Chitosan/Corn Cob Biocomposite Films by Cross-linking with Glutaraldehyde

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Corn cob (CC) was used as a filler in chitosan (CS) biopolymer films. The effect of glutaraldehyde (GLA) as a crosslinking agent was studied in an effort to improve the properties of CS/CC biocomposite films prepared *via* solvent casting. The tensile strength and elongation at break values decreased, but the modulus of elasticity increased with CC content. However, the tensile properties of CS/CC biocomposite films improved when modified with GLA. The Fourier transform infrared (FTIR) results indicated the presence of imine bonds (C=N) and ethylenic groups due to the cross-linking reaction between CS and GLA. The thermal stability of CS/CC biocomposite films reduced with increasing CC content. The modification of CS/CC with GLA enhanced the thermal stability of the biocomposite films. Moreover, the wettability and adhesion of the CC-CS system were enhanced by modification with GLA, as demonstrated by a morphological study. The crosslinking agent glutaraldehyde positively affected the tensile strength, modulus of elasticity, and thermal stability of the biocomposite films.

Keywords: Chitosan; Corn cob; Glutaraldehyde; Biocomposite; Films

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INTRODUCTION

In recent years, researchers have been looking at ways of using biopolymer or biocomposite plastics, which are made from renewable resources and can be naturally recycled by biological processes (Pilla 2011). Their use can help conserve limited natural resources like fossil fuels and reduce greenhouse gas emissions such as carbon dioxide (CO_2). Additionally, biopolymers or biocomposites can substitute for petroleum-based composites and provide equivalent strength-to-weight ratios compared to synthetic plastics. There are four types of biodegradable polymers: (i) agro-polymers (*e.g.*, polysaccharides) obtained from biomass by fractionation; (ii) polyesters obtained by fermentation from biomass or from genetically modified plants (*e.g.*, polyhyroxyalkanoate (PHA)); (iii) polyesters obtained by synthesis from monomers and obtained from biomass (*e.g.*, polylactic acid (PLA)); and (iv) polyesters totally synthesized by petrochemical processes (*e.g.*, polycaprolactone (PCL), aliphatic or aromatic copolyester) (Averous and Digabel 2006; John and Thomas 2008).

Chitosan (CS) is a biopolymer that is derived from chitin or by-products of seafood processing, such as crab shell, lobster shell, and prawn shell waste (Mathew and Abraham 2008; Park *et al.* 2004). Chitosan is the most abundant natural polysaccharide after cellulose and hemicelluloses (González-Campos *et al.* 2009; Onesippe and Lagerge 2008; Singh *et al.* 2009). It is a semicrystalline polysaccharide that contains a considerable amorphous fraction (Mathew *et al.* 2009) and has T_g values from 30 to 222 °C (González-Campos *et al.* 2009). Among biopolymers, chitosan has been considered as one of the most promising materials for future applications on account of its excellent biocompatibility, biodegradability, anti-microbial activity, non-toxicity, and its economic advantages (Rutnakornpituk *et al.* 2006; Singh *et al.* 2009). Besides, when placed into a solution of relatively low pH, chitosan can be dissolved as a cationic polyelectrolyte (Tuhin *et al.* 2012). Chitosan is readily soluble in dilute acidic solutions below pH 6.0 and can therefore be considered a weak base. The pH-dependent nature of chitosan can be attributed to the presence of primary amine groups (Pillai *et al.* 2009).

Through reaction with a cross-linking agent, chitosan may obtain hydrogel-like properties, which allows it to be used in a wide range of applications such as food packaging, wastewater treatment, and drug delivery systems (Thanpitcha *et al.* 2006; Tuhin *et al.* 2012). There have been numerous studies on chitosan, such as chitosan blended with natural polymer (Garcia *et al.* 2006; Senna *et al.* 2012; Zhai *et al.* 2004), synthetic polymer (Salmah and Azieyanti 2011; Salmah *et al.* 2011, 2012a), and modified chitosan (Ambri *et al.* 2013; Beppu *et al.* 2007; Rutnakornpituk *et al.* 2006). However, there is a lack of literature on the development of natural filler in chitosan biocomposite films.

Most researchers are more interested in the utilization of agricultural wastes such as corn cob (Chun and Husseinsyah 2013), palm kennel shell (Salmah *et al.* 2013), coconut shell (Chun *et al.* 2012; Salmah *et al.* 2012b), and chitosan (Salmah and Azieyanti 2011; Salmah *et al.* 2011) to produce biocomposites that reduce cost as well as enhance the properties and biodegradability of biocomposites. Corn (*Zea mays*) is a biomass resource that is cultivated around the world. A greater weight of corn is produced each year than other grains. Corn cob as a natural filler in polymer could have economic advantages; however, natural filler-filled polymer may result in poor properties compared to neat polymer due to poor filler-matrix adhesion and wettability. Chemical modification is one of the ways to enhance the properties of biocomposites.

Cross-linking is an example of a chemical modification of chitosan to enhance the properties of biocomposite films (Beppu *et al.* 2007; Tsai and Wang 2008; Xiong *et al.* 2009; Yu *et al.* 2011). Cross-linking reactions usually occur between the active groups of a cross-link agent (*e.g.*, aldehyde groups, acid groups, and epoxy groups) and the amino groups of CS (Robinson 2008). Most studies have reported that glutaraldehyde is one type of crosslinking agent that can improve tensile and thermal properties of biocomposites (Uragami *et al.* 1994). Thus, a three-dimensional network is formed, which reduces the mobility of the polymer chain because of the formation of new inter-chain linkages (Bhatia 2012; Robinson 2008). Furthermore, cross-linking modification of chitosan can alter the degradation profile of chitosan (Sarmento and Neves 2012). Among cross-linking agents, glutaraldehyde (GLA) is the most commonly used in chitosan (Bhatia 2012; Robinson 2008; Sarmento and Neves 2012; Mathew *et al.* 2009). The reaction with glutaraldehyde occurs through Schiff base reaction between aldehyde groups of GLA and some amino groups of chitosan to form imine bonds (Bhatia 2012; Robinson 2008).

