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Research article

Characterization and Properties of Biodegradable Thermoplastic Arrowroot Starch Crosslinked by Glutaraldehyde Processed by Compression Molding Technique

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Abstract

Keywords

arrowroot starch;
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crosslinking;
thermoplastic starch

Although starch is available and biodegradable, hydrophilicity and mechanical properties are still main disadvantages for many applications. In this study, arrowroot starch, a perennial herb found in tropical climates and extracted from the tubers of the arrowroot plant was used. The arrowroot starch was chemically modified by crosslinking with different amounts of glutaraldehyde in order to overcome the starch disadvantages. The crosslinked starch was then prepared as thermoplastic starch by plasticizing with glycerol, compounding in an internal mixer and finally shaping in a compression molding machine. An increase of gel fraction and decrease of swelling as well as the moisture uptake of different thermoplastic crosslinked arrowroot starch samples were observed, all of which indicated a crosslinking reaction of glutaraldehyde with the starch molecules. The thermal degradation temperature of thermoplastic crosslinked arrowroot starch, determined from thermogravimetric analysis technique, increased when compared with thermoplastic arrowroot starch. The extensibility of the thermoplastic crosslinked arrowroot starch also improved via glutaraldehyde crosslinking. Higher content of glutaraldehyde also caused lower swelling and moisture uptake including higher gel fraction and extensibility. Moreover, crystallinity, morphology and biodegradability were also examined.

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1. Introduction

Biodegradable polymers from renewable resources, particularly natural polysaccharides of starch, are one of the most plentiful and high available biopolymers worldwide. Starch is composed of branched polymers of amylopectin with α-D-(1,6-glycosidic linkages) and linear polymers of amylose with α-D-(1,4-glycosidic linkages). Several types of starch, such as cassava, corn, potato, rice or arrowroot starch, exist [1].

Arrowroot is obtained from the rhizomes of *Tacca leontopetaloides*, extracted from the arrowroot plant. The plant is naturally cultivated in Africa, Asia and Australia [2]. Arrowroot powder contains gluten-free, therefore, it is commonly used as an ingredient in gluten-free cooked food including baby meals. It is commonly used for thickening sources, soups and other foods. Arrowroot can also be applied as an ingredient in body care and body powder products. Arrowroot starch contains approximately 22% amylose and 77% amylopectin [3]. Arrowroot starch contains the same amylose content as cassava starch; therefore, it can be used as a replacement option [3].

In general, starch exists naturally in granular structure. When glycerol plasticizer is incorporated into starch, it can destroy the granular structure of starch. As a result, the plasticized starch can flow and be processed using high shear force and high temperature, commonly known as thermoplastic starch (TPS). TPS polymers from several types of starch have been studied, i.e. corn [4], cassava [5], wheat [6], rice [7] and maize starch [8]. However, all TPS prepared from various sources of starch still show low mechanical properties and high hydrophilicity.

Chemical modification via crosslinking is an effective way to reduce hydrophilicity of starch. Several types of crosslinking agents such as glutaraldehyde, epichlorohydrin, sodium trimetaphosphate have been utilized for chemical reaction with the hydroxyl groups of starch [9]. It was reported that the addition of glutaraldehyde while mixing with poly(lactic acid)/TPS from tapioca starch reinforced with bacterial cellulose fibers caused a decrease of moisture content and tensile strength but a slight increase of elongation at break [10].

Most researchers focused on using glutaraldehyde as a crosslinking agent for starch using a casting method. Casted cassava starch film plasticized by glycerol and poly(ethylene glycol) and crosslinked with glutaraldehyde presented decrease of water vapor transmission rate without significant change to tensile strength and extendibility [11]. In addition, post-crosslinking of glutaraldehyde by soaking in corn starch blended with poly(vinyl alcohol) casted film led to a drop in swelling and elongation but an increase in tensile strength and modulus [12]. In addition, with increasing content of glutaraldehyde, the tensile strength of corn starch blended with poly(vinyl alcohol) casted film was found to increase but swelling and solubility decreased [13, 14]. Pullulan film prepared by the casting method and crosslinked by glutaraldehyde was claimed to show lower swelling and its maximum tensile strength was found with 5% glutaraldehyde [15]. Moreover, crosslinking with glutaraldehyde in chitosan/starch casted film caused the reduction of tensile strength and elongation; however, the moisture uptake was not affected by different content of glutaraldehyde [16].

