

## 에폭시기를 가진 천연고무와 Sodium Alginate를 이용한 Carbendazim의 인캡슐레이션

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## Encapsulation of Carbendazim with Epoxidized Natural Rubber/Sodium Alginate

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**Abstract:** This work aimed to study the properties of epoxidized natural rubber (ENR) having 19% mole epoxidation crosslinked with glutaraldehyde (GA) and its application in encapsulation of carbendazim (CAD). The swelling ratio in toluene and the elongation at break of cured ENR decreased with increasing dipping time in GA and the GA concentration. The weight loss of the sample after being buried in soil indicated its biodegradability. The blend of cured ENR with sodium alginate (NaAlg) which was then crosslinked by  $\text{Ca}^{2+}$  or  $\text{GA}/\text{Ca}^{2+}$  was successfully used for encapsulation of CAD. Results showed that the release rate of CAD was controlled by  $\text{GA}/\text{Ca}^{2+}$  and ENR/NaAlg ratios.

**Keywords:** natural rubber, epoxidized natural rubber, glutaraldehyde, encapsulation.

### Introduction

In order to improve the properties of natural rubber (NR), the chemical modification techniques including the epoxidation, cyclization, hydrogenation, and grafting have been applied. Due to epoxide group in epoxidized natural rubber (ENR) structure, the epoxidation is frequently used for improving the weak properties e.g., gas barrier resistance, oil resistance and weathering resistance, of NR.<sup>1,2</sup> In general, ENR is prepared from the epoxidation reaction by using the combination of formic acid and hydrogen peroxide under heating. Similar to NR, ENR must be cured or vulcanized before use. The mechanical properties, elasticity and weathering resistance of the vulcanized rubber are higher compared to the uncured sample. ENR has been cured with sulphur,<sup>3,4</sup> peroxide,<sup>5,6</sup> formic acid,<sup>7</sup> dicarboxylic acid<sup>8</sup> and other curing agents, e.g., poly(lactic acid)/ethylene glycol triblock copolymer<sup>9</sup> and, it is difficult to degrade the sulphur-cured ENR in nature.<sup>10</sup> ENR

can be also modified by blending with other polymers, e.g., polypropylene (PP). The 75/25 ENR/PP blends was vulcanized with sulphur, peroxide and a mixture of sulphur and peroxide-cured systems.<sup>6</sup> Due to the formation of S-S, C-S combined with C-C linkages in ENR phase, the mixing torque, shear stress, shear viscosity, tensile strength and elongation at break of the 75/25 ENR/PP blend using the mixed-cure system exhibited higher values than those of the sulphur and peroxide-cured systems. However, during shearing at high temperature of the peroxide and mixed-cure systems, the peroxide caused degradation of PP molecules. Dodecanedioic acid (DA) was then used for curing reactive functional rubber containing 10 and 25 mol% epoxide groups at 180 °C.<sup>11</sup> Since long heat treatment (3 h) was necessary to complete the reaction, the mechanical properties of the cured rubber were deteriorated. In addition, this curing agent must be used in only solid form while ENR was generally synthesized in latex form. It is interesting in searching for a new crosslinker with fast rate of crosslinking for ENR latex and glutaraldehyde (GA) was a candidate. In the previous works, GA was used as a crosslinker of sodium alginate (NaAlg),<sup>12,13</sup> gelatin,<sup>14,15</sup> and poly(vinyl

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alcohol) (PVA).<sup>16,17</sup> The mixture of  $\beta$ -cyclodextrin and chitosan crosslinked with GA was applied as an absorbent.<sup>18</sup> Based on the interaction between free amino acids from gelatin and aldehyde group of GA, the microcapsules containing Zanthoxylum limonella oil were prepared from gelatin/GA by the coacervation technique.<sup>19</sup> In addition, alginate crosslinked with GA was used as a membrane for the encapsulation of natural pesticide, i.e., neem.<sup>12</sup> The results indicated that the swelling ratio of polymer beads decreased as a function of exposure time to GA and, hence, the rate of release pesticide reduced. GA was used a crosslinker for PVA to use an ultrafiltration membrane with the particle size greater than 100 nm.<sup>20</sup> Until now, there was no any report about the crosslinking of ENR with GA.

The objective of this work was to study the encapsulation of carbendazim (CAD) with ENR having 19% mole epoxidation/sodium alginate (NaAlg). The effect of the GA content on the swelling ratio of the cured ENR in toluene was investigated. The chemical structure of the cured ENR was observed by ATR-FTIR whereas their modulus, tensile strength and elongation at break were tested according to ASTM D412-98a. The feasibility of encapsulation a benzimidazolic compound, i.e., carbendazim (CAD), using ENR blended with sodium alginate (NaAlg) as a matrix was examined. CAD was initially found to be a bioactive metabolite of the fungicide benomyl, and is widely used in crop protection as a fungicide to protect crops from decay caused by various fungal pathogens.<sup>21</sup> It is also used as a pesticide and herbicide for the protection of flowers and flower bulbs. The release rate of CAD was also determined by using UV spectroscopy.