The aim of this work was to investigate the effect of CC content on mechanical, thermal, and morphological characteristics of CS/CC biocomposite films. The effect of glutaraldehyde (GLA) was evaluated as a crosslinking agent in chitosan in an effort to improve the properties of CS/CC biocomposites films.

EXPERIMENTAL

Materials

Chitosan (CS) (used as matrix) was supplied by Hunza Nutriceuticals Sdn. Bhd. (Malaysia), with an average size of 80 µm and degree of deacetylation (DD) of 90%. The average molar mass of CS is 1000000 g/mol. Corn cob (CC) was obtained from a market in Perlis, Malaysia. Firstly, the CC was cleaned manually, then crushed and ground into powder form. After that, the CC powder was dried at 80 °C for 24 h. The particle size of CC was analyzed using a Malvern particle size analyzer. The average particle size of CC was 38 µm. Glutaraldehyde was supplied by Sigma-Aldrich. The main composition of CC was 41.27% cellulose, 46% hemicellulose, and 7.4% lignin (Wang *et al.* 2010; Wanitwattanarumlug *et al.* 2012).

Preparation of Unmodified and Modified CS/CC Biocomposite Films

The unmodified and modified CS/CC biocomposite films were produced using a solvent casting method. Chitosan powder (10 g) was dissolved in acetic acid (1 v/v %) and stirred for 30 min. Then, the CC powder was added and stirred until it became homogenous (15 min). After that, unmodified CS/CC biocomposite solution was poured into a mould and dried at room temperature for 48 h. The acrylic plastic mould was used for casting films with dimensions of 15 x 15 cm. For modified biocomposite films, the first GLA was dissolved in distilled water to produce a 1 v/v % GLA solution. Then, 1% of GLA solution was mixed with (1.5 w/v %) chitosan solution, and corn cob was added slowly to the solution. The CS/CC biocomposite films were prepared in ratios CS: CC of 100:0; 90:10; 80:20; 70:30; 60:40 with and without the addition of GLA as crosslinking agent.

Fourier Transform Infrared (FTIR)

FTIR analysis was carried out with a Perkin Elmer, Model L1280044 instrument. The attenuated total reflectance (ATF) method was used. Four scans in the wavenumber (cm^{-1}) range 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1} were recorded for each sample.

Tensile Testing

The tensile test was conducted using an Instron universal testing system, Model 5569, according to ASTM D 882. The tensile properties (tensile strength, modulus of elasticity, and elongation at break) of biocomposite film can be obtained from tensile tests. A cross-head speed of 15 mm/min was used and the test was carried out at 25 ± 3 °C. Specimens of size of 100 × 15 mm were cut from each biocomposite film. At least five specimens were tested for each sample and the average value was recorded. The biocomposite films tensile test was repeated three times to get the accuracy value.

Thermogravimetric Analysis (TGA)

TGA was used to determine the composition and thermal stability of CS/CC biocomposite films. The TGA analysis was performed by a TGA Pyris Diamond (Perkin-Elmer). Before starting thermal degradation tests, the samples were dried at 50 ^{o}C to remove moisture until constant weight. The samples, about 7 ± 2 g in weight, were heated at a rate of 10 °C/min. Measurements were taken from 30 °C to 600 °C and nitrogen gas was used as the purge gas at a flow rate of 50 mL/min.

Morphological Study

The tensile fracture surface of the CS/CC biocomposite film was analyzed using a scanning electron microscope (SEM), model JEOL JSM-6460 LA, at a voltage of 5 kV. The fracture surfaces of samples were coated with a thin layer of palladium for conductive purposes.

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR) Analysis

The FTIR spectra of unmodified and modified CS/CC biocomposite films are shown in Fig. 1. The broad peak at 3800 to 3000 cm^{-1} was assigned to the –OH group. The absorption peak at 2920 cm^{-1} was ascribed to C-H stretching. The peaks at 1634 cm^{-1} and 1550 cm^{-1} indicated the N-H bending of NH_2. Moreno-Osorio *et al.* (2010) reported that the peak at 1560 cm^{-1} was assigned to NH_3-CH_3COO- in chitosan. However, there was no peak that related to the free aldehydic group near 1720 cm^{-1}. The peak at 1408 cm^{-1} was attributed to –CH_2 deformation vibration from cellulose or C-H deformation in lignin. The C-H group deformation was illustrated by the band at 1328 cm^{-1}. Furthermore, the sharp peak at 1151 cm^{-1} corresponded to the ether bond C-O-C of chitosan. The broad peak in the range of 1000 to 1150 cm^{-1} indicated C-O-C and C-O groups, respectively. Chitosan showed a saccharide structure due to the presence of peaks at 1151, 1063, 1022, and 897 cm^{-1}. Similar observations were reported by Dhawade and Jagtap (2012). Additionally, the peak at 897 cm^{-1} was attributed to the C-H bending vibration. After modification with GLA, the intensity increased from 1550 cm^{-1} to 1547 cm^{-1} due to the ethylenic C=C bonds from the CS-GLA cross-linking chain overlapped with N-H of CS.

