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Synthesis and properties of carrageenan grafted copolymer with poly(vinyl alcohol)

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ABSTRACT

The aim of this work was to prepare a carrageenan-g-poly(vinyl alcohol) (CG-g-PVA) polymer using potassium persulphate as an initiator. The effect of different ratios of the polymer blends on the parameters of the grafted polymer was investigated. The grafting ratio decreased with an increase of the CG content in the graft copolymer. The resulting CG-g-PVA was characterized by ATR-FTIR, tensile strength, elongation at break, swelling ratio, contact angle and biodegradation in soil. From the ATR-FTIR the 3,6-anhydride-galactose of the CG showed a peak at 927 cm^{-1} that was absent in the CG-g-PVA and the ether linkage of PVA-g-CG between the hydroxyl group of PVA and the 3,6-anhydride-galactose of CG showed a peak at 1089 cm^{-1} in the graft copolymer. The tensile strength and elongation at break decreased with an increase of the CG due to its phase separation. The highest tensile strength was observed at 2:8 CG/PVA. In addition, the swelling ratio decreased and the contact angle increased as a function of the increase of the CG in the grafted copolymer. The best ratio of CG-g-PVA was 2:8 CG/PVA. This graft copolymer was easily biodegraded in natural soil.

1. Introduction

At the present time, biodegradable natural polymers produced from proteins and polysaccharides are being widely used in the pharmaceuticals and biomedical field. Among such polysaccharides are a family of biodegradable natural polymers, called, carrageenans (CG). They consist of linear sulfated polysaccharides extracted from red seaweeds. There are three main types of CG, namely k-carrageenans that have one sulfate per disaccharide, iota-carrageenan with two sulfates per disaccharide and lambda containing three sulfates per disaccharide (Tanaka, Lu, Yuasa, & Yamaura, 2001). Considering their applications, k-carrageenan is mainly used in food applications but other applications include cosmetics, paints, pharmaceuticals and for applications in the biomedical field (Dafader, Ganguli, Sattar, Haque, & Akhtar, 2009). In addition, it is used to help form scaffolds in tissue engineering, for biosensors, wound dressing, cell encapsulation, enzyme immobilization and drug delivery. However, its drawbacks are that it has a low weathering resistance and poor mechanical properties. In previous work, the poor properties of the biopolymer have been modified by blending with other polymers such as poly(vinyl alcohol) to form a (PVA)/k-carrageenan blend (Tanaka et al., 2001), and an acrylamide/k-carrageenan blend (Dafader et al., 2009), and poly(*N*-vinyl pyrrolidone)/k-carrageenan blend (Maolina, Hongfeia, Yoshiib, & Makuuchi, 2000). For example, after PVA was blended with k-carrageenan, its endothermic peaks shifted to lower temperatures as the content of the k-carrageenan increased while the PVA crystal in the blend films did not change (Tanaka et al., 2001). Many methods have been used to improve the properties of polymer blends, such as crosslinking, forming complexes and graft copolymers. The literature reports of crosslinking in polymer blends, and one claimed that $CaCl_2$ can be used as a crosslinking agent for an alginate/CG blend (Paşcalău et al., 2012) and genipin was used as a crosslinker for a CG/PVA blend (Hezaveh & Muhamad, 2013) and a chitosan/CG blend (Devi & Maji, 2010). In the case of complex methods with no added chemical agents an i-PVA/CG complex has been produced (Kantoglu, Caykara, & Guven, 2013), a CG complex with gelatin (Lii, Chen, Lu, & Tomasik, 2003) and a chitosan–carrageenan polyelectrolyte complex (Li, Hein, & Wang, 2013). The mechanical properties of CG have been improved by grafting with *N*-vinyl formamide (Mishra, Yadav, Sand, Tripathy, & Behari, 2010) and poly(sodium acrylate) (Sadeghi, Ghasemi, & Kazemi, 2012). For example, the thermal properties of a cured CG/PVA blend with genipin were higher than that of an uncrosslinked blend. The objective of the present work was to develop the properties of CG by grafting with PVA. PVA is known to be biocompatible, hydrophilic, with excellent chemical resistance, a high tensile strength and is relatively easy to

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modify (Tang, Sun, Li, Wu, & Lin, 2009). It is made from poly (vinyl acetate) that has been hydrolyzed to produce a high percentage of the repeat units with pendent hydroxyl groups. In our previous work, the PVA has been grafted with other polymers such as polyacrylonitrile (Taghizadeh & Darvishi, 2001), poly(hydroxy acid) (Lejardi, Etxeberria, Meaurio, & Sarasu, 2012), polyethylene glycol (Heuschmid et al., 2013), *N*-isopropylacrylamide (Yang, Hua, & Zhang, 2012), methacryloxyethyl trimethylammoniumchloride (Zheng, Chen, Lu, Wu, & Lin, 2005), starch (Xiao & Yang, 2006) and *N*-trimethyl chitosan (Martins et al., 2013). After starch was grafted onto PVA, the swelling ratio of the hydrogels increased with the molecular weight of the PVA used and the crystallinity of the starch-g-PVA was lower than that of starch (Xiao & Yang, 2006). In this work, the effect of the polymer blend ratios on the grafted copolymer was studied. The grafted copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD) studies, their swelling ratio in water, their dissolution ratio, contact angle, percentage degree of grafting, mechanical properties, biodegradation and observations by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Commercial reagent grade kappa-carrageenan (Bangkok, Thailand) was used as received. PVA with a number average molecular weight of 8.9×10^4 g/mol and 89% hydrolysis (Nippon Gohsei Co., Ltd., Singapore) was used for the present study. Potassium persulphate ($K_2S_2O_8$) used as a water soluble initiator was manufactured by RFCL Ltd. (India).

