

Preparation and Mechanical Properties of Chitosan-graft Maleic Anhydride Reinforced with Montmorillonite

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Abstract. The research aims to develop biodegradable composites as bio-based plastics from chitosan. The composites were prepared *via* solution casting method by introducing the maleic anhydride (MAH) as grafting agent and montmorillonite (MMt) as reinforcement. The grafting process of chitosan was conducted by varying concentrations of MAH which were 10, 20, and 30% w/w. It was observed that the chitosan-graft-maleic anhydride (Cs-g-MAH) containing 10% w/w of MAH increased its tensile strength by 70%. Reinforcement material was added to the Cs-g-MAH by varying MMt concentrations, e.g. 3, 6, 9 and 12% w/w. It was noted that the presence of 9% w/w of MMt in the Cs-g-MAH gave the best mechanical properties of the Cs-g-MAH/MMt composite.

1. Introduction

The use of synthetic polymer materials which are usually derivate products of petroleum have been increased enormously. Petroleum-derived polymer are not biodegradable, worsening the problem of the waste disposal. Therefore, the use of biodegradable materials bio-based polymers from renewable resources is a growing demand for limited availability of petroleum resources and environmentally-friendly [1-4].

Chitosan is a natural polymer which is a de-acetylated product of the chitin. It is non-toxic, biocompatible and biodegradable with antimicrobial activity [5]. Chitosan has been applied for bioplastic materials which have notable mechanical properties. However, their water sensitivity, mechanical strength and barrier properties are not as good as synthetic polymer plastics. Therefore, these disadvantages need to be solved so that these bioplastics can compete with the synthetic polymers [6]. Graft copolymerization is one of the technique which can be used for chemical modification of natural and synthetic polymers [5]. It has been a growing interest in grafting of chitosan which allows the formation of functional derivatives onto the chitosan backbone by covalent binding of a molecule with amino and hydroxyl groups of chitosan. The carboxylation of chitosan can be achieved easily by the reaction between its amine groups and anhydride groups from various anhydride derivatives such as succinic anhydride, phthalic anhydride and maleic anhydride (MAH) [7-13]. In this work, MAH was used to increase the mechanical properties of chitosan polymer matrix.

The inclusion of a small amount of clay particles such as bentonite, halloysite, kaolin, or montmorillonite (MMt) into a polymeric matrix has received considerable research attention due to the improvement in mechanical and thermal properties [14-15]. When clay is blended with a polymer, clay particles are dispersed within the polymer matrix and these interactions increase the mechanical properties [16]. MMt is commonly used as cationic clay of the smectite group for preparation of

polymer nanocomposites. In this work, MMt was used as reinforcement to enhance the mechanical properties of the biocomposites. The aim of this research was to fabricate novel bioplastic composites based on chitosan to improve their properties by MAH grafting and adding of MMt.

2. Experimental

2.1. Materials

Chitosan (Cs) was purchased from PT Biotech Surindo, Indonesia. All chemicals were used are analytical grade from e-Merck, otherwise is stated. Montmorillonite K10 (Aldrich) was prepared by calcination at 400°C for 12 h before used.

2.2. Synthesis of chitosan-g-poly(maleic anhydride) (Cs-g-MAH)

Chitosan (2 g) was dissolved in 70 mL of acetic acid at room temperature at constant stirring condition. Maleic anhydride (MAH) as much as 10, 20 and 30% w/w, 5% w/w benzoyl peroxide (BPO) and 10 mL acetic acid were dispersed using sonicator for 30 mins. This mixtures were then added into chitosan solution (Table 1). Co-polymerization was conducted at 80°C for 1 h. The mixtures were poured into stainless steel templates and dried for 12 h at 50°C. The composites were then airing for acetic acid removal for 12 h.

Table 1. Chitosan-g-poly(maleic anhydride) (Cs-g-MAH) composite compositions.

Composites	Composition (g)		
	Chitosan	MAH	BPO
Cs	2	0	0
Cs-g-MAH-10	2	0.2	0.01
Cs-g-MAH-20	2	0.4	0.02
Cs-g-MAH-30	2	0.6	0.03

2.3. Synthesis of chitosan/montmorillonite g-poly(maleic anhydride) (Cs-g-MAH/MMt)

The fabrication of chitosan/montmorillonite co-poly(maleic anhydrides) (Cs-g-MAH/MMt) composites were conducted using the same procedures for the synthesis of Cs-g-MAH. The MMt as much as 3, 6, 9, and 12% w/w was added after 1 h of blending the chitosan, MAH and BPO (Table 2). The mixtures were blended for 1 h and then poured into stainless steel templates.