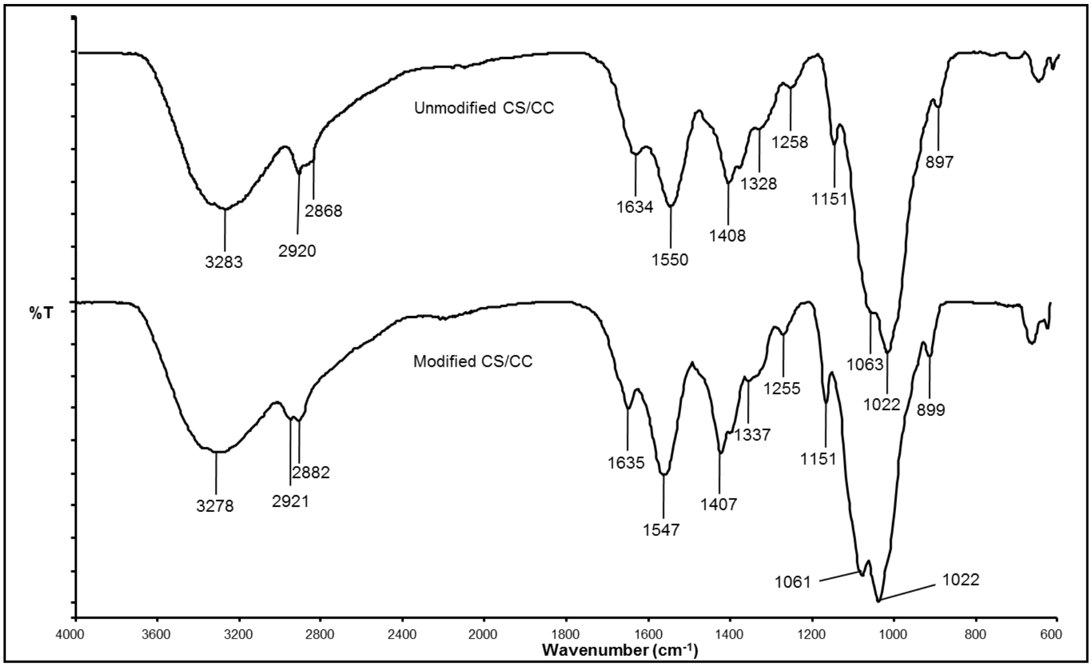

Fig. 1. FTIR analysis of unmodified and modified biocomposite films

The intensity of the band at frequency 1634 cm^{-1} also increased due to the formation of C=N imine bonds in GLA cross-linked with CS through Schiff base reactions between amino groups of CS and aldehyde groups of GLA. Monteiro and Airoldi (1999) reported that the presence of imine C=N and ethylenic C=C bonds is associated with CS-GLA interaction.

Tensile Properties

The stress-strain curves of unmodified and modified CS/CC biocomposite films are shown in Fig. 2. These curves reveal the brittle nature of the CS films. The addition of CC filler reduced the ductility of CS. It can be observed that the modified CS/CC biocomposite films with GLA showed higher tensile stress as compared to the unmodified films. This is attributed to the presence of GLA, which formed bonding imine linkages with CS, and thus improved the interfacial interaction of CS and CC biocomposite films.

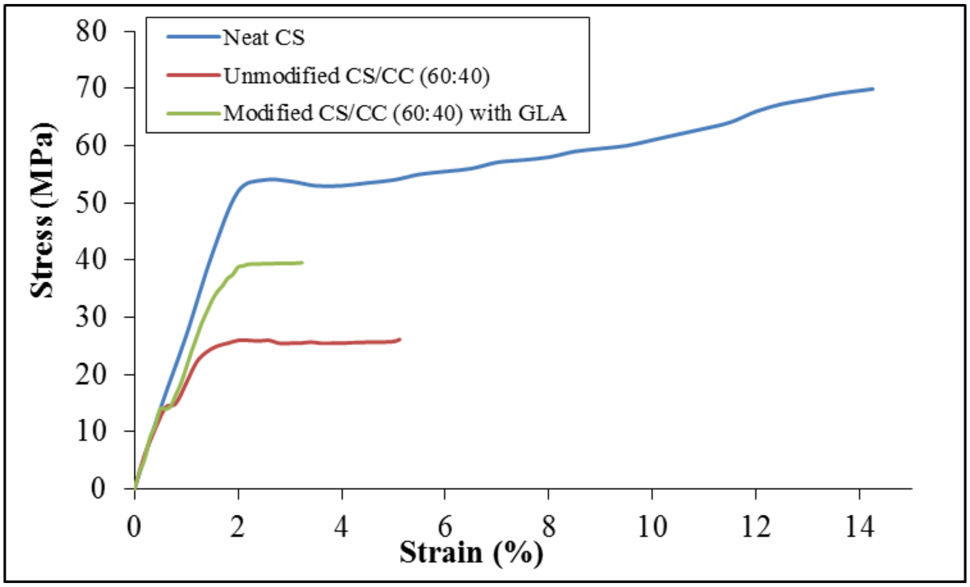

Fig. 2. Stress-strain curves of neat CS, unmodified, and modified biocomposite films

Figure 3 exhibits the tensile strength of unmodified and modified CS/CC biocomposite films. The results show that the tensile strength decreased with increasing CC content due to weak interfacial bonding and wettability between CC filler and CS matrix. This phenomenon was supported by the SEM study of CS/CC biocomposite films.