2.2. Synthesis of CG-g-PVA

PVA was dissolved in distilled water to produce PVA solutions of 5% (w/w). The ungrafted CG was extracted by water then placed in an oven at 50 °C for 24 h and kept in a desiccator before characterization. The blends were prepared by mixing the CG solution and PVA to obtain a homogeneous solution in the presence of $K_2S_2O_8$ while heating at 65 °C for 1 h. Then the mixture was cast into a film on a Petri dish at 30 °C.

2.3. Characterization

The CG-g-PVA samples was analyzed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Bruker EQUINOK 55 measuring in the range of 4000–500 cm^{-1}. The grafted samples were examined by extraction of the samples in boiling water for 24 h using a soxhlet apparatus. The extracted samples were dried in an oven at 50 °C until a constant weight was achieved. The grafting ratio was calculated by the following Eq. (1):

$$\%\text{Swelling ratio} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_1 and W_0 are the weights of the dried samples after extraction and before extraction, respectively (Maolina et al., 2000).

The dissolution behaviors of the CG-g-PVA and CG/PVA blend was carried out by the following method. The samples were cut into 1×1 cm lengths and their weights measured (W_0). Subsequently, the samples were immersed in distilled water and heated at 80 °C for different times. Then, the wet samples were dried and the weights (W_1) were recorded. The dissolution ratio of CG-g-PVA was evaluated by Eq. (2).

$$\text{Dissolution ratio}(R) = \frac{W_1}{W_0} \times 100 \quad (2)$$

The tensile property of the resulting samples was determined by a standard testing procedure according to ASTM D412C using a LLOYD instrument LR10K Tensile Machine. Three to five specimens were measured for each particular sample and an average value was reported with the standard deviation showing the error range. The swelling ratio was measured in distilled water at room temperature. The dried CG-g-PVA was immersed in 25 mL of distilled water for 0.5, 1, 2, 4, 24 and 48 h. The swelling ratio was obtained according to the Eq. (3).

$$\%\text{Swelling ratio} = \frac{W_2 - W_1}{W_1} \times 100 \quad (3)$$

where W_1 was mass of the dried CG-g-PVA (g) and W_2 was the mass of the swollen CG-g-PVA (g) (Paşcalău et al., 2012).

The sessile drop method was used to determine the contact angle with a contact angle goniometer and an optical subsystem to capture the profile of a liquid on a solid substrate. The angle formed between the liquid/solid interface and the liquid/vapor interface was the contact angle. The degradation in soil was measured after being mixed with soil for 30 days. The biodegradation of the resulting sample in soil was obtained according to the Eq. (4). For thermal analysis, a TGA7 (Perkin Elmer) was used for testing a sample (5–6 mg) under N_2 with a flow rate of 45 mL/min, from 50 to 850 °C at a heating rate of 10 °C/min.

$$\%\text{Biodegradation} = \frac{W_2 - W_1}{W_1} \times 100 \quad (4)$$

where W_1 was the mass of the initial dried CG-g-PVA (g) and W_2 was the mass after being incubated in soil for 30 days and dried.

3. Results and discussion

3.1. Synthesis of the graft copolymer, % grafting of the copolymer and the ATIR-FTIR results

At the first step, after the KPS was heated, it decomposed into sulfate free radicals as shown in Fig. 1. The resulting free radical abstracts hydrogel from the hydroxyl group of CG that possesses repeating galactose units and 3,6 anhydrogalactose (3,6-AG) with the units joined by alternating alpha 1–3 and beta 1–4 glycosidic linkages to form the corresponding alkoxy radicals. At the same time, these macroradicals initiate PVA grafting onto the CG backbones to form the graft copolymer (CG-g-PVA). Another way, is for the free radicals from the $K_2S_2O_8$ PVA molecules to graft the copolymer at the C-3 carbon of the CG ring because of the electrostatic attraction during heating (Sarasu et al., 2012). Then, the anionic radical attacked the C-4 carbon and transferred the radical to the C-4 carbon by subtracting the hydrogen from it. The presence of a free radical at the C-4 carbon weakened then homolytically broke the next C—O bond at the C-1 carbon and transferred the free radical to the C-1 carbon. One had a free radical on the C-1 carbon at the end, and the other had a carbonyl group at the C-4 carbon in the terminal ring as shown in Fig. 1 (2).

The synthesized copolymers from CG and PVA were characterized for their functional groups using ATR-FTIR (Fig. 2I). The FTIR spectra of the pure CG and PVA films present both common and specific absorption bands. The ATR-FTIR spectra for the CG, PVA and CG-g-PVA hydrogels show notable differences in the region of 1475 and −1775 cm^{-1} (Fig. 2I). The FTIR spectrum of PVA shows a broad peak around 3334 cm^{-1} that indicates stretching of a hydroxyl group and peaks at 2924 and 2854 cm^{-1} due to C—H stretching (Hezaveh & Muhamad, 2013). The FTIR spectrum of the CG showed a broad peak around 3323 cm^{-1} that was attributed to stretching of a hydroxyl group. Three important bands at 844, 920 and 1262 cm^{-1} can be attributed to a D-galactose-4-sulfate, 3,6-anhydride-galactose and an ester sulfate stretching,

