Corn Starch Reactive Blending with Latex from Natural Rubber in Presence of Na⁺ Ions of Carboxymethyl Cellulose as a Catalyst

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Abstract

Corn starch (CS) was blended with glycerol, latex natural rubber (LNR), and carboxymethyl cellulose (CMC). The addition of 10 phr of CMC improved the Young's modulus (6.7 MPa), tensile strength (8 MPa), and elongation at break (80%) of the CSG/LNR blend. The morphology of the CSG/LNR/CMC blends showed a uniform distribution of LNR particles (1–3 μm) in the CSG matrix. The addition of CMC enhanced the swelling ability and water droplet contact angle of the blends owing to the swelling properties, interfacial crosslinking, and amphiphilic structure of CMC. Fourier transform infrared spectroscopy confirmed the reaction between the C=C bond of LNR and the carboxyl groups ($-\text{COO}^-$) of CMC, in which Na^+ ions in CMC acted as a catalyst. Notably, the mechanical properties of the CSG/LNR/CMC blend were improved owing to the miscibility of CSG/CMC and the CMC/LNR interfacial reaction.

Introduction

Biodegradable polymers have attracted considerable attention because they are environmentally friendly with excellent degradation abilities. They can be especially competitive in certain sectors of the plastic market, such as food packaging [1, 2] at both the industrial and street food levels, where hygiene must be practiced to prevent packaging contamination [3]. Petroleum polymers generated from petroleum resources subjected to depletion have detrimental effects on the environment. Therefore, biodegradable polymers are widely investigated to replace petroleum polymers, such as polylactic acid (PLA) [4], polybutylene succinate (PBS) [5], and thermoplastic starch (TPS) [6].

Starch is a natural polymer possessing desirable traits, such as complete biodegradability, low cost, and renewability. Starch is produced from plants that are widely consumed by humans. Starch is a semi-crystalline biopolymer whose structure contains starch granules with different amylose/amylopectin ratios depending on the starch resources and gelling properties of water and heat [7]. Starch processing involves chemical reactions, including melting, gelatinization, and water diffusion [8]. Some common starch resources have been investigated, such as cassava [9] and corn [10], along with the development of special enzymes that can degrade starch under harsh conditions [11]. Corn starch (CS) is the world's largest starch resource [12] and is widely used in food processing [13].

Natural rubber (NR) is extracted from some plants to obtain a latex. This latex from NR (LNR) has a relatively high water content and up to 60% rubber content. Ammonia is a common chemical used to prevent coagulation and bacterial growth in LNR [14]. Because of its excellent properties, LNR is used extensively to manufacture several products (e.g., gloves, balloons, rubber boots, and condoms). LNR is also the main natural polymer resource for the global agricultural economy; however, NR prices have dropped because of economic conditions [15]. There are some studies on NR blending utilizing starch [16]. The mechanical properties of NR blends can be improved by crosslinking certain functional groups in rubber using various methods [17].

CMC is a cellulose derivative obtained from alkali cellulose and sodium salt reactions [18]. The main applications of CMC include food, paper, printing, medicine, and packaging. CMC has carboxylic groups with Na^+ ions [19] and exhibits high viscosity and non-toxic properties. CMC can also act as a compatibilizer to improve the properties of starch [20].

However, few studies have investigated the mechanical property improvement in starch blended with NR undergoing a reaction with CMC. Therefore, in this study, CS was blended with glycerol, LNR, and CMC to improve the blend properties. High compatibility of CS/CMC, and reaction between CMC and LNR were suggested to improve mechanical properties of the blends. A tough, transparent, water-resistant biodegradable material having high tensile properties was developed. The effects of CMC addition and presence of Na^+ ions in CMC were investigated. The tensile properties, morphology, water resistance, and reaction mechanisms were also evaluated.

Results And Discussions

Mechanical properties. CS was blended with glycerol, CMC, and LNR through solution mixing at 80°C for 1 h. The mixed solutions were cast onto films, followed by drying at 60°C for 24 h. Figure 1 shows the stress–strain curves of the CSG/LNR blends with 0–20 phr of CMC. The Young's modulus was calculated from the slope at the early stage of the stress–strain curve. The CSG/LNR blend showed a low Young's modulus of 0.3 MPa, a maximum tensile strength of 0.5 MPa, and an elongation at break of 30% (Table 1). The addition of CMC resulted in an increase in the values of Young's modulus and maximum tensile strength. The CSG/LNR/CMC10 blend exhibited a Young's modulus of 6.7 MPa, a maximum tensile strength of 8 MPa, and an elongation at break of 80%, all the values higher than those for the blends where CMC was added at 0, 2, and 5 phr. The CSG/LNR/CMC20 blend exhibited the highest Young's modulus (18.2 MPa) and maximum tensile strength (18 MPa) and the lowest elongation at break because of the high tensile strength and brittle properties of CMC. The toughness and tensile properties of the CSG/LNR blend were improved by adding CMC, particularly for the CSG/LNR/CMC10 sample. The toughness of the sample is related to the area under the stress–strain curve [21]. The Young's modulus of starch increased with the CMC content [22], and a high interfacial reaction improved the mechanical properties of the polymer blends, which has been reported previously [23]. The improvement in the tensile properties was attributed to the compatibility of CSG/CMC, occurrence of the interfacial reaction of CMC/LNR, and crosslinking inside the LNR phase.