A micrograph of CC filler is shown in Fig. 4. The irregular shape of corn cob filler with a low aspect ratio led to poor adhesion between CC filler and CS matrix when stress was applied, resulting in a decrease of tensile strength. Similar observations have been reported by many researchers (Chun *et al.* 2013; Amri *et al.* 2013). The tensile fracture surface of neat CS showed a homogeneous surface and matrix tearing (Fig. 5). The SEM micrograph of unmodified CS/CC biocomposite film at 40 wt% CC content is shown in Fig. 6. The micrograph of CS/CC biocomposite film exhibited a rough surface. The micrograph showed the agglomerates pulled out of CC from the CS matrix. This micrograph indicates poor wettability and interfacial interaction between CS matrix and CC filler, resulting in a decrease of tensile strength at higher content of CC. Nevertheless, modification with GLA improved the tensile strength of CS/CC biocomposite films. This is due to GLA forming covalent imine bonds with the amino groups of CS *via* Schiff base reactions, enhancing the adhesion between CC filler and CS matrix. The schematic reaction between GLA and CS is illustrated in Fig. 7. This result was proven by micrograph SEM of modified biocomposite film in Fig. 8 that showed better dispersion and less pulled out of CC. It can be confirmed that modification with GLA improved the wettability and interfacial adhesion between CS and CC.

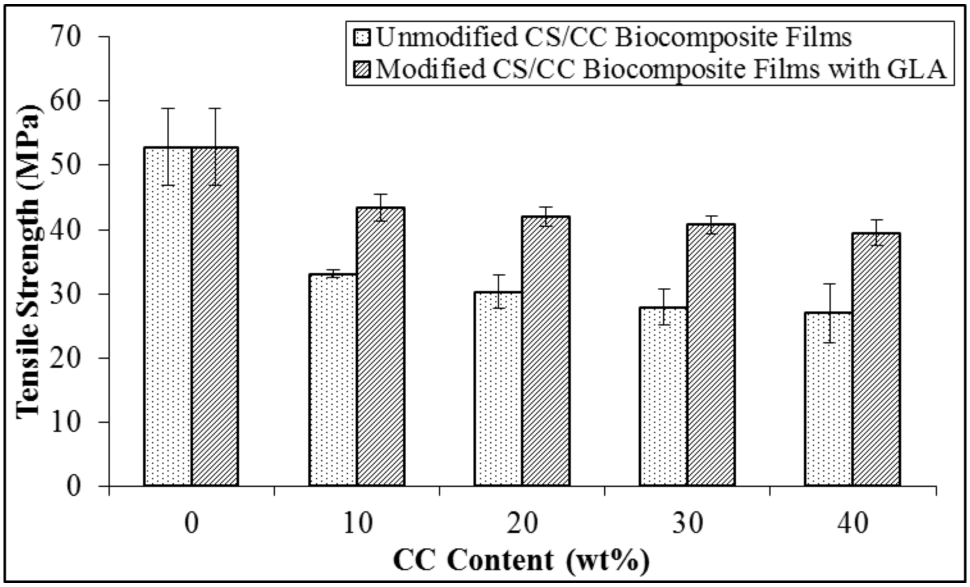

Fig. 3. Effect of CC content on tensile strength of unmodified and modified CS/CC biocomposite films