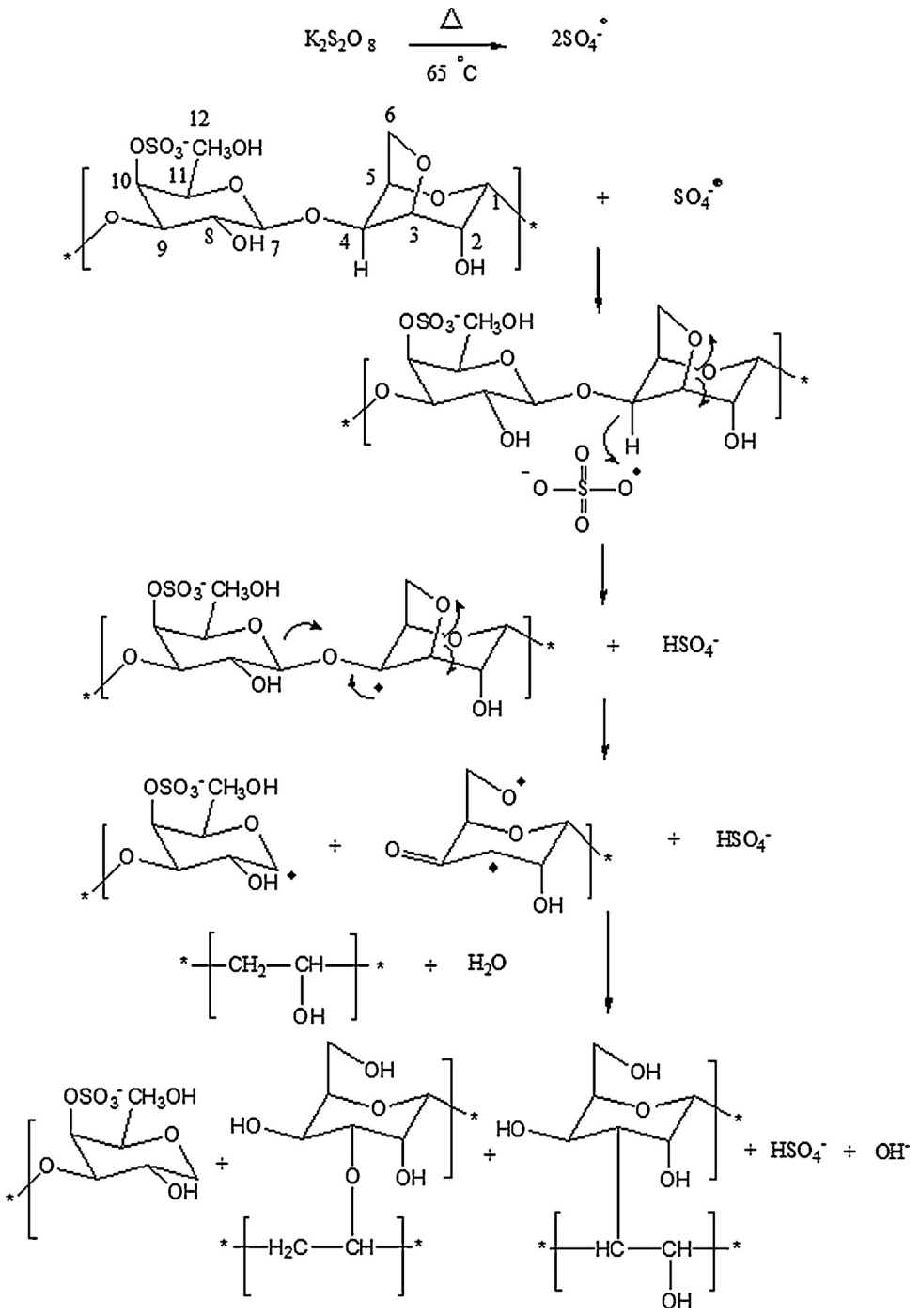

Fig. 1. Possible reactions of CG during its grafting with PVA using $K_2S_2O_8$.

respectively (Paşcalău et al., 2012). After the CG was grafted with PVA the peak at 920 cm^{-1} in the CG disappeared and showed that grafting had occurred to form a copolymer and the ether linkage of the CG-g-PVA between the hydroxyl group of PVA and the 3,6-anhydride-galactose of CG exhibits a peak at 1089 cm^{-1} that is referred to the graft copolymer. The peak at 1626 cm^{-1} in the CG spectrum can be assigned to the hydrogen bonding coupled with COO^{-1} stretching. As the PVA only shows a small shoulder at 1658 cm^{-1} due to water absorption, the increase in the intensity of the peak at about 1630 cm^{-1} indicated the presence of CG in the polymer hydrogel.

The XRD patterns of CG, PVA, and CG-g-PVA at 3:7 and CG-g-PVA 2:8 are displayed in Fig. 2(II). The diffraction patterns show the amorphous structure of all the analyzed films, that produce halloo at different values of the 2θ angle. The pure CG and PVA displays two halloo that correspond to different amorphous regions (Heuschmid et al., 2013). The 2θ XRD patterns of PVA were located at around 20.5° and 40.6°, while that of the CG was found at around 28.38° and 58.78°. The first one has a clear crystalline peak at scattering angles of $2\theta = 20.5°$ in which the first one has a clear crystalline peak at a scattering angle of $2\theta = 20.5°$ that corresponds to a (1 0 1) spacing (Riyajan, Chaiponban, & Tanbumrung, 2009). The second halo at 40.6° has a low intensity and a broad shape that corresponds to noncrystalline zones within the crystalline polymer matrix. This result confirmed previous work (Riyajan et al., 2009). In the case of the CG-g-PVA, there were many XRD patterns

