol, and CA was gelatinised in one-pot at temperature <100 °C without any catalyst and no further thermal curing. The FTIR

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and NMR analysis confirmed the crosslinked structure of the film even at lower temperature i.e. 70-85 °C and the water vapor barrier was also improved.

In this project, CA was used as a crosslinker and the one-pot method (Seligra et al., 2016) was adopted to prepare the crosslinked starch film. To date, no reports are found on the effects of CA content on the thermal and the tensile properties of the crosslinked starch film that employ the one-pot method. This CA crosslinked-starch film has the potential to be used as food and medical packaging since the ingredients are non-toxic materials. The film is also biodegradable which can contribute to the environmental sustainability.

2. Experimental section

2.1 Materials

Tapioca starch and citric acid used were purchased from Sigma Aldrich Sdn. Bhd. Glycerol was supplied by Fisher Scientific. All the materials were used without further purification.

2.2 Preparation of the crosslinked starch film

The crosslinked starch film was prepared by in-situ gelatinisation where all the materials (Table 1), were mixed simultaneously. The solution was stirred for 30 min at 80 °C, degassing under a vacuum environment before casting onto Teflon mould using a 100 µm bar coater. The crosslinked film was oven-dried overnight at 50 °C.

Table 1: Ratio of S:G:CA to the dry basis of 100 g system

Sample	Distilled water (g)	S	G	CA
B1	93	3	1	0.0
B2	93	3	1	0.4
B3	93	3	1	0.6
B4	93	3	1	0.8
B5	93	3	1	1.0

2.3 Characterisations of the crosslinked starch film

2.3.1 Fourier Transform Infra-Red

The changes of the functional groups in the starch films were analysed using a Shimadzu IR Tracer 100, Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR) spectrometer. The spectra were obtained in the range of 4,000-600 cm^{-1} with 16 scans in 4 cm^{-1} resolution mode.

2.3.2 Degree of crosslinking

The degree of crosslinking (DC) was calculated using Eq(1) by immersing the film in dimethylsulphoxide (DMSO) as reported by (Seligra et al., 2016) with some modifications.

$$DC = \frac{m_1 - m_0}{m_0} \times 100\ \% \tag{1}$$

where, m_0 is the initial weight of the film and m_1 is the final weight of the film after drying at 50 °C.

2.3.3 Thermal properties

A Perkin Elmer (TGA 4,000) was used to evaluate the thermal stability of the starch film. The weight loss of the film was recorded from 25-900 °C at a heating rate of 10 °C /min under nitrogen atmosphere. TG and DTG of the starch film were recorded.

2.3.4 Tensile properties

Tensile properties of the film were measured using a Zwick Roell Tensile Tester according to ASTM D882-18. The reported results were representing the average of five replicates for each formulation.

3. Results and discussions

3.1 FTIR analysis

Figure 1 presents the FTIR spectra of the native starch and crosslinked starch at different ratio of CA. There is a new peak appeared at 1,720 cm^{-1} upon addition of CA which corresponding to the ester C=O stretching. The detection of the new peak was the evidence of the esterification of CA, suggesting that crosslinking occurred in the system as presented in Figure 1d (Seligra et al., 2016). The broad peaks exhibited at 3,296 cm^{-1} and

2,927 cm^{-1} were due to the hydroxyl group (OH) stretching and C-H stretching (Prachayawarakorn and Tamseekhram, 2019) of starch, glycerol and CA. This finding is consistent with the literature reported by Reddy and Yang (2010) and Qin et al. (2019).