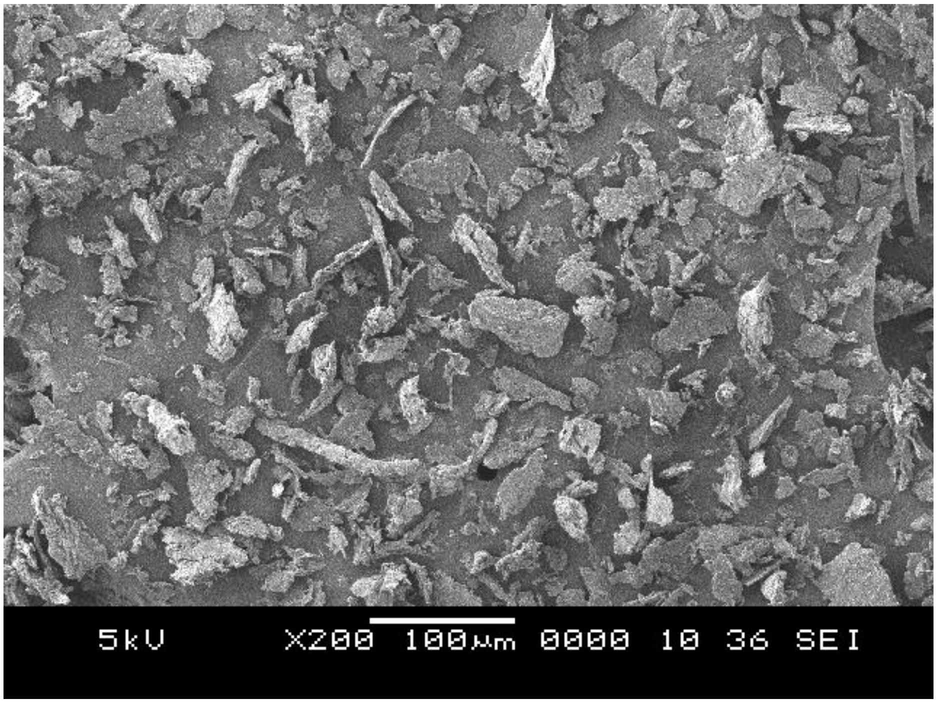

Fig. 4. SEM micrograph of corn cob

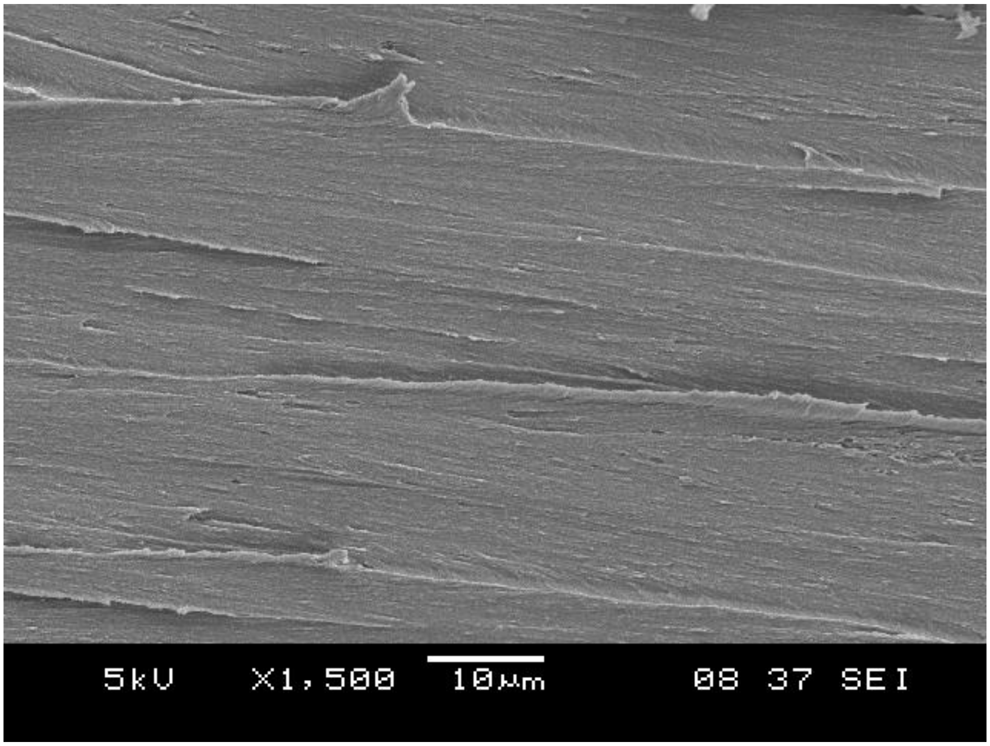

Fig. 5. SEM micrograph of neat CS

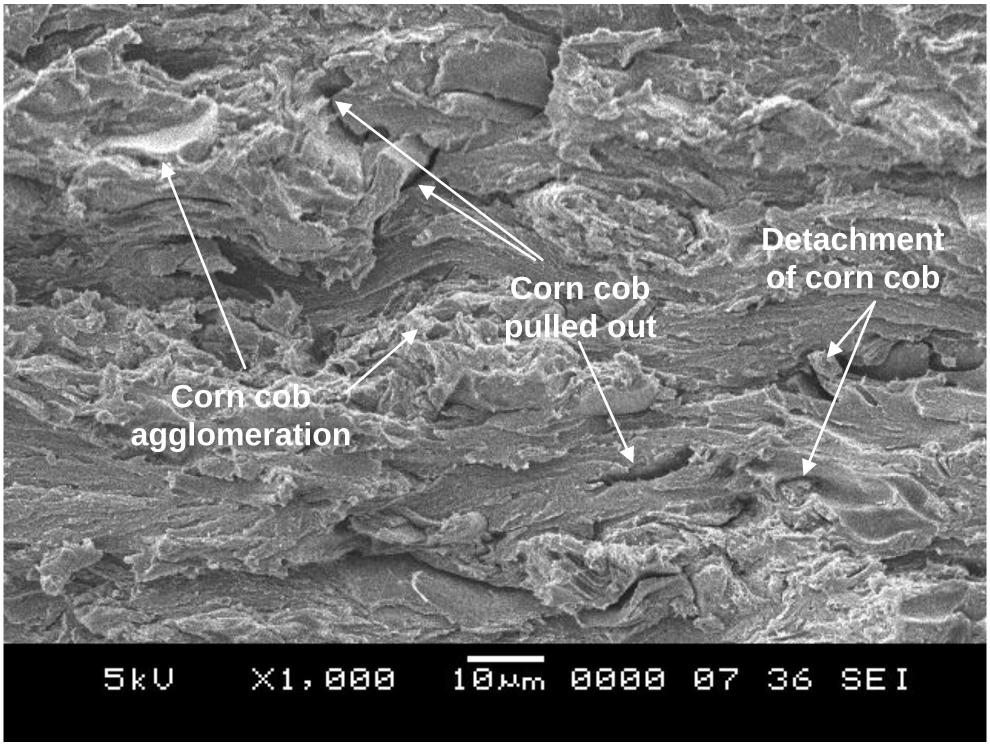

Fig. 6. SEM micrograph of unmodified CS/CC biocomposite film at 40 wt% CC content