Table 1

Young's modulus, maximum tensile strength, and elongation at break of CSG/LNR blends with 0–20 phr CMC.

Sample	Young's modulus (MPa)	Maximum tensile strength (MPa)	Elongation at break (%)
CSG/LNR	0.3 ± 0.08^a	0.5 ± 0.08^a	30.1 ± 2.40^b
CSG/LNR/CMC2	2.4 ± 0.07^b	1.7 ± 0.12^b	35.4 ± 2.89^c
CSG/LNR/CMC5	2.8 ± 0.08^c	2.9 ± 0.21^c	33.3 ± 3.21^c
CSG/LNR/CMC10	6.7 ± 0.08^d	8.0 ± 0.43^d	79.9 ± 4.35^d
CSG/LNR/CMC20	18.2 ± 0.08^e	18.0 ± 2.1^e	7.80 ± 0.51^a
Means with different lowercase superscript letters in the same column are significantly different ($P < 0.05$).			

Morphology. The morphologies of the samples were observed using SEM. The samples were disintegrated in liquid nitrogen, and then the LNR phase on the fracture surface was extracted using an immersion technique in toluene at 60°C for 1 h. Figure 2 shows the fracture surface images of the CSG/LNR and CSG/LNR/CMC blends with 2, 5, 10, and 20 phr of CMC. The CSG/LNR blend exhibited a black circle representing the LNR particles extracted using toluene because NR was dissolved in toluene [24]. The LNR particle sizes of the CSG/LNR blend were 1–3 μm . The addition of CMC at 2, 5, 10, and 20 phr resulted in the dispersion of the LNR rubber particles (1–3 μm) in the CSG matrix. The LNR formed small rubber particles in the CSG matrix, while the addition of CMC did not reduce the particle size of the LNR. The improvement in the tensile properties was probably due to the high tensile properties of CMC, interfacial crosslinking of CSG/LNR, and crosslinking inside the LNR phase.

Solubility and swelling. The solubility and swelling of the samples were measured by dissolving the samples in distilled water at 25°C for 24 h. The CSG film was prepared through a controlled mixing of starch with glycerol (70/30 %w/w). The solubility and swelling degree of the CSG/LNR film were 41 and 65%, respectively (Fig. 3). The solubility of CSG/LNR/CMC2 decreased to 22% owing to the formation of interfacial crosslinking between the CMC and LNR. The elevated CMC content increased the solubility of the CSG/CMC/LNR blends because of the large amount of hydrophilic materials. The degree of swelling increased with the CMC content. CS is a hydrophilic material [25], whereas CMC forms a gel in water [18, 26]. The increase in the swelling degree was an evidence of the hydrophilic properties of CS and CMC [25, 27], the swelling ability of CMC [28], and the interfacial crosslinking of CSG/LNR through CMC.

Contact angle. The water droplet contact angle is related to the hydrophilicity and surface tension of materials. Figure 4 shows the contact angle of CSG and the CSG/LNR blends with 0–20 phr of CMC at 3 min. The CSG exhibited a low contact angle of 61°. The contact angle of the CSG/LNR blends increased with increasing CMC content, especially for 20 phr. CS is a polar material, whereas amphiphilic CMC

combines polar and non-polar structures [27]. The increase in the contact angle of the CSG/LNR blend was probably caused by small hydrophobic rubber particles that were finely dispersed in the CSG matrix. The increase in the contact angle of CSG/LNR/CMC2 was possibly due to the interfacial crosslinking between LNR and CMC and the non-polar portion of CMC. The addition of 5–20 phr of CMC increased the contact angle to 85–90°, respectively, owing to the enhanced non-polar portion of CMC.