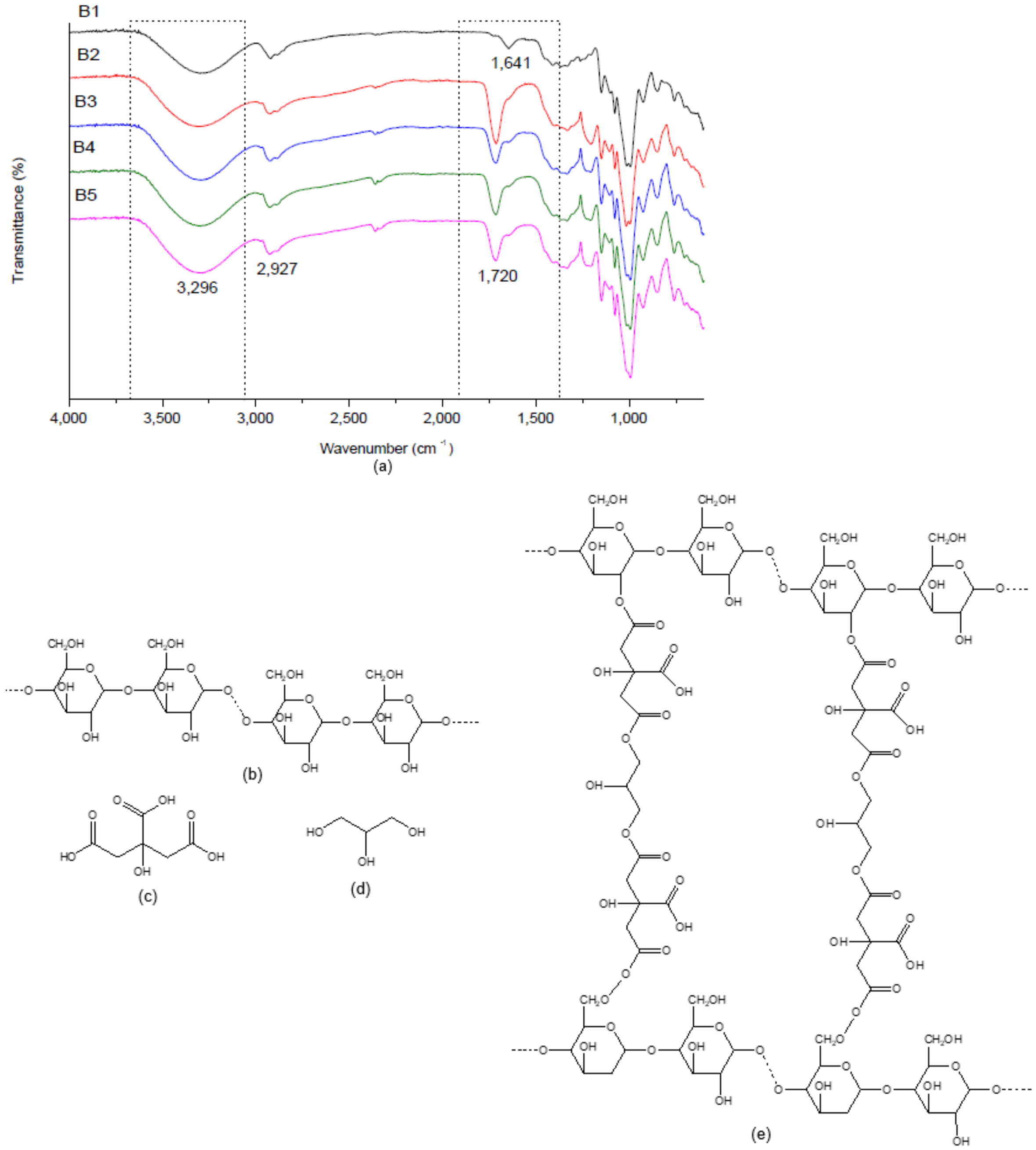

Figure 1: (a) FTIR spectra of the starch film at different CA content and chemical structure of the raw materials used, (b) Starch; (c) CA; (d) Glycerol; and (e) possible crosslinking structure of S,G and CA

3.2 Degree of crosslinking

DC of the starch film was determined by calculating the insoluble part of the film. The effects of CA to the degree of crosslinking of the starch film was shown in Figure 2. The DC of the starch film was increased when CA was added into the system from 0 to 56 %. This coincided with the FTIR spectra reported earlier when the crosslinking occurred upon addition of CA. Above 0.6 wt% CA content, the DC experienced approximately 28.6 % reduction. This reduction can be related to the starch hydrolysis under acidic environment (Menzel et al., 2013). Olsson et al. (2013) also demonstrated that the hydrolysis of S/G/CA film occurred in a low pH system (pH ≤ 4), which caused the cleavage of glycosidic linkages in starch. The occurrence of acid hydrolysis can be supported by FTIR, where the intensity of the waveband at 1,720 cm^{-1}, corresponding to the crosslinking by esterification, reduced with increasing CA contents (i.e. less crosslink). Since the crosslinking occurred between starch-CA and glycerol, by fixing the amounts of glycerol and starch had led to an excess of CA. The excess acid had hydrolysed the starch, resulting the detection of broad peaks of OH groups at 3,296 cm^{-1} (samples B4 and B5).