To the best of our knowledge, thermoplastic arrowroot starch prepared by compression molding technique, a promising method for producing commodity synthetic thermoplastics, has never been reported. In this present study, arrowroot starch crosslinked with different loadings of glutaraldehyde, i.e. 0, 0.25, 0.5, 1, 2 and 4 phr was firstly prepared. Thermal processes using an internal mixer and a compression molding machine was performed to formulate thermoplastic crosslinked arrowroot starch (TPCAS), in comparison with TPS from arrowroot starch (TPAS). The effects of glutaraldehyde content on gel fraction, moisture uptake, swelling, mechanical properties and biodegradability were investigated. In addition, X-ray diffraction, scanning electron microscopy and thermogravimetric analysis were employed to characterize the different starch samples.

2. Materials and Methods

2.1 Materials

Arrowroot starch, composed of approximately 22 %wt amylose and 77%wt amylopectin, was obtained from E.T.C, Co. Ltd. (Thailand). Glycerol (plasticizer) was obtained from Lab System Co. Ltd. (Thailand). Glutaraldehyde (AR grade) was purchased from Fluka, Co. Ltd (Thailand) and citric acid (food grade) was purchased from UCS 1986, Co. Ltd. (Thailand).

2.2 Sample preparation

Firstly, glutaraldehyde crosslinked arrowroot starch was formulated by blending 50 g of arrowroot starch, 50 ml of distilled water and 20 g of glycerol at 300 rpm for 1 h. Different amounts of glutaraldehyde, i.e. 0.125, 0.025, 0.05, 1 and 2 g, corresponding to 0, 0.25, 0.5, 1, 2 and 4 phr were gradually included into the mixture. A hot plate (IKA, Germany) was used to heat the mixture with continuous stirring for 15 min at the gelatinization temperature of 70°C. During the gelatinization, citric acid (a catalyst) was added to adjust pH of the mixture to 4.0. After that, the mixture was dried for 24 h at 80°C in a hot-air oven (Memmert, Germany) and was then milled before thermal processing.

Next, either arrowroot starch or glutaraldehyde crosslinked arrowroot starch was mixed with glycerol plasticizer in plastic bags and left overnight. The ratio of the starch to glycerol was retained at 65:35 by weight. Compounding was performed using an internal mixer (Chareon, Thailand) at 40 rpm rotor speed and 150°C for 5 min to obtain a homogeneous TPAS or TPCAS material. The compounded samples were subsequently compressed into 2 mm thick plates using a compression molding machine (LabTech Engineering, Thailand) with the pressure of 1300 psi at 150°C for 7 min.

2.3 Swelling

A sample, with the size of $25 \times 25 \times 2$ mm^3, was weighed and placed in distilled water for 2, 4 and 6 h at ambient temperature. Then, a filtered paper was used to blot the sample. The film weight was determined regularly with a balance (Presica Instrument, UK) until it reached the equilibrium. Swelling was calculated using equation (1):

$$\text{Swelling} = \frac{m_2 - m_1}{m_1} \times 100 \qquad (1)$$

where m_1 was the film weight before swelling and m_2 was the film weight after swelling.

2.4 Gel fraction

The gel fraction was considered by the loss in weight of the crosslinked starch [17]. A $25 \times 25 \times 2$ mm^3 sample was weighed and then immersed in 85% formic acid for 5 h at 50°C. The immersed sample was thoroughly washed, dried and finally weighed. The gel fraction was evaluated as per the following equation:

$$\text{Gel fraction (\%)} = \frac{W_2}{W_1} \times 100 \qquad (2)$$

where W_1 and W_2 were the weights of the film sample before and after immersing in formic acid, respectively.

2.5 Moisture uptake

A moisture uptake test was performed using ASTM D-570. A film sample was dried and then preserved in a tight storage box at 100% RH. The absorbed water was assessed for 15 days. The moisture uptake of the film sample was calculated as follows:

$$\text{Moisture uptake} = \frac{W_2 - W_1}{W_1} \times 100 \tag{3}$$

where W_2 and W_1 were the wet weight and the dried weight of the film sample, respectively.