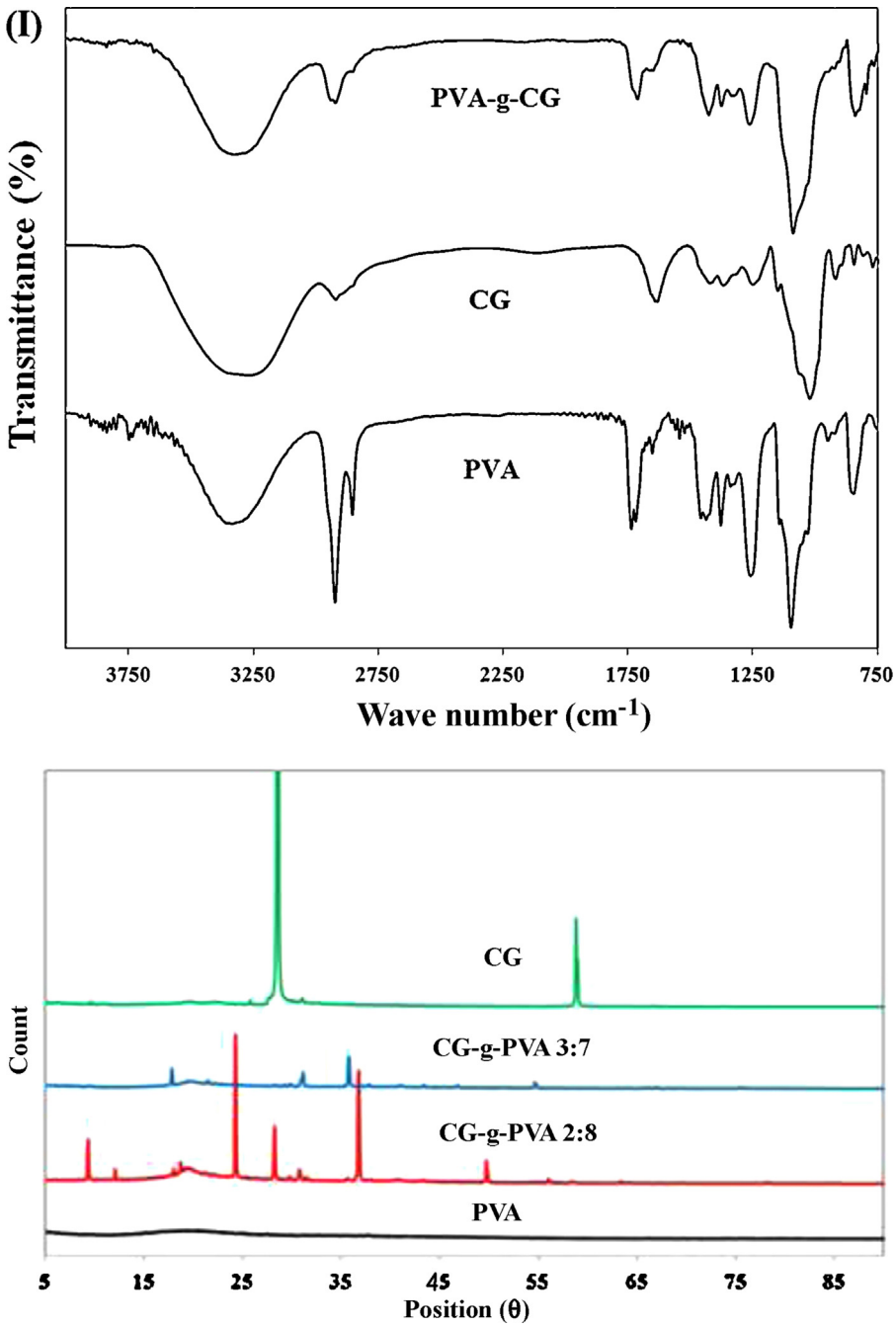

Fig. 2. (I) ATR-FTIR spectra and (II) the XRD patterns of PVA, CG and CG-g-PVA.

due to the new arrangements of the CG and PVA in the grafted copolymer.

The grafting ratio of the CG-g-PVA is shown in Fig. 3(I). The grafting ratio decreased with an increase of the CG content in the graft copolymer due to its chain scission.

With an increase in the concentration of CG, the % percentage of the graft copolymer decreased continuously, and reached a minimum value when the concentration was 6:4 CG:PVA. This was due to the chain scissions (Riyajan & Sukhlaaied, 2013). The highest percentage of grafting was found at a ratio of 1:9. When the CG content increased, the percentage of the graft copolymer decreased due to a reduction in the active sites and the increase in the CG concentration may be due to the amount of CG that was more helpful to copolymerization than to the grafting in the concentrations used.

3.2. The % swelling ratio and the % dissolution ratio

The swelling ratio of the polymer hydrogel in water could be practically used to approximate the chemical change in the graft copolymer (Fig. 3II). This indicated that a chemical reaction had occurred between the CG and PVA using the $K_2S_2O_8$ as an initiator. The swelling ratio of the polymer hydrogel in water could be used practically to approximate the chemical change in the graft copolymer and these results are shown in Fig. 3(II). The swelling ratio of the polymer hydrogel dramatically decreased as a function of the CG in the CG-g-PVA copolymer. The swelling ratio of the CG-g-PVA at 5:5 CG:PVA was 160%, while the swelling ratio of the polymer hydrogel with 2:8 CG/PVA was 270%. This result indicated that higher interactions such as hydrogen bonding occurred between the CG and the PVA. This result supports those of