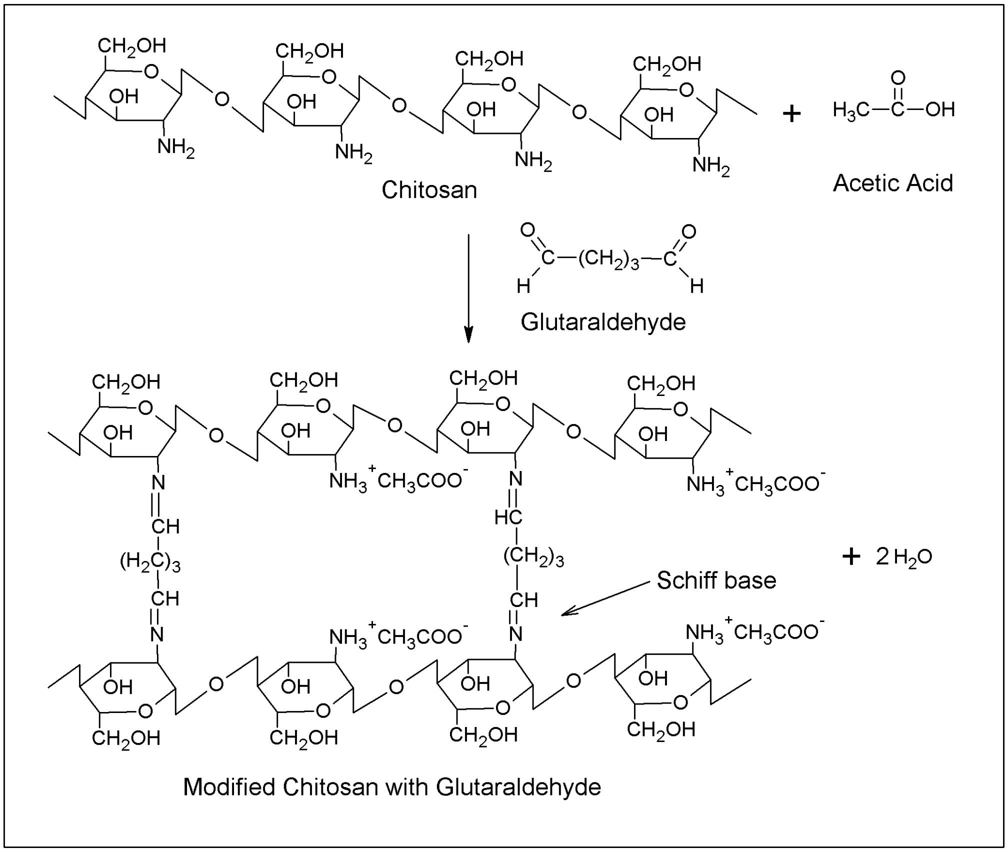

Fig. 7. Schematic reaction between GLA and CS

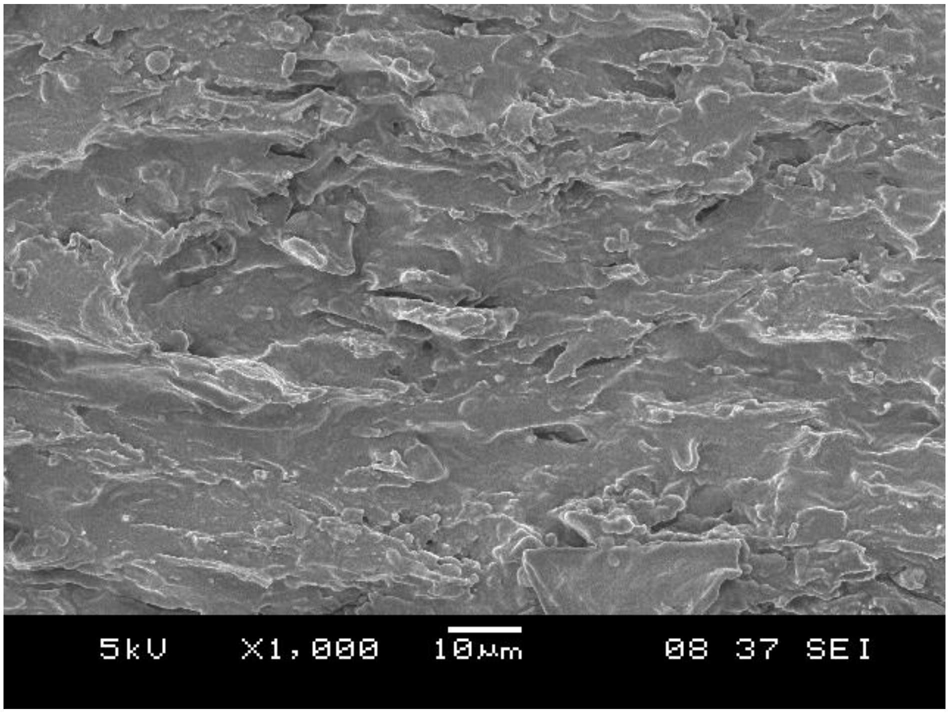

Fig. 8. SEM micrograph of modified CS/CC biocomposite film at 40 wt% CC content

In addition, the modulus of elasticity of unmodified and modified CS/CC biocomposite films is shown in Fig. 9. The modulus of elasticity of biocomposite films increased with increasing CC content. The addition of CC into CS increased the stiffness of the biocomposite films and decreased the ductility of CS matrix. On the other hand, the modulus of elasticity of modified CS/CC biocomposite film was higher than that of the unmodified film. The formation of imine linkage increased the stiffness of the CS/CC biocomposite films. The increased modulus elasticity film was attributed to the formation of three-dimensional network between GLA and CS.