2.6 X-ray diffraction

An X-ray diffractometer (D8 Advance, Bruker, Madison, USA), operating with CuK_α radiation (wavelength 0.1542 nm), was used for X-ray diffraction measurements with 40 kV and 35 mA. The scattering angle (2θ) was 10° to 80° (θ was the Bragg angle) with stepped sampling intervals of 0.02° and 10s, respectively. The relative crystallinity of a film sample was determined by equation (4):

$$\text{Relative crystallinity (\%)} = \frac{A_c}{A_c + A_a} \times 100 \tag{4}$$

where A_c and A_a denoted the crystallinity area (2θ of 10-30°) and the amorphous area (2θ of 10-80°) of starch on the diffractogram, respectively.

2.7 Thermogravimetric analysis

Sample thermograms were recorded on a Thermogravimetric analyzer (TGA) (Perkin Elmer, Pyris 1, USA). Each film sample was investigated over the range of 50-600°C and 10°C/min heating rate under nitrogen atmosphere. Thermal degradation temperatures were established at maximum degradation rate, and the temperature a 50% weight loss were then reported.

2.8 Morphology

A scanning electron microscope (EVO®MA 10, Jena, Germany) was used to examine film morphology. To prevent electrical charge, each tested sample was coated with a thin gold layer. In addition, each sample was thoroughly dipped under liquid nitrogen before fracturing to obtain cross-section morphology.

2.9 Mechanical properties

A mechanical test was performed according to ASTM D-638 at the relative humidity of 60±5% and temperature of 23±1°C using a Universal Testing Machine (LR 5K, Lloyd Instrument, West Sussex, UK) with a 1 kN load cell and 40 mm/min crosshead speed. Averaged data were obtained from at least 10 independent specimens.

2.10 Biodegradation

Biodegradation was examined from the soil burial test. A tensile specimen was buried under the soil. The temperature and water content were kept at 32±2°C and 5-10%, respectively. The change in tensile properties was determined at day 5 and day 10.

3. Results and Discussion

Glutaraldehyde can be used to crosslink arrowroot starch chains via hydroxyl groups; as a result, hemiacetal or acetal linkages are formed. Chemical reaction between starch molecules and glutaraldehyde can form via S_N1 type nucleophilic addition using acid as a catalyst [18]. Four possible chemical structures of glutaraldehyde crosslinked arrowroot starch are shown in Figure 1. Hemiacetal linkage was shown in Figure 1(a) and Figures 1(b)-1(d) represent acetal linkages. The chemical structure in Figure 1(c) reveals both hemiacetal and acetal linkages.