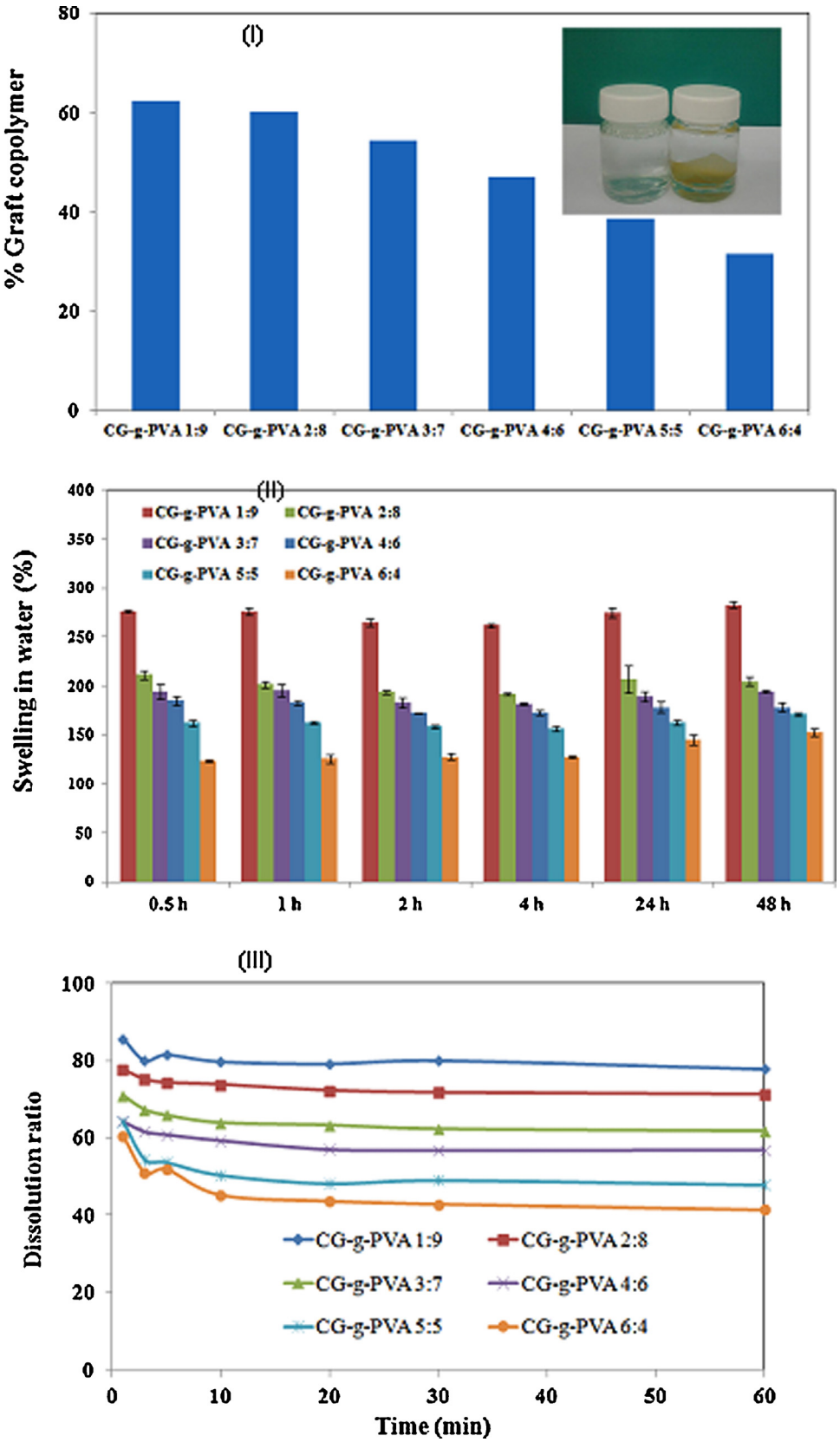

Fig. 3. Effect of the CG content on (I) the %age grafted copolymer, (II) the %age swelling ratio in water and (III) the dissolution ratio of the CG-g-PVA in water at 80 °C.