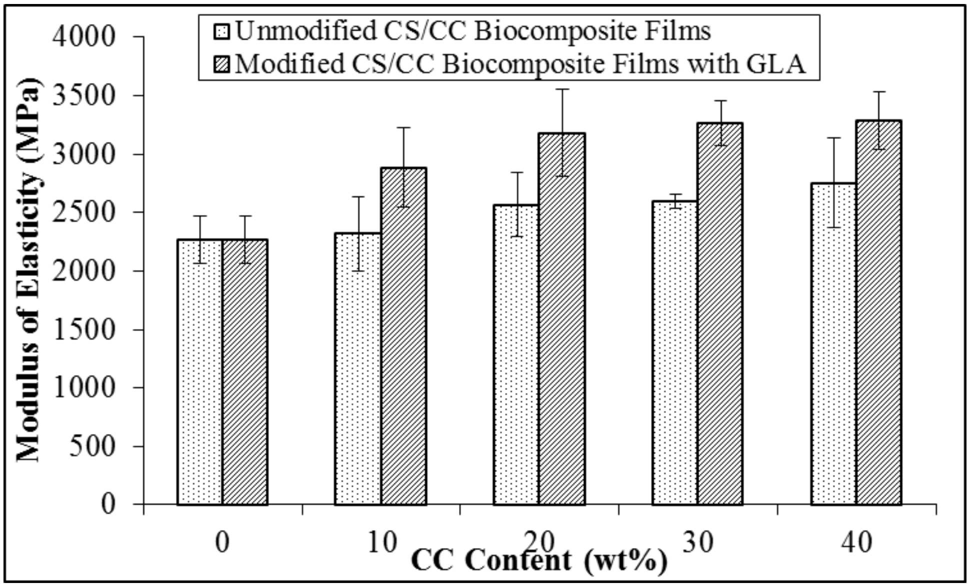

Fig. 9. Effect of CC content on modulus of elasticity of unmodified and modified CS/CC biocomposite films

Figure 10 illustrates the elongation at break of unmodified and modified CS/CC biocomposite films.

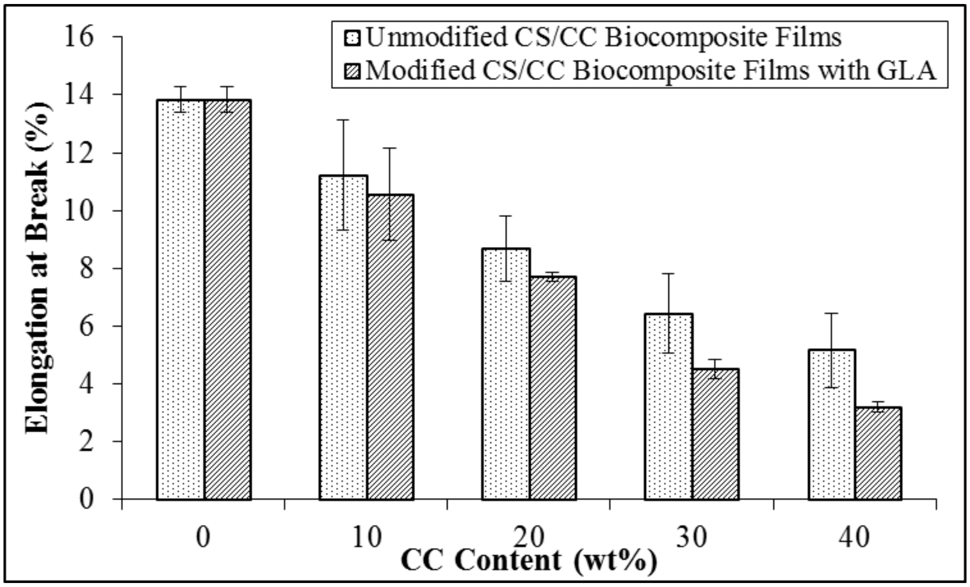

Fig. 10. Effect of CC content on elongation at break of unmodified and modified CS/CC biocomposite films

It can be seen that the elongation at break of biocomposite films was reduced with increasing CC content. The incorporation of CC filler reduced the chain mobility and enhanced the rigidity of CS/CC biocomposite films. However, the modified film had lower elongation at break compared to unmodified biocomposite films. This indicated that the improvement of interfacial interaction between CS and CC with GLA has reduced the elongation at break of modified biocomposite films.

Thermogravimetric Analysis (TGA)

Figures 11 and 12 show the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of unmodified and modified CS/CC biocomposite films. The TGA and DTG data are summarized in Table 1. From the DTG curve, the neat CS exhibited two stages of weight loss. The first stage of weight loss of chitosan was 16%, starting at about 50 °C, followed by a weight loss of 41% from 200 °C to 300 °C. The first stage of weight loss was associated with the evaporation of absorbed water, whereas the second stage was assigned to the decomposition of chitosan and vaporization and elimination of volatile products. This is due to the fact that pyrolysis of polysaccharides starts with a random splitting of glysidic bonds, followed by further decomposition (Neto *et al.* 2005). CC also decomposed in two stages. The first stage of weight loss at 55 °C was attributed to loss of water, and the second stage showed a decomposition peak within the range 200 to 400 °C, which was assigned to the decomposition of hemicellulose, cellulose, and lignin. However, the decomposition of unmodified and modified CS/CC biocomposite films occurred in three stages. Both of the films showed weight loss at a temperature of 300 °C, which was attributed to the thermal decomposition of hemicelluloses in CC. A shoulder peak for each of the CS/CC biocomposite films occurred in the temperature range of 310 to 350 °C.