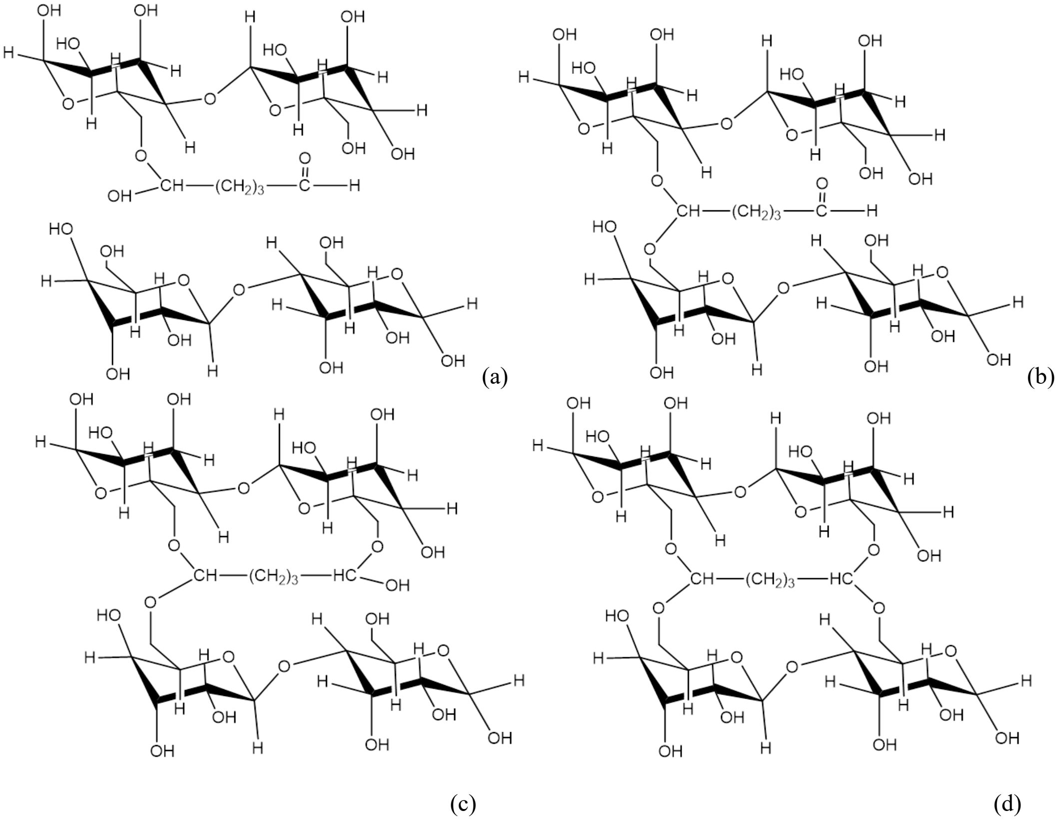

Figure 1. Chemical crosslinking of arrowroot starch molecules with glutaraldehyde

3.1 Swelling and gel fraction

Swelling ability indirectly indicates crosslink density in starch molecules. It can be observed in Table 1 that swelling of TPAS and all TPCAS samples increased with increasing times. However, the increase of glutaraldehyde content clearly led to decrease of percentage of swelling. As expected, TPCAS4 and TPAS presented the lowest and highest degrees of swelling, respectively. The drop in swelling obviously corresponded to crosslink density confirmed by the increment of gel fraction results in Table 1. When glutaraldehyde content increased, gel fraction significantly increased, indicative of increase crosslink density. The increment in the crosslink density restricted the ability of water molecules to penetrate into starch molecules. Moreover, the crosslinking reaction caused

Table 1. Swelling, gel fraction, moisture uptake and relative crystallinity of TPAS and different TPCAS polymers

Samples	Swelling (%)			Gel fraction (%)	Moisture uptake (%)			Relative crystallinity (%)
	2h	4h	6h		Day 5	Day 10	Day 15	
TPAS	129.9	147.6	176.1	0	37.6	47.5	53.8	42.9
TPCAS0.25	124.4	140.6	166.0	8.4	36.5	46.9	52.3	41.2
TPCAS0.5	120.6	136.2	163.8	13.5	36.4	46.5	50.6	39.5
TPCAS1	117.1	131.6	159.2	29.6	36.3	46.2	49.4	30.7
TPCAS2	106.5	124.2	153.0	41.9	36.0	45.5	48.0	29.0
TPCAS4	92.7	107.3	129.4	56.2	35.5	44.7	46.8	25.0

more hydrophobicity of starch molecules due to the substitution of hydroxyl groups by hemiacetal or acetal groups. Similar results were also mentioned for casted cassava starch film crosslinked by lactic, malic or citric acids [19].

3.2 Moisture uptake

Moisture uptake is an important property for packaging applications. Table 1 shows percentage of moisture uptake of TPAS and different TPCAS samples at days 5, 10 and 15. The moisture uptake tended to increase with increasing time for all samples. Nevertheless, increasing glutaraldehyde content caused decrease of moisture uptake, especially for TPCAS4. This was because glutaraldehyde crosslinking led to less hydrophobicity of TPCAS. The results of moisture uptake also corresponded with our swelling results and with the report by El-Tahlawy *et al.* [20] who stated that glutaraldehyde crosslinking agent caused lower hydrophilicity of microcellular foam prepared from corn starch.

3.3 XRD

XRD was used to examine the crystallinity of various starch samples since crystallinity was directly related to the mechanical properties of the starch samples. XRD diffractograms of TPAS and various TPCAS specimens are shown in Figure 2. In general, starch granules can be gelatinized and the glucosidic chains are consequently retrograded into the V form type [21]. TPAS sample gave V-type diffraction patterns with the main diffracted peaks at 2θ of 15.2°, 17.5° and 20.8°. For different crosslinked TPCAS samples (Figure 2), the intensity of the peak at 2θ of 17.5° tended to decrease, indicating that the crystal structure of TPCAS had changed.