Reaction mechanism. The reaction mechanisms of CSG, CMC, and LNR were investigated using FTIR. Figure 5 shows the FTIR spectra of CMC, CSG, and the CSG/LNR blends with 0–20 phr of CMC. The FTIR spectra of LNR (cis-1,4 polyisoprene) exhibited C–H stretching (2960, 2927, and 2852 cm^{-1}), C = C stretching (1661 cm^{-1}), C–H deformation of stretching $-\text{CH}_2-$ (1448 cm^{-1}), C–H deformation of $-\text{CH}_3$ (1376 cm^{-1}), and C = C–H (835 cm^{-1}) [29]. The CSG spectra exhibited peaks at 1643 (–OH bending), 1016, and 929 cm^{-1} (–CO stretching) [30]. The CMC spectra exhibited peaks at 3040 (–OH stretching), 2897 (–CH stretching), 1602 (COO^-), and 1427 cm^{-1} (COO^-Na^+) [31]. The spectra of the CSG/LNR blend exhibited a combination of the individual CSG and LNR spectra. The CSG/LNR/CMC blend presented an increase in peak intensities at 1602 (COO^-) and 1427 cm^{-1} (COO^-Na^+) of CMC. To study the reaction mechanism of the blend, the LNR phase was extracted from the CSG/LNR and CSG/LNR/CMC blends. The spectra of CSG, CMC, LNR, and the extracted LNR are shown in Fig. 6. The extracted LNR from the CSG/LNR (Fig. 6d) exhibited spectra similar to those of pure LNR (Fig. 6c) with peaks at 1661 (C = C stretching) and 835 cm^{-1} (C = C–H). Furthermore, in the LNR extracted from the CSG/LNR/CMC blend, the peak at 1661 cm^{-1} (C = C) shifted to 1657 cm^{-1} and increased in intensity (Fig. 6e). This indicated a new –C–O peak due to the reaction between CMC and LNR. The intensity of the peak at 835 cm^{-1} (C = C–H) decreased (Fig. 6e) compared to that of pure LNR (Fig. 6c) owing to the reduction of the C = C–H structure in the LNR chain. The Na^+ ion in CMC is considered a Lewis acid catalyst [32]. The crosslinking at the C = C structure of NR is accelerated by a Lewis acid catalyst, as reported previously [33]. It was confirmed that the C = C of the LNR structure reacted with the COO^- of CMC as the Na^+ ion in CMC acted as a catalyst. The suggested reaction is shown in Fig. 7. CSG showed high compatibility with CMC owing to their structural similarity and interaction between the –OH groups (Fig. 7a); whereas, a reaction occurred between the C = C of LNR and COO^- of CMC (Fig. 7b). These interactions and reactions improved the interfacial crosslinking, LNR crosslinking, mechanical properties, and water resistance of the CSG/LNR/CMC blends.

Conclusions

A new biopolymer film with improved mechanical properties and water resistance was successfully developed by blending CSG with CMC and LNR. The incorporation of CMC into the CSG/LNR blend enhanced the tensile properties of the blend because of the improvement in the interfacial reaction, miscibility of CSG/CMC, LNR crosslink, and mechanical properties of CMC. Interfacial crosslinking of CMC/LNR improved the solubility of the CSG/CMC/LNR blend. The swelling properties were enhanced with CMC content due to the gel formation of CMC. The contact angle increased with the CMC content

owing to the hydrophobic nature of LNR, interfacial crosslinking of CMC/LNR, and non-polar structural portion of the amphiphilic CMC. The FTIR results confirmed the reaction between the COO^- groups of CMC and the $\text{C}=\text{C}$ groups of LNR in presence of the Na^+ ions acting as a Lewis acid catalyst. This reaction and the compatibility of CSG/CMC improved the mechanical properties and water resistance of the CSG/CMC/LNR blend. The CSG/CMC/LNR blend, with its excellent properties, can be used in packaging, agriculture, and medical applications.

Methods

Materials. CS (Super-Find brand with MW of 2.54×10^8 g/mol) was procured from R&B Food Supply Public Co. Ltd., Bangkok, Thailand. Glycerol (99%) was procured from Yok Inter Trade (Chiang Mai) Co. Ltd., Chiang Mai, Thailand. Food grade CMC (FVH6-3, DS = 0.65–0.85) was procured from Guoyu Environmental S&T Co. Ltd., Changzhou, Jiangsu, China. LNR (Mastex brand) was procured from Mastex Co. Ltd., Nakornpathom, Thailand.

Sample preparation. Starch and glycerol (CSG) were mixed at a ratio of 70/30 (% w/w) with water (50 g/100 mL) through agitation in a water bath at 80°C for 30 min. CMC was added during the mixing process at a concentration of 2–20 phr (parts/hundred) of CSG. The formulations of the CSG/LNR/CMC blends are listed in Table 2. The solutions were cast on a clean glass plate and then dried in a hot-air oven at 60°C for 24 h.