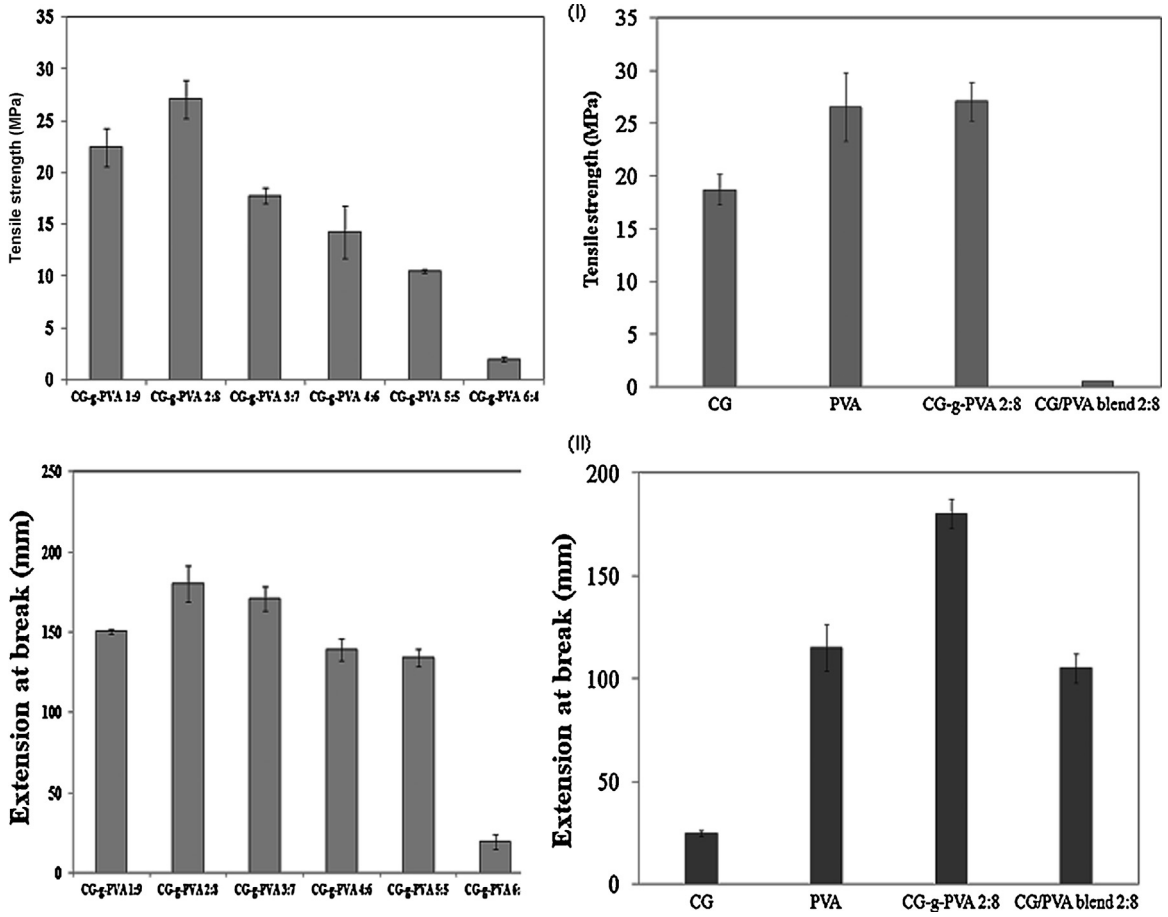

Fig. 4. Effect of the CG concentration on (a) the tensile strength and (b) the elongation at break of the CG-g-PVA.

Nagahama and co-worker (Nagahama et al., 2009). They studied the swelling behavior of a chitosan/gelatin blend compared to the chitosan hydrogel. This sample showed more water resistance because it had stronger hydrogen bonds compared to chitosan and gelatin. In addition, this result was used to confirm the chemical structure of the CG-g-PVA and was in agreement with the ATR-FTIR result. The water resistance of CG-g-PVA was confirmed again through the dissolution behavior in water at 80 °C. The dissolution behavior of CG-g-PVA with different polymer ratios in hot water at 80 °C is shown in Fig. 3(III). At a low CG content in the polymer hydrogel, the CG-g-PVA showed only a small variation of the dissolution ratio after heating at 80 °C for 1 h. In contrast, with a high CG content in the graft copolymer there was a significant change of dissolution over the same time. These results are due to good miscibility between the CG and the PVA at a lower CG content in the sample. However, when the CG in the polymer hydrogel increased, a poor miscibility was found between the CG and PVA leading to a high dissolution in hot water. In the case of the CG/PVA blend, it dissolved completely in water within 10 min. These results indicated that the dissolution of the CG-g-PVA in hot water had very little influence when compared to its blend due to the good chemical interactions between PVA and CG.

3.3. Mechanical studies

The tensile strength of the polymer hydrogel samples is a vital factor in its biomedical applications. Thus, it was important to establish if the tensile strength of the polymer hydrogel sample was improved by grafting the copolymer when compared to the individual PVA. The effect of the CG/PVA ratio on the tensile strength of the polymer hydrogel is shown in Fig. 4(I). The tensile strength (TS) initially increased with an increase of the CG content in the blend and after reaching a maximum value, the TS value began to decrease. The increase in the TS was due to the increase of the interaction between the polymer blends. At a higher CG content than 30% in the blend, the tensile strength of the polymer hydrogel dramatically decreased. This was due to phase separation of the polymer blend as observed by the SEM (Fig. 5). The highest TS value of the CG-g-PVA was obtained from a 20:80 CG/PVA and amounted to 27 MPa. In the case of a blend at the same ratio, the TS was very poor and its TS was equal to 1.2 MPa. These results confirmed that the CG had been successfully grafted with the PVA. In the case of the elongation at break, the elongation at break of the polymer hydrogel samples was a function of the CG to the highest elongation at break and then the elongation at break of this sample significantly decreased (Fig. 4**II**). This might be used as evidence for the existence of a chemical grafting between the CG and PVA. These results agreed with the change in tensile strength. It was a surprise to find that the elongation at break of the polymer hydrogel based on a 2:8 CG/PVA reached 180% when the CG concentration reached 20% (w/w). The tensile strength and elongation at break decreased with the increase of the CG content in the graft copolymer due to its phase separation (Devi & Maji, 2010). The highest tensile strength and elongation at break was found at 2:8 CG/PVA and its tensile strength and %age elongation at break were about 27 MPa and 180, respectively.

3.4. Morphology

Fig. 5 presents the SEM images of a liquid nitrogen fractured surface of the CG-g-PVA with different CG:PVA ratios. At a low