The relative crystallinity of TPAS and various TPCAS samples is also shown in Table 1. It can be seen that increase of glutalradehyde content resulted in decrease of crystallinity. The lowest percentage of relative crystallinity was found in TPCAS4 because glutaraldehyde crosslinking restricted orientation of starch molecules, hindering crystal formation. This result was in agreement with the swelling and moisture uptake results. The drop of the crystallinity was also reported for casted cassava starch film crosslinked with citric acid [22].

3.4 Thermal properties

TGA is an important technique for studying the thermal properties of various types of materials. TPAS had 3 degradation steps, as shown in Figures 3(a) and 3(b) for TGA and DTG, respectively.

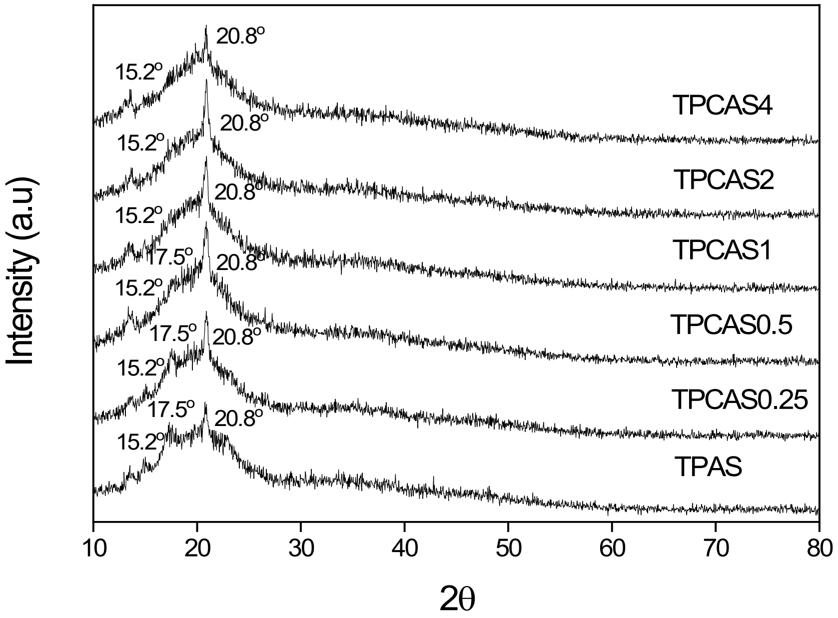

Figure 2. XRD diffractograms of TPAS and different TPCAS polymers

The first step was that of the glycerol plasticizer at the temperature of about 170°C. The second step at the temperature of 280-300°C was probably the degradation of decomposed starch, which had previously been processed at high shear force and temperature. The final step, the main degradation step, occurred from the degradation of starch (310-325°C).

Table 2 presents the thermal decomposition temperatures of TPAS and different TPCAS specimens. It is clear that thermal decomposition temperature of the starch (Step 3) increased with the incorporation of glutaraldehyde. This is because the crosslinking reaction had led to an improved thermal decomposition temperature of TPCAS. The increase of the thermal decomposition temperature corresponded with the SEM micrographs in Section 3.5. The degradation temperatures at 50% weight loss of TPCAS4 and TPCAS1 were similar; however, the thermal degradation temperatures at step 3, the main decomposition temperature of TPCAS4, attributed to starch decomposition, was obviously higher than that of TPCAS1. This was clearly caused by the effect of the gel fraction increment. A similar result was reported for distarch phosphate crosslinked starch blended with native starch [23].