Table 2
Designation and formulation of the CSG/LNR/CMC blends.

Sample	CSG (wt%)	LNR (wt%)	CMC (phr/CSG)
CSG/LNR	90	10	-
CSG/LNR/CMC2	90	10	2
CSG/LNR/CMC5	90	10	5
CSG/LNR/CMC10	90	10	10
CSG/LNR/CMC20	90	10	20

Tensile properties. The tensile properties of the samples were evaluated using a tensile tester (Tensilion UTM-II-20; Orientec Co. Ltd., Tokyo, Japan) at a crosshead speed of 2 mm/min. Bone-shaped samples were prepared using a die-cutting mold with gauge lengths, widths, and thicknesses of 10, 3, and 0.2 mm, respectively.

Scanning electron microscopy. Morphological images of the samples were obtained through scanning electron microscopy (SEM) (SM-200, Topcon Corp., Tokyo, Japan). The samples were disintegrated in liquid nitrogen, and then the fractured surfaces of the samples were extracted using toluene at 60°C for 1

h. The extracted fractured surfaces of the samples were coated with a thin layer of gold and measured at an acceleration voltage of 10 kV.

Swelling measurement. The swelling percentage of the samples in water was measured for a specimen size of 50 mm × 50 mm × 0.05 mm (width × length × thickness). The samples were dried at 60°C for 24 h and soaked in 50 mL of distilled water at 25°C for 24 h. The swelling ratio was calculated using Eq. 1 [34].

$$\text{Swelling ratio (\%)} = \frac{W_a - W_b}{W_b} \times 100 \quad (1)$$

where W_a is the swollen weight and W_b is the dried weight.

Solubility measurement. The sample specimen size was 50 mm × 50 mm × 0.05 mm (width × length × thickness). The sample films were dried at 60°C for 24 h and placed in a 250 mL Erlenmeyer flask containing 50 mL of distilled water. The samples were shaken at a speed of 25 rpm for 24 h using a shaker (OS-300, Hysc Lab, Scilution Co. Ltd., Nonthaburi, Thailand). The supernatant was filtered and the remaining samples were collected. The residue on the filter paper was dried in a hot-air oven at 80°C for 24 h. The water solubility percentage was calculated using Eq. 2 [35].

$$\text{Solubility (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

where W_1 is the initial weight and W_2 is the dried weight of the filtered sample.

Fourier transform infrared spectrometer (FTIR). FTIR (FT/IR-480 plus, Jasco Corp., Japan) was used to observe the reactions in the CSG/LNR/CMC blends. The samples were prepared as thin films using the solution cast method. The measurement was performed from 600 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Statistical analysis. One-way ANOVA using SPSS software was used to analyze the results. Statistically significant differences at a confidence interval of 95% ($P < 0.05$) were estimated using Duncan's test. Five data of replication for each sample were used for the evaluation.

Declarations

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AUTHOR CONTRIBUTIONS

K.J., and N.L. designed the research study; K.J. prepared sample and investigated; K.J., N.L., T.C., P.R., P.J., W.R., P.S. contributed to data analysis; K.J., N.L., T.O., C.T., S.R.S. discussed the results; K.J., N.L., and Y.P., were involved in drafting and edit this work.

COMPETING INTERESTS

Authors have no competing interests.

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Figures

Figure 1

Tensile stress–strain curves of the CSG/LNR blends with CMC of (a) 0, (b) 2, (c) 5, (d) 10, and (e) 20 phr ($n = 5$).

Figure 2

SEM images of (a) CSG/LNR and CSG/LNR/CMC blends with CMC of (b) 2 phr, (c) 5 phr, (d) 10 phr, and (e) 20 phr.

Figure 3

Solubility and swelling of the CSG/LNR/CMC blends with 0, 2, 5, 10, and 20 phr of CMC (n = 5). Means with different lowercase letters of solubility and uppercase letters of solubility are significantly different ($P < 0.05$).

Figure 4

Contact angles of CSG and the CSG/LNR blends with 0–20 phr of CMC at 3 min ($n = 5$). Means with different lowercase superscript letters are significantly different ($P < 0.05$).

Figure 5

FTIR spectra of (a) CMC, (b) CSG, (c) CSG/LNR, (d) CSG/LNR/CMC2, (e) CSG/LNR/CMC5, (f) CSG/LNR/CMC10, and (g) CSG/LNR/CMC20.

Figure 6

FTIR spectra of (a) CSG, (b) CMC, (c) LNR, (d) extracted LNR from CSG/LNR, and (e) extracted LNR from CMC/LNR.

Figure 7

Suggested reaction of (a) interaction between CSG and CMC and (b) reaction between CMC and LNR.