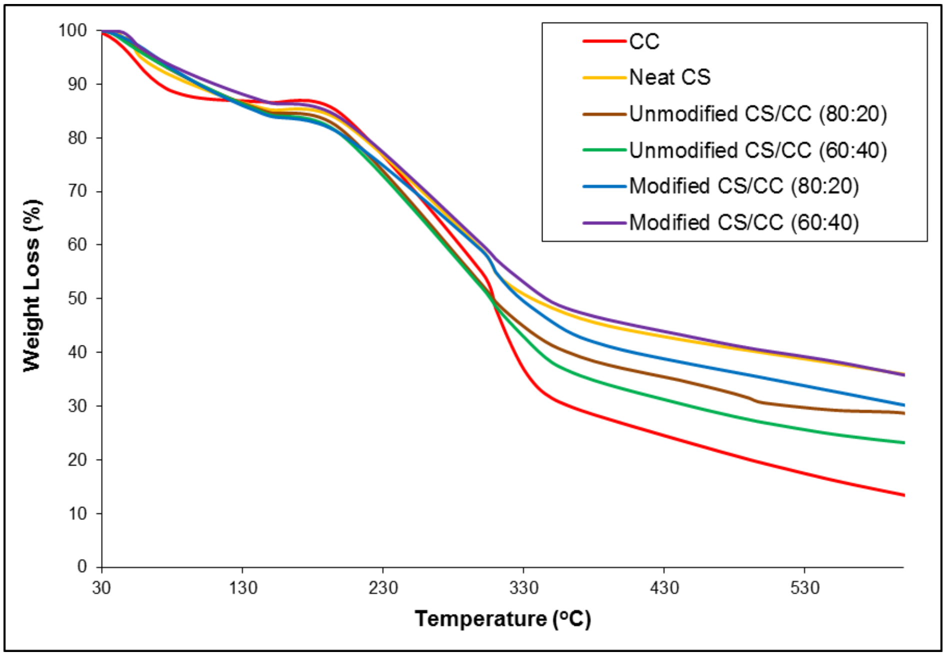

Fig. 11. TGA curve of unmodified and modified CS/CC biocomposite films

The T_{dmax} and char residue at 200 °C and 600 °C of unmodified CS/CC biocomposite films decreased with increasing CC content. Nevertheless, the char residue of the modified biocomposite films at 600 °C was higher than unmodified. This is due to the fact that GLA as crosslinking agent enhanced the degradation of biocomposite films.

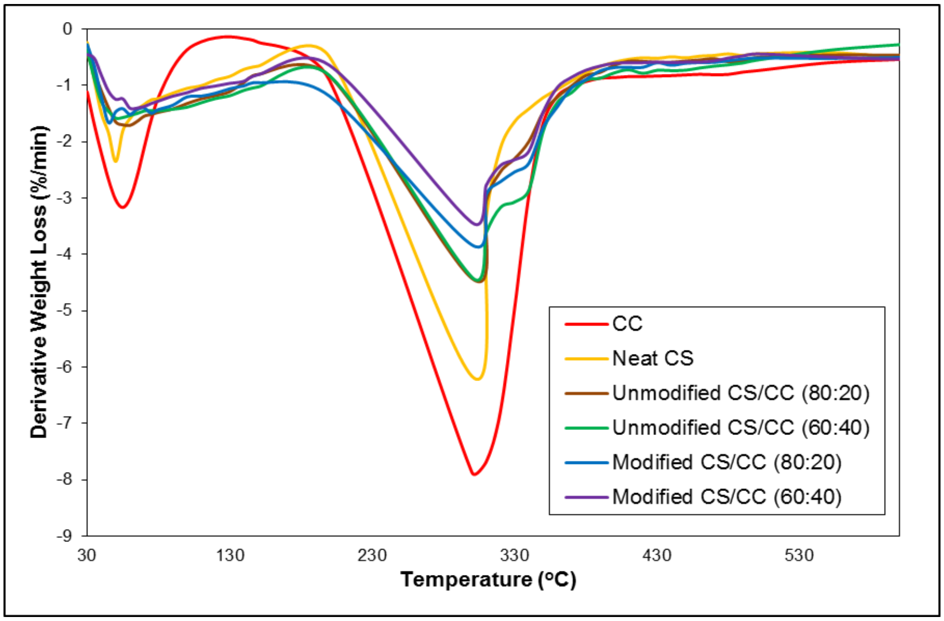

Fig. 12. DTG curve of unmodified and modified CS/CC biocomposite films

Table 1. TGA and DTG Data of Unmodified and Modified CS/CC Biocomposite Films

Material		Char residue (%)	
	T_{dmax} (°C)	200 °C	600 °C
CC	300	84	13
Neat CS	293	83	36
Unmodified CS/CC (80:20)	285	81	29
Unmodified CS/CC (60:40)	272	80	23
Modified CS/CC (80:20) with GLA	284	82	30
Modified CS/CC (60:40) with GLA	274	84	36

CONCLUSIONS

1. The utilization of corn cob in chitosan biocomposite films enhanced the modulus of elasticity, but it reduced the tensile strength and elongation at break with increasing CC content.
2. The biocomposite films modified with GLA had enhanced tensile properties, which meant higher tensile strength and modulus of elasticity, but lower elongation at break than unmodified CS.
3. The modified CS/CC biocomposite films showed better thermal stability than unmodified due to the presence of imine linkages. GLA also improved the CC dispersion, wettability, and interfacial interaction of biocomposite films.

4. The FTIR results of biocomposite films showed that the GLA formed imine C=N and ethylenic C=C bonds, indicating interaction between CS and GLA in CS/CC biocomposite films.

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