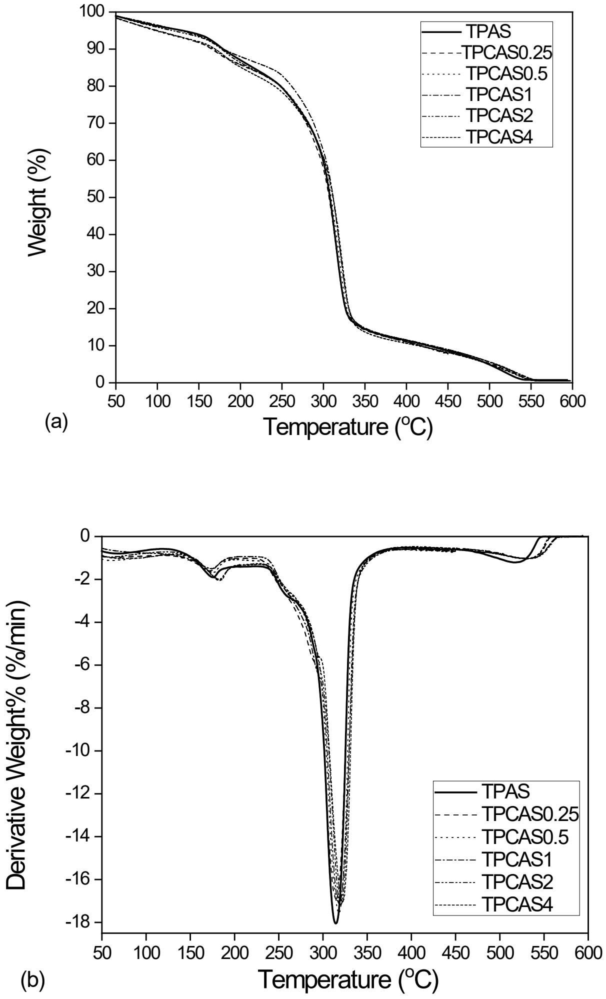

Figure 3. (a) TGA and (b) DTG thermograms of TPAS and several TPCAS polymers

Table 2. Thermal decomposition temperatures of TPAS and different TPCAS polymers

Samples	**Thermal decomposition temperature (°C)**			**Temperature at 50% weight loss (°C)**
	Stage 1 (glycerol)	**Stage 2 (decomposed starch)**	**Stage 3 (starch)**	
0TPCAS	176.0	290.7	314.5	306.1
TPCAS0.25	171.3	289.7	315.0	307.7
TPCAS0.5	174.5	291.8	318.0	309.1
TPCAS1	173.0	293.1	318.3	311.6
TPCAS2	181.8	294.7	320.3	311.2
TPCAS4	182.4	296.8	321.9	311.6

3.5 Morphology

The phase morphology of TPS samples was examined using SEM technique. The fractured surface morphology of TPAS and TPCAS crosslinked by different amounts of glutaraldehyde is shown in Figure 4. It can be seen in Figure 4(a) that TPAS presented with smooth surface morphology without unmolten starch. Nevertheless, surface roughness was observed for various TPCAS samples. Increase of glutaraldehyde content caused more surface roughness due to the presence of unmolten starch. Some starch granules cannot be destroyed and flow under the processing conditions. This corresponded to the higher thermal decomposition temperatures from TGA technique which caused the difficulty for starch melting, especially for TPCAS4 (Figure 4(f)). This morphology confirmed the increase of thermal decomposition temperature in Section 3.4.