Table 2. Chitosan/montmorillonite g-poly(maleic anhydride) (Cs/MAH/MMt) composite compositions.

Composites	Composition (g)			
	Chitosan	MAH	BPO	MMt
Cs-g-MAH/MMt -3	1.940	0.194	0.009	0.060
Cs-g-MAH/MMt -6	1.880	0.188	0.009	0.120
Cs-g-MAH/MMt -9	1.820	0.182	0.009	0.180
Cs-g-MAH/MMt -12	1.760	0.176	0.009	0.240

2.4. The characterization of composites

The composites were characterized for their functional groups by FT-IR spectrophotometer. The mechanical testing of Cs-g-MAH and Cs-g-MAH/MMt were performed according to ASTM D-638. The specimen tests were prepared with 6 mm of section width, 33 mm of section length and under 4 mm of thickness. Mechanical tests were conducted using Mechanical Testing Machine Ray-Run M500 50CT, with 5 mm/min of applying speed.

The water absorption tests were performed for analysing the swelling phenomena of Cs-g-MAH and Cs-g-MAH/MMt. The initial weights of samples were recorded as W_o . The sample with $1 \times 1 \text{ cm}^2$ (A_o) of dimension were placed into chamber containing distilled water for 1 h. The final sample weight were recorded as W_t . The samples were also measured for swelling area by calculating the area before (A_o) and after 1 h of soaking in water (A_t). Water absorption (WA) and swelling area (SA) of samples were then calculated using equation (1) and (2).

$$WA = \frac{(W_t - W_o)}{W_o} \times 100\% \text{-----} (1)$$

$$SA = \frac{(A_t - A_o)}{A_o} \times 100\% \text{-----} (2)$$

3. Result and discussion

3.1. Composites of chitosan-g-poly(maleic anhydride) (Cs-g-MAH)

The chitosan-g-poly(maleic anhydride) (Cs-g-MAH) composites were prepared and their mechanical properties such as tensile strength, strain and young's modules were investigated. Increasing of the tensile strength (TS) after copolymerization chitosan matrixs with MAH were noted (Table 3). The highest TS was achieved when the amount of 10% w/w of MAH was applied. In this composite, compatibilized matrixs with MAH had a significant effect on both tensile strength and strain at break. TS increased from 21.11 to 35.90 Mpa and strain decreased from 13.46 to 9.18%. An increased of young's modulus was also observed from 156.78 to 892.28 MPa. It indicated that the addition of MAH reduced the brittle of chitosan plastics. This is consistent with several studies involving polymer matrixs compatibilized MAH system [17, 18].

Table 3. The mechanical properties of Cs-g-MAH composites.

Composites	Tensile stength (MPa)	Strain (%)	Young's modulus (MPa)
Cs	21.11	13.47	156.78
Cs-g-MAH-10	35.90	9.18	494.61
Cs-g-MAH-20	30.97	3.42	892.28
Cs-g-MAH-30	33.94	4.29	781.95

Water absorption is the key to indicate the bioplastics moisture sensitivity which is an important aspect for packaging applications. The swelling behaviors at 100% relative humidity were evaluated for 1 h. Figure 1 shows the swelling properties of Cs-g-MAH composites. In respect to the chitosan, the swelling degrees decreased upon the addition of MAH. The addition of 10% w/w of MAH insignificantly decreased the swelling degree by 11.76%, nevertheless the addition of 20 and 30% w/w of MAH significantly decreased the swelling degree by 45.38 and 44.45%, respectively. In was noted that the addition of 10% of MAH did not affect the swelling area, whereas the addition of 20 and 30% w/w of MAH decreased the swelling area significantly by 77.27 and 52.27%, respectively. It was reported that compatibilization of natural polymers decreased the tendency of the composites to absorb water [19, 20]. Increasing cross-linking decreased water absorption due to the reduction of hydroxyl group available to absorb water [19, 21]. In this work, the Cs-g-MAH-10 composite was observed to have best water resistance, where the swelling degree and swelling area remained almost unaffected by water.

Based on the mechanical properties and the swelling behaviour data, the Cs-g-MAH-10 composite has been chosen for further studies. Montmorillonite as reinforcement was then added to the composite giving Cs-g-MAH/MMt composites in order to improve their properties.