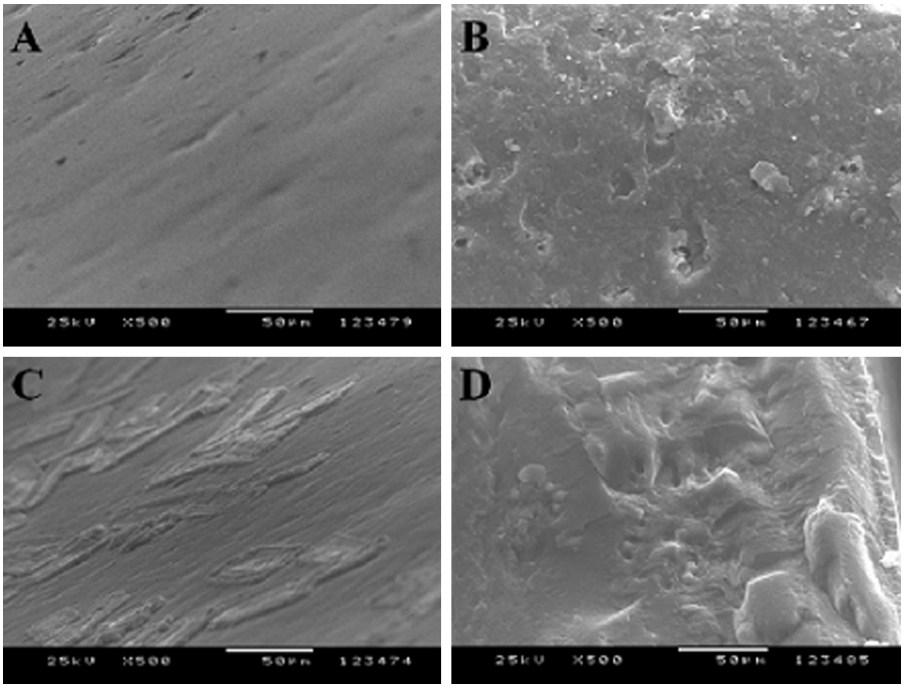

Fig. 5. SEM images of CG-g-PVA with (A) 1:9 (B) 2:8 (C) 3:7 and (D) 4:6 CG:PVA ratios.

amount of CG in the blend, the CG was chemically compatible to PVA, and the hydroxyl groups from the PVA and CG were essentially within the hydrogen bond network. Therefore it was hard to connect the hydroxyl groups from both components by building new hydrogen bonds and chemically bonding them. This resulted in an inferior interfacial interaction of the polymer hydrogel (Paşcalău et al., 2012). When the CG in the graft copolymer increased, a phase separation of the polymer hydrogel occurred as seen in the SEM. These results were a reflection of the tensile strength.

3.5. Contact angle studies

The measurement of the contact angle between pure water and the graft copolymer surface was one of the easiest ways to characterize the hydrophilicity of the graft copolymer surface. A hydrophobic surface with a low free energy produces a high contact angle with water, whereas a wet high-energy surface allows the drop to spread, i.e., produces a low contact angle (Guilizzoni, 2011). Fig. 6 shows the variant dependence of the static contact angle (SCA) of the CG, the PVA and the CG-g-PVA at 1:9 and 3:7 CG:PVA. The plot indicates that the SCA of the samples underwent a significant change. For the original PVA, the surface was very hydrophobic, and the measured water contact angle was 93.6°, while the measured water contact angle of the CG was 11.55°. After the CG was grafted with the PVA, the water contact angle declined gradually to 43–58°. This behavior is likely to be associated with the graft copolymer of the polymer molecule in the polymer matrix. In addition, this behavior is primarily caused by the reorientation of

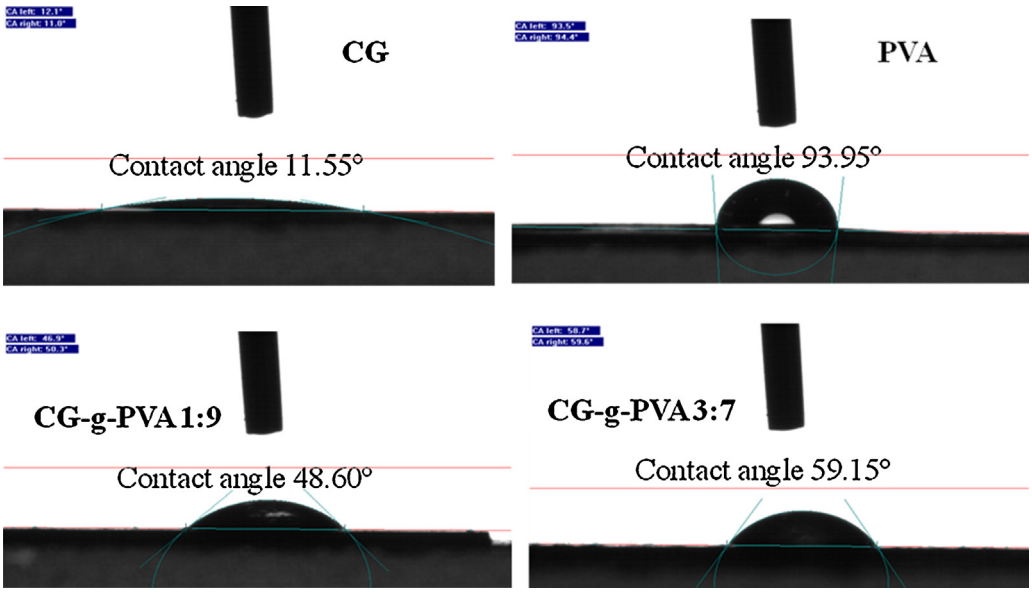

Fig. 6. Contact angle of the PVA, CG, and CG-g-PVA.

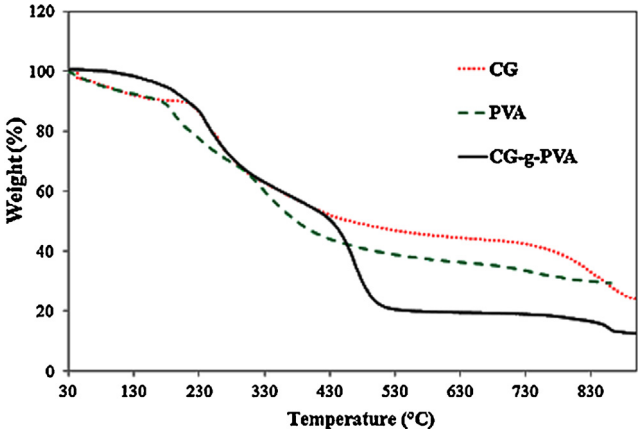

Fig. 7. TGA curves of PVA, CG and PVA-g-CG.

the polar function groups toward the outer surface of the sample film.