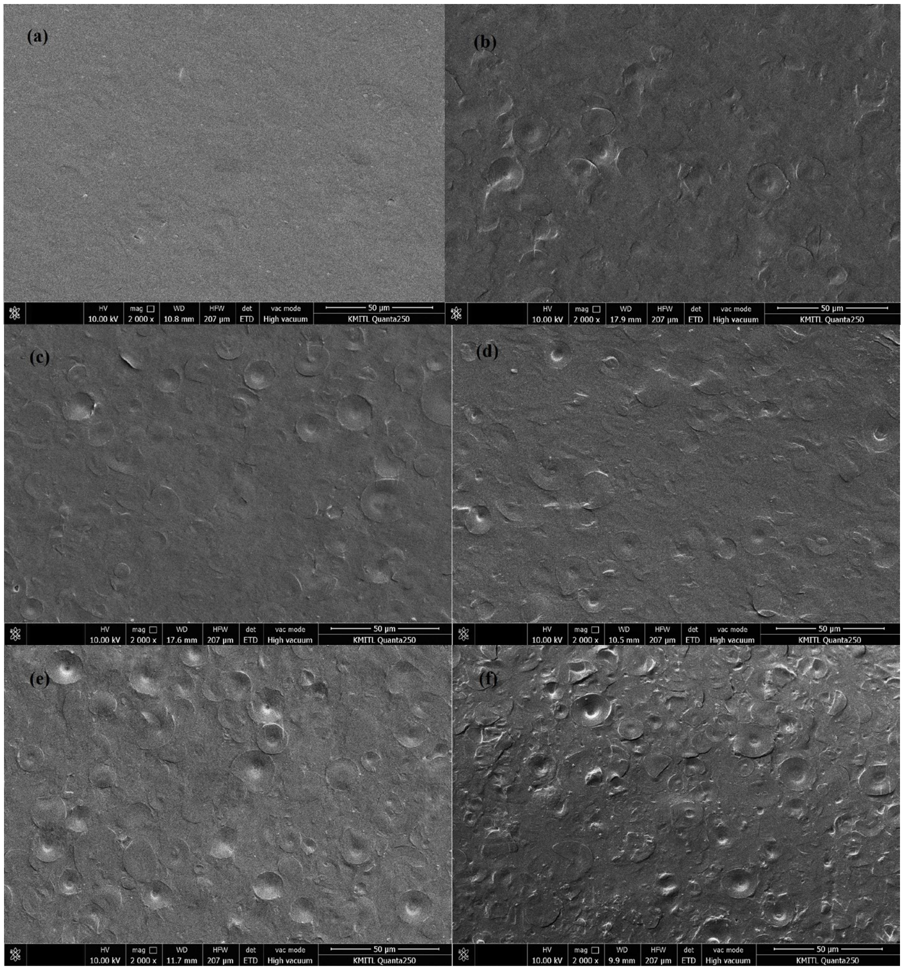

Figure 4. SEM micrographs of (a) TPAS (b) TPCAS0.25 (c) TPCAS0.5 (d) TPCAS1 (e) TPCAS2 and (f) TPCAS4

3.6 Mechanical properties

Mechanical properties are considered as one of the most essential properties for many applications. In Figure 5, TPAS presented the highest stress at maximum load and Young's modulus including the lowest strain at maximum load. However, the use of glutaraldehyde crosslinking agent brought about the decrease of stress at maximum load and Young's modulus but a slight increase of strain at maximum load. This was caused by crosslinked starch structure as glutaraldehyde restricted starch orientation and crystallization (Section 3.3) as well as by some unmolten starch morphology (Section 3.5). At the same time, crosslinking made starch molecules more flexible; therefore, strain at maximum load increased. Stress at maximum load and Young's modulus was in the following order: TPAS > TPCAS0.25 > TPCAS 0.5 > TPCAS1 > TPCAS 2 > TPCAS4. The lowest and highest strain at maximum load was obtained for TPAS and TPCAS4, respectively. The reduction of tensile strength and the increment of elongation at break were also mentioned for PLA/TPS blends with the increase of glutaraldehyde contents [10]. The improvement of the extendibility after crosslinking was also reported for other crosslinked starch films [24, 25].

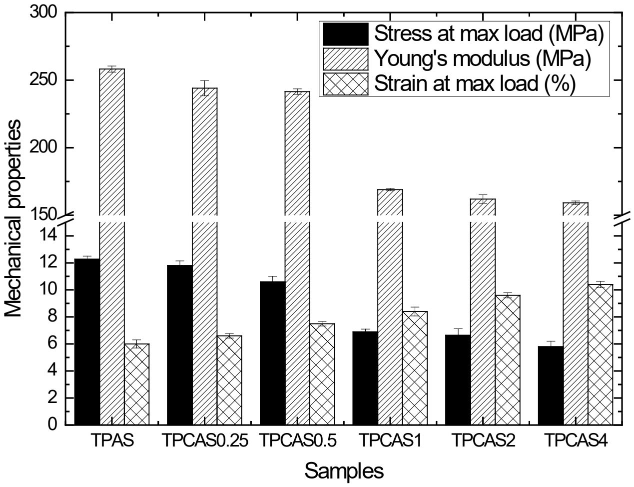

Figure 5. Mechanical properties of TPAS and various TPCAS polymers

3.7 Biodegradability

The biodegradability of TPAS and various TPCAS samples was determined by the decline of mechanical properties after being buried in soil for 5 and 10 days. It can be observed from Figure 6 that all mechanical properties of TPAS and all TPCAS samples decreased markedly after the soil burial test. The decline in mechanical properties was mainly due to hydrolysis from moisture in soil [26]. When glutaraldehyde content increased, the biodegradability of TPCAS samples tended to decrease. It could be observed by the lower drop in the mechanical properties due to the lower hydrophilicity and the more complex glutaraldehyde crosslinked starch structure. Nevertheless, all samples showed biodegradation in the soil burial test.