3.2. Composites of chitosan/montmorillonite g-poly(maleic anhydride) (Cs-g-MAH/MMt)

The mechanical properties of the Cs/MAH/MMt composites are shown on Table 4. In respect to composite without MMt, which was Cs-g-MAH-10 composite, the increased of TS was observed upon addition of MMt and the highest TS of 42.14 Mpa was reached when the amount of 9% w/w of MMt was used. The decreased of strain from 9.18 to 7.14% were observed. The brittle of biocomposite diminished which was indicated by increasing of young's modulus from 494.61 to 707.68 MPa. Improving the mechanical properties upon addition of MMt indicated that the composite of Cs-g-MAH-10 was compatible with MMt due to the interaction among the polar hydroxyl group of chitosan, polar carbonyl group of MAH and polar hidroxyl group of montmorillonite [17].

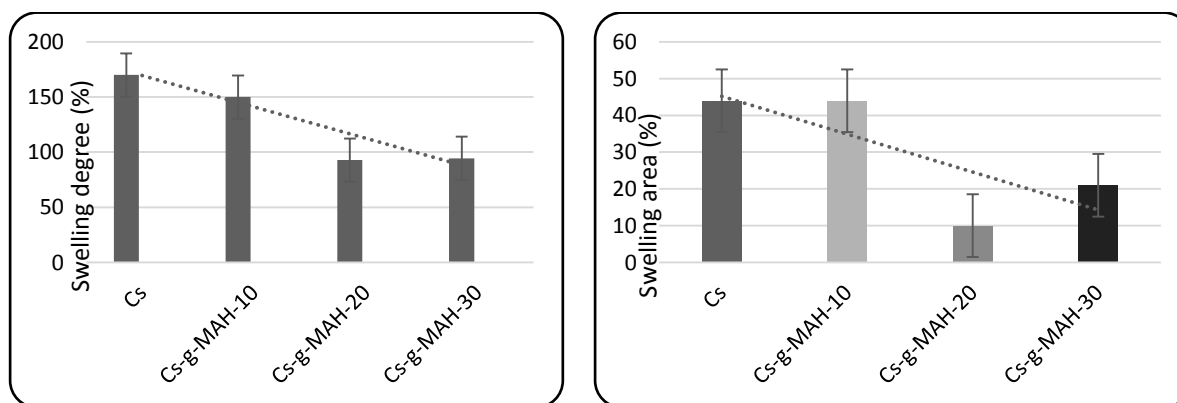


Figure 1. Swelling degree (a) and swelling area (b) of Cs-g-MAH composites.

Table 4. The mechanical properties of Cs-g-MAH/MMt composites.

Sample	Tensile strength (MPa)	Strain (%)	Young's modulus (MPa)
Cs-g-MAH-10	35.90	9.18	494.61
Cs-g-MAH/MMt-3	26.97	9.49	333.95
Cs-g-MAH/MMt-6	39.14	7.14	552.12
Cs-g-MAH/MMt-9	42.14	6.04	707.68
Cs-g-MAH/MMt-12	41.92	5.49	766.96

The swelling properties of Cs-g-MAH/MMt composites are shown in Figure 2. The addition of MMt into Cs-g-MAH-10 composite increased the swelling degree and swelling area of Cs-g-MAH/MMt composites. Upon addition of MMt into matrix polymer increased the water absorption due to the hydrophilic activity of clay [22]. The Cs-g-MAH/MMt-9 composite was observed to have best water resistance since it had the lowest swelling degree respect to the Cs-g-MAH-10 composite. The swelling degree of Cs-g-MAH/MMt-9 composite increased from 170 to 233 %.

3.3. FTIR analysis chitosan, Cs-g-MAH-10 and Cs-g-MAH/MMt-9

Figure 3 shows the FT-IR spectra of chitosan, Cs-g-MAH-10 and Cs-g-MAH/MMt-9 composites. The FT-IR spectrum shows characteristics peaks for chitosan [23]. The spectrum shows a peak at 3080 cm^{-1} due to the overlapped of -NH symmetric stretching vibration and -OH stretching vibration. Peaks at 1664 , 1588 and 1324 cm^{-1} were observed due to vibration of C=O secondary amide, protonated amide and stretching vibration of -CH₃ tertiary amide of chitosan, respectively. A peak at 2886 cm^{-1} was obtained due to the asymmetric stretching vibration of aliphatic (-CH₂), peaks at 1422 and 1388 cm^{-1}

appeared for the characteristic peaks of $\delta(\text{C-H})$ and a peak at 894 cm^{-1} was characteristic for wagging of C-H. The peaks at 1150 and 1033 cm^{-1} were characteristics for the symmetric and asymmetric stretching vibration of C-O-C. The characteristic peaks of C-O and C-N stretching vibration appeared at 1033 and 1422 cm^{-1} , respectively.