3.6. Thermal properties

TGA was used to understand the thermal stability of the polymer hydrogels. The TGA curves for CG, PVA and CG-g-PVA are shown in Fig. 7. The first peak of the PVA in Fig. 7 corresponded to the loss of water (Paşcalău et al., 2012). The other peaks corresponded to the total decomposition of the polymeric structure. The three peaks in the temperature range of 190–280 °C, were responsible for the glass transition temperatures and the melting point of the PVA (Riyajan et al., 2009). The CG showed a weight loss in three stages, the first stage of the CG from the TGA occurred in the range of 30–200 °C and the %weight loss of 9.33% was probably due to a loss of moisture from the samples. The results corresponded to those of previous work (Paşcalău et al., 2012). It had been reported that in studying the thermal degradation of the sodium alginate/CG blend, their weight loss stages, under 100 °C, between 100 and 200 °C and 200–260 °C, can be distinguished and assigned to the three kinds of water from the polysaccharide. The second peak was found at a range of between 206 and 730 °C and the %weight loss of this peak was 59.39%. The third peaks were located over the range of 730 and 900 °C, when the % weight loss was 9.97%. In the case of the graft copolymer, the TGA patterns of this sample changed from the individual PVA and CG and there were three stages of weight loss observed by the TGA. The thermal stability of the graft copolymer was higher than that of the pristine CG and PVA.

3.7. Biodegradation

The degradation percentage in soil of CG-g-PVA is shown in Fig. 8(I). It is clear that the degradation percentage of the graft copolymer in soil increased with the increasing CG content in the graft copolymer. This is due to a higher biodegradation of CG. In addition, these results show that the graft copolymer is less susceptible to biodegradation and similar results have also been reported in Lii et al. (2003). The graft copolymer can be made less susceptible to bacterial attack (Li et al., 2013).

The appearance of the CG-g-PVA with different polymer blend ratios before and after being buried in the soil for 1 month is illustrated in Fig. 8(II). It is clear that the shape of the graft copolymer altered after being buried in soil for 1 month (Fig. 8II). When the amount of CG in the graft copolymer increased, the shape of the graft copolymer dramatically changed since there were different environmental conditions. The natural soil environment contains fungi, bacteria and moisture (Riyajan, Intharit,

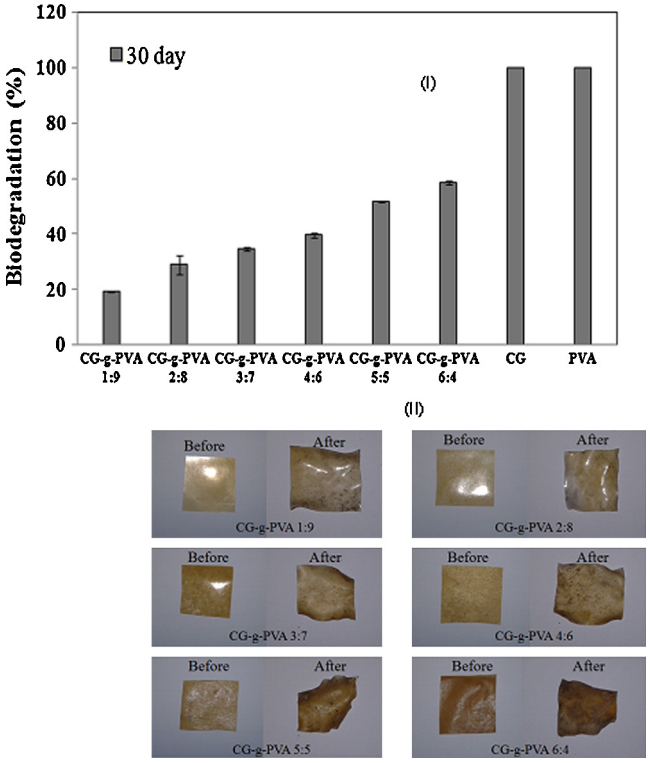

Fig. 8. (I) Biodegradation and (II) photograph images of CG-g-PVA in natural soil after 1 month.

& Tangboriboonrat, 2013). The growth of many fungi can cause small-scale swellings and splitting of the hydrogel as the fungi penetrate the polymer. In addition, the moisture in natural soil together with the water added every week for 1 month penetrates into the CG-g-PVA. Three physical forces: physical, chemical, and biological, cause a deterioration of the polymer hydrogel surfaces and create new surfaces for reacting with chemical and biochemical agents, a critical phenomenon in the degradation of solid polymers (Riyajan et al., 2013). The soil environment can initiate the depolymerization of many biopolymers such as CG, cellulose, and hemicelluloses (Riyajan et al., 2013). In addition, there are many enzymes in the soil water, that might initiate the breakdown of the polymers.

4. Conclusion

The synthesis of novel CG-g-PVA polymers was achieved by the solution method using $K_2S_2O_8$ as an initiator. The chemical structure of the CG-g-PVA was confirmed by ATR-FTIR and XRD. The tensile strength, elongation at break and swelling ratio decreased with an increasing CG content. A smaller dissolution of the graft copolymer CG-g-PVA with a low CG content was observed because of the chemical grafting and the good miscibility between the CG and PVA. The contact angle and the biodegradable percentage increased with an increasing CG content in the graft copolymer. The biodegradation of this graft copolymer degraded easily in natural soil. The best ratio of the CG-g-PVA was 2:8 CG/PVA as evaluated from their mechanical properties and swelling ratio results. The possible application of this work will include preparing cover material for wounds.

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