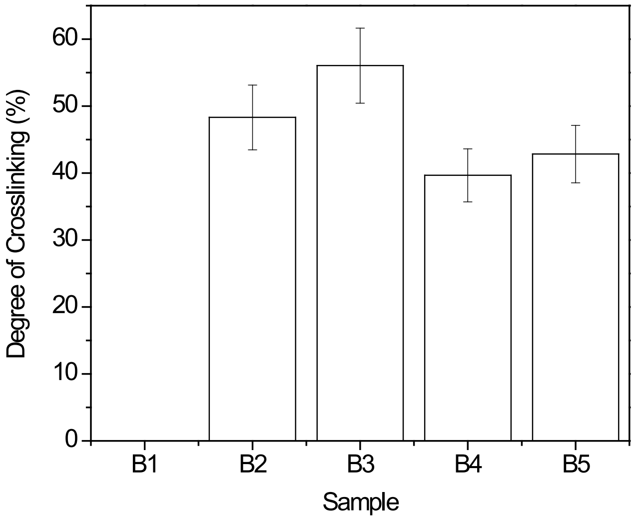

Figure 2: The effect of the CA content on the starch film degree of crosslinking (%)

3.3 Thermal properties of the crosslinked starch film

The thermal degradation of the starch film is illustrated in Figure 3. It can be observed that there was noticeable weight loss at 100 °C, which attributed to the evaporation of water and moisture (Gilfillan and Doherty, 2016). The second weight loss was correspondent to the decomposition of starch components around 320 °C (Liu et al., 2013). From the DTG (2nd region), decomposition temperature (T_d) of starch was shifted to a higher temperature (325-333.8 °C) when CA was added. This confirmed that the CA had successfully improved the thermal stability of the starch film by developing the crosslinked structure in the system. Reddy and Yang (2010) also reported that the crosslinked starch exhibited higher thermal stability than the non-crosslinked starch.

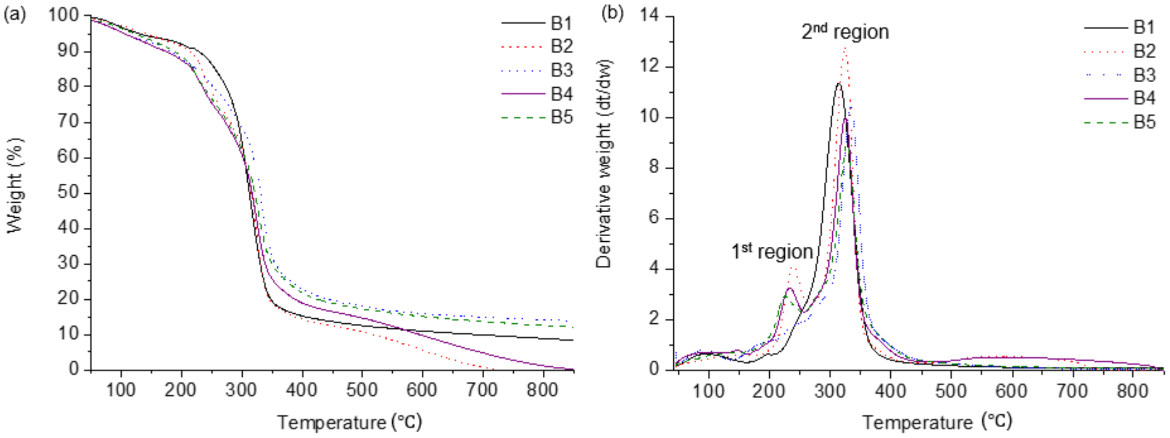

Figure 3: Thermal properties of the starch film (a) Weight against temperature (DT);(b) Derivative weight against temperature (DTG)

The thermal stability of the starch film reflects its degree of crosslinking. For instance, sample B3 had higher T_{80} (temperature for 80 % of weight loss) i.e. 441.7 °C compared to sample B1 which T_{80} was 347.7 °C. This is because higher CA contents are able to form more crosslinks with the starch (covalent bond) as shown in Figure 1d) and need more energy to break the molecular chains (i.e. high thermal stability). Besides that, the presence of strong intermolecular interactions such as hydrogen bonding between the –OH group of starch and CA also contributed to the high thermal stability (Shi et al., 2007). Further increased the CA contents had reduced the thermal stability. This is due to the acid hydrolysis that reduced the degree of crosslinking. These observations were reflected in the T_{80} shown by sample B4 (388.8 °C) and sample B5 (423.2 °C). Besides that, the presence of hydrolysed starch was detected at 224-233 °C for samples B4 and B5 as illustrated in DTG (1st region). This was in agreement with the decomposition temperature of hydrolysed starch reported in the literature, T_d = 220-300 °C (Reddy and Yang, 2010) and T_d =220-270 °C (Prachayawarakorn and Tamseekhram, 2019).