## Experimental

**Materials.** ENR latex (20% TSC, 19% epoxidation) was prepared in our laboratory as described elsewhere.<sup>1</sup> Glutaraldehyde (99%, RFCL Ltd (India), sodium alginate (AR grade, Zhejiang, China), carbendazim (AR grade, Sigma-Aldrich®, Seelze, Germany), Terric® 16A16 (AR grade, Lucky Four, Bangkok, Thailand) and dimethyl sulphoxide (DMSO) (AR grade, RCI Labscan Ltd, Bangkok, Thailand) were used as received.

**Preparation and Characterizations of ENR Crosslinked with GA.** ENR latex (17 g) in the presence of 10% w/w Terric® 16A16 (1 g) was mixed with GA (0, 25, 50, 100 or 150 phr) and stirred by using magnetic stirrer at 60 °C for 3 h. The mixture was cast on a glass plate and then left at room temperature for 3-4 days. After drying in an oven at 50 °C for

24 h, the sample was kept in a desiccator before characterization.

The chemical structure of cured ENR was investigated by using attenuated total reflection-fourier transform infrared spectrophotometer (ATR-FTIR) (Equinox 55; Bruker) for 100 scans. Their degree of swelling ratio was estimated from the equation (1):

$$\text{Swelling ratio} = (W_2 - W_1)/W_1 \quad (1)$$

where  $W_1$  is the original weight of the sample and  $W_2$  is the weight of swollen sample after immersion for 5 days. Experiments were run in triplicate.

The crosslinking density was estimated using eq. (2).<sup>22</sup>

$$\nu = 1/2 M_c = -[\ln(1 - V_r) + V_r + \chi V_r^2]/[2\rho_r V_o (V_r^{1/3} - V_r)] \quad (2)$$

$\nu$  = crosslinking density per gram of rubber

$M_c$  = molecular weight between crosslink

$V_r$  = rubber volume fraction

$\chi$  = Huggin interaction constant

$\rho_r$  = density of the rubber

$V_o$  = molar volume of the solvent

$\rho_s$  = density of solvent

The physical testing of five dumbbell test pieces was analyzed by a universal testing machine (LR10K, Lloy Instruments) based on ASTM D 412 at a rate of 500 mm/min. For the biodegradable study, the cured ENR (2×2 cm<sup>2</sup>) was buried under soil (100 g) at 7 cm depth from top soil (Hat Yai, Province of Songkhla, Thailand). In this experiment, water (50 mL) was poured in sample every week for 1 month. Each week, the sample was carefully taken out, washed with distilled water and dried at 45 °C for 2 days before being weighed. The % weight loss of the residual sample was calculated from the eq. (3).

$$\% \text{ Weight loss} = \frac{W_e - W_1}{W_1} \quad (3)$$

where  $W_e$  is the weight of residual sample after being buried in soil for various times.

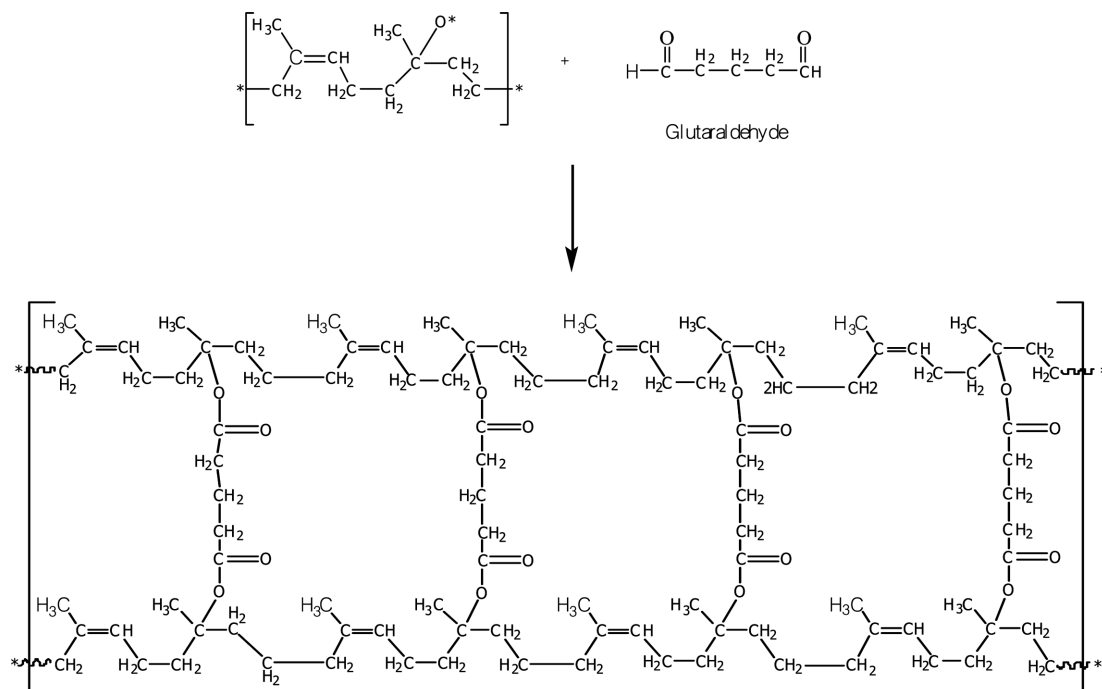
**Encapsulation of CAD with ENR/NaAlg Blend and the Release Study.** ENR latex (10 g) was mixed with 4% aqueous NaAlg solution (40 g) while stirring with a magnetic stirrer. Then, 50% CAD in DMSO (2 g) was added into polymer blend under stirring for 1 min. The mixture containing CAD