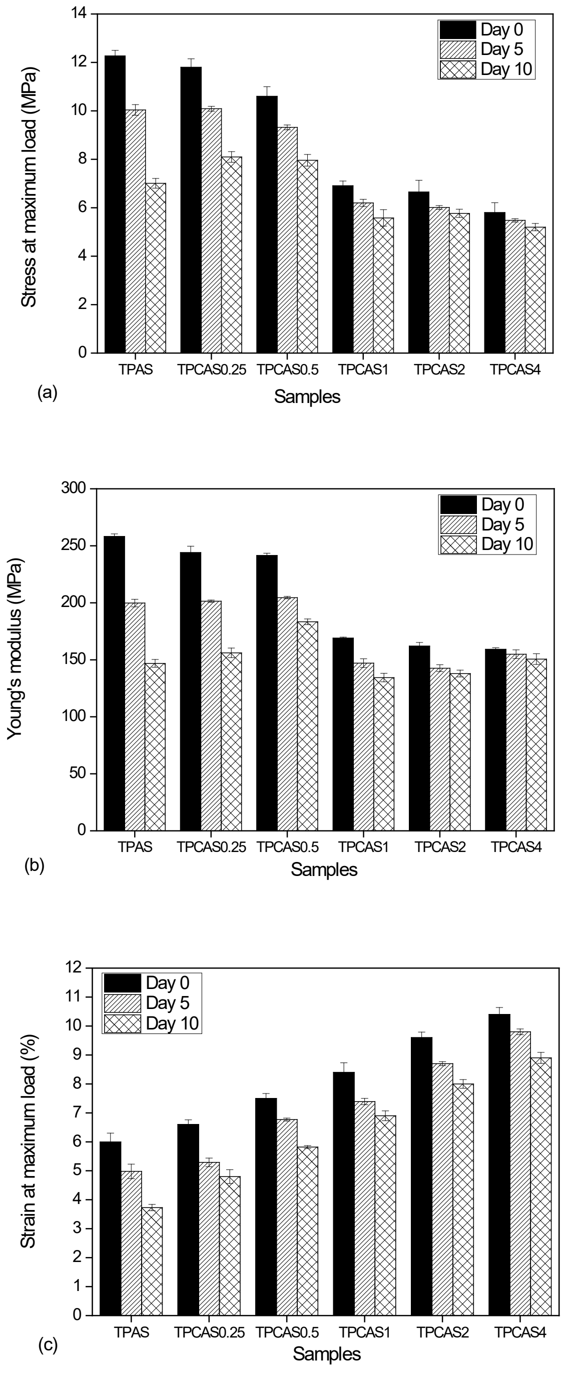

Figure 6. (a) Stress at maximum load (b) Young's modulus and (c) strain at maximum load of TPAS and different TPCAS polymers after soil burial test

4. Conclusions

TPAS and TPCAS samples with various glutaraldehyde content were successfully prepared by the compression molding technique. Glutaraldehyde addition caused the starch crosslinking and resulted in property improvement of the crosslinked starch samples. TPCAS showed decrease in swelling, moisture uptake and crystallinity, attribute to the crosslinking reaction by glutaraldehyde. Furthermore, gel fraction and thermal degradation temperature of different TPCAS specimens increased, leading to the rough fractured surface morphology as observed by SEM technique. In addition, stress at maximum load and Young's modulus decreased with increasing glutaraldehyde content but strain at maximum load increased. All TPAS and TPCAS samples also presented biodegradable properties as examined by the decrease of mechanical properties after the soil burial test. The TPCAS samples, especially TPCAS4, presented high extendibility and low moisture uptake, indicative of the potential application as biodegradable agricultural products such as biodegradable plant pots.

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