3.4 Tensile properties of the crosslinked starch film

The tensile properties of the starch film are represented in Figure 4. By increasing the CA content up to 0.6 wt% had increased the rigidity of the samples. This was manifested by the values of Young's modulus and tensile strength (TS) of the starch film. Sample B3 exhibited higher modulus (10 MPa) and tensile strength (0.16 MPa) due to a higher degree of crosslinking. The crosslinked networks hold the starch polymer chains and prevent the chains from slide past each other during stretching. Consequently, the elongation at break (EB) of sample B3 was reduced. Further, increased the CA content had decreased the modulus and TS (samples B4 and B5). As previously discussed, high CA content caused acid hydrolysis to occur which cleavaged the bond in starch, reducing the degree of crosslinking in the samples. Apart from crosslinking, the presence of intermolecular interaction such as hydrogen bonding had also contributed to the increase of modulus and TS as shown by sample B2 (Ghanbarzadeh et al., 2011). Sample B1 had the highest EB as it contains no CA, and there is no crosslinking network to restrict the mobility of the polymer chain upon stretching.

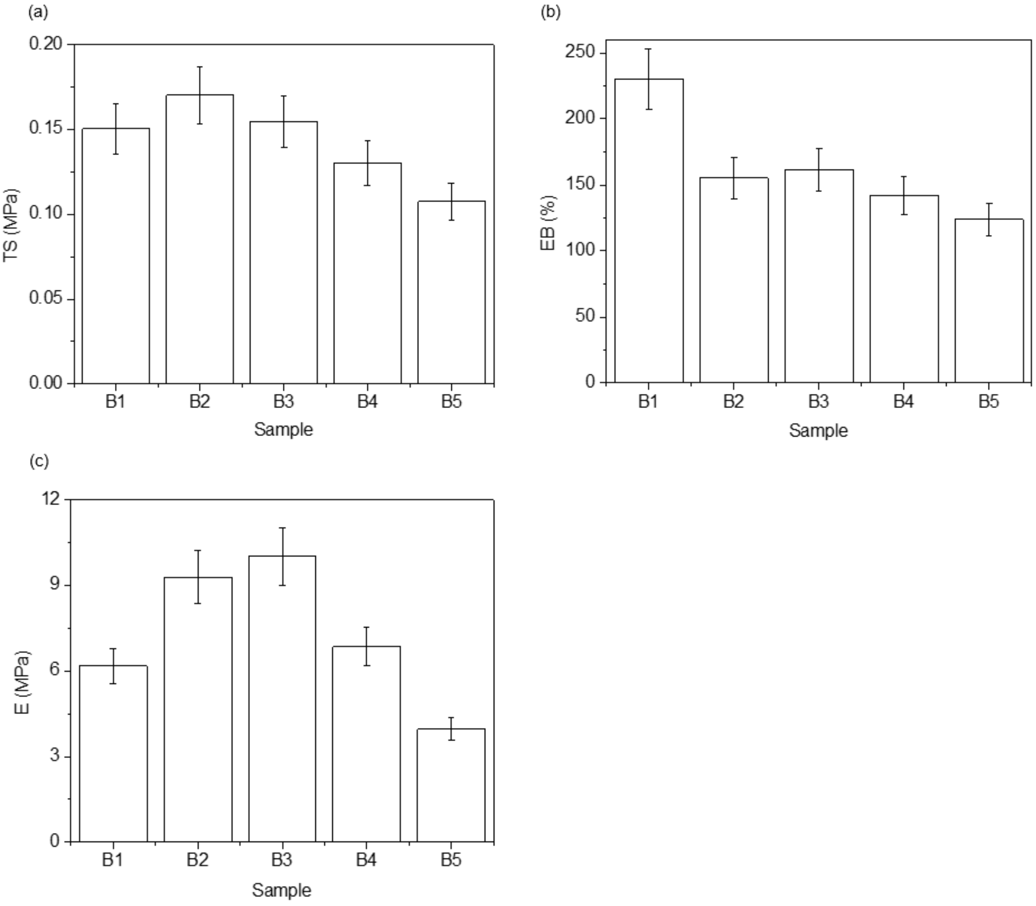

Figure 4: Tensile properties of the film (a) Tensile strength (MPa), (b) Elongation at break (%) and (c) Young's modulus at various CA ratio

4. Conclusions

The thermal and the tensile properties of the crosslinked tapioca starch film have been successfully improved by using CA as a crosslinking agent. Results showed that higher CA contents had affected both thermal and tensile properties of the film. Higher degree of crosslinking (DC) means more starch-CA-glycerol chains were inter-bonded which needed higher tensile force or heat to break or degrade the chains. The effects were manifested by sample B3 (0.6 wt% CA) which had the highest DC (56 %), improved tensile properties and good thermal stability. On the contrary, higher CA content (above 0.6 wt%) relatively had reduced the pH of the system which initiated the hydrolysis of starch (i.e. cleavage of glycosidic linkages in starch), resulting in poor tensile and thermal properties.

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