The spectrum of Cs-g-MAH-10 showed that a peak at 3080 cm^{-1} was disappeared and a peak at 3435 cm^{-1} was appeared. A strong band at 1566 cm^{-1} was observed due to C=C bond. In addition, the Cs-g-MAH-10 FT-IR spectrum showed a new absorption peak at 1704 cm^{-1} corresponding to the CO stretching vibration of carboxyl groups [14]. These results provided evidences that the MAH was interacted with chitosan matrix [23].

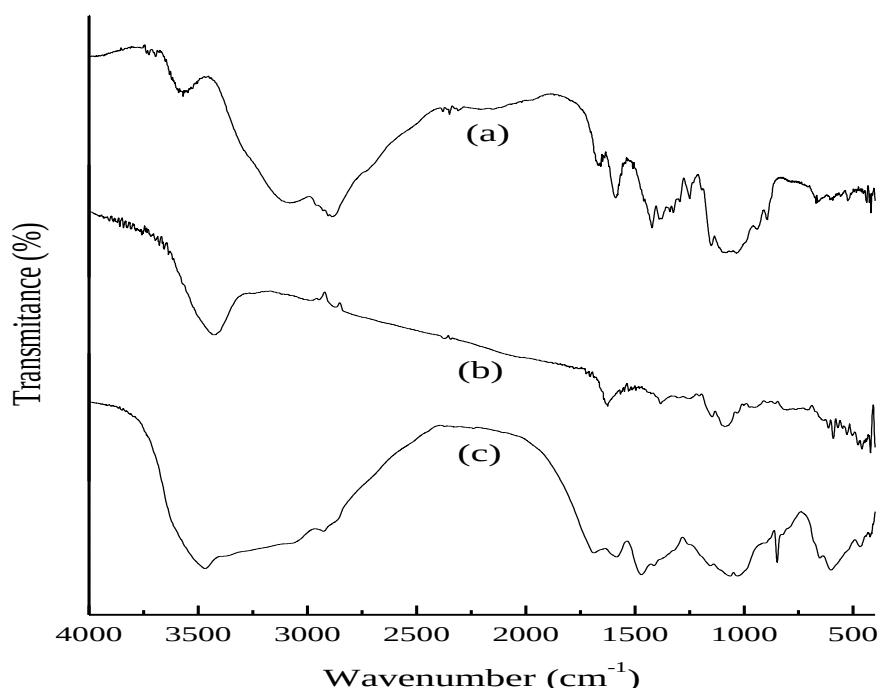


Figure 3. FT-IR spectra of: (a). chitosan, (b). Cs-g-MAH-10 and (c). Cs-g-MAH/MMt-9.

The peaks at 814 , 835 and 946 cm^{-1} shown in Cs-g-MAH-10 FT-IR spectrum were shifted to the 823 , 848 and 903 cm^{-1} in Cs-g-MAH/MMt-9 spectrum, respectively. Those peaks were due to the bending vibration of Al-Mg-OH, Al-Fe-OH and Al-Al-OH. The characteristic absorption bands corresponding to the water molecules associated with the samples and with the protonated amine group in the chitosan chain were also shifted. The peaks at 1588 and 1644 cm^{-1} in chitosan spectrum were shifted into 1566 and 1625 cm^{-1} in Cs-g-MAH-10 FT-IR spectrum and 1583 and 1688 cm^{-1} in Cs-g-MAH/MMt-9 spectrum. These results confirmed that there were interactions between MMt and the chitosan-MAH composite.

4. Conclusions

The graft co-polymer of chitosan-maleic anhydride reinforced with montmorillonite composites have been successfully produced. FTIR analysis revealed that compatibilizing matrix among chitosan, MAH and MMt was fully achieved. A chitosan composite containing 10% w/w MAH and 9% w/w MMt was observed to have the best mechanical properties. However, the water resistance decreased upon addition of MMt into a chitosan-maleic anhydride composite. Further studies by varying amount of the each component and the thickness of composites still need to be evaluated to produce the bioplastics with better water resistance.

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