was added dropwise, via a 25 mL hypodermic syringe (0.8 mm diameter), into an aqueous solution of 2% calcium chloride 100 mL/mixture of 2% calcium chloride/9% GA 200 mL with constant stirring. The beads formed were filtered, washed with distilled water and then dried at 50 °C in an oven. The efficiency of CAD entrapment was calculated from the ratio between the initial mass of CAD to be encapsulated and its mass in the final product. The total loaded CAD per gram polymer was calculated as in the following. In order to determine the amount of CAD in bead, a known amount of microcapsules (ca. 10 mg) was broken in 50/50 DMSO/H<sub>2</sub>O mixture and stirred for 2 days at room temperature. Subsequently, the suspension was filtered and the CAD content dissolved in the 50/50 DMSO/H<sub>2</sub>O mixture solution was determined by UV spectrometer (Shimadzu UV-1601) at 290 nm ( $\lambda_{\text{max}}$ ). At definite intervals of time, an aliquot (5 mL) was taken for the analysis of CAD by using UV spectrometer (Shimadzu UV-1601) at 290 nm ( $\lambda_{\text{max}}$ ). Experiments were performed thrice. In case of soil medium, the sample (2×2 cm<sup>2</sup>) was buried under soil (100 g) at 7 cm depth from top soil (Hat Yai, Province of Songkhla, Thailand). The water in the soil was allowed to elute in five-day intervals and the eluted solution (50 mL) was collected. The CAD content in the eluted solutions was tested in order to study the release behaviour of the CAD system.

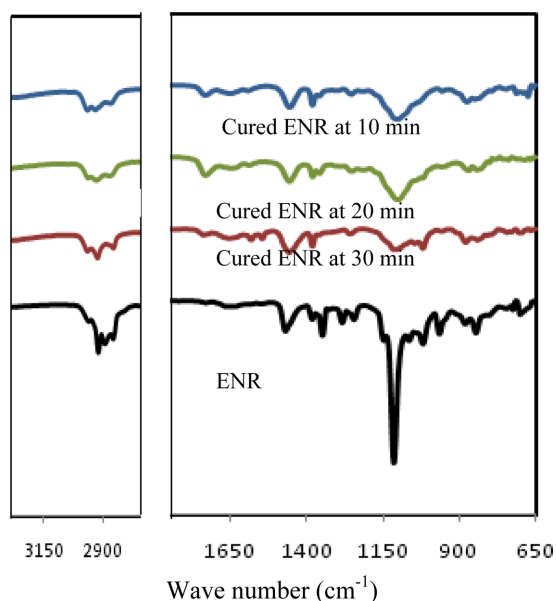
## Results and Discussion

**ATR-FTIR of Cured ENR.** The possible mechanism of crosslinking of ENR with GA is presented in Figure 1. The epoxide ring of ENR was opened by adding small amount of hydrochloric acid and was consequently converted into hydroxyl group.<sup>22</sup> By heating, the aldehyde group of GA attacked the hydroxyl group from ENR molecules and the two reactions, i.e., crosslinking and chain scission, took place.

The chemical structure of ENR crosslinked by immersing in GA for various times was confirmed by ATR-FTIR. As shown in Figure 2, the absorption bands of ENR were found at 2861 cm<sup>-1</sup> (C–H stretching), 1664 cm<sup>-1</sup> (C=C stretching), 1451 cm<sup>-1</sup> (–CH<sub>2</sub>– deformation), 1374 cm<sup>-1</sup> and (methyl C–H deformation)<sup>5</sup>. The new peaks at 1750–1740 cm<sup>-1</sup> and at 1100 cm<sup>-1</sup> of crosslinked ENR compared to pristine ENR were assigned to ester linkage between ENR and GA and to ether group, respectively. The intensity of hydroxyl group from cured ENR decreased due to the chemical reaction. The two vital bands at 2850 and 2750 cm<sup>-1</sup> of C–H stretching related to aldehyde groups in cured ENR. These results agreed well with those concerning PVA crosslinked with GA which was used as a membrane for encapsulation of neem.<sup>12</sup> In that case, a strong band at 1720–1740 cm<sup>-1</sup> from carbonyl groups was verified. The intensity of O–H stretching vibration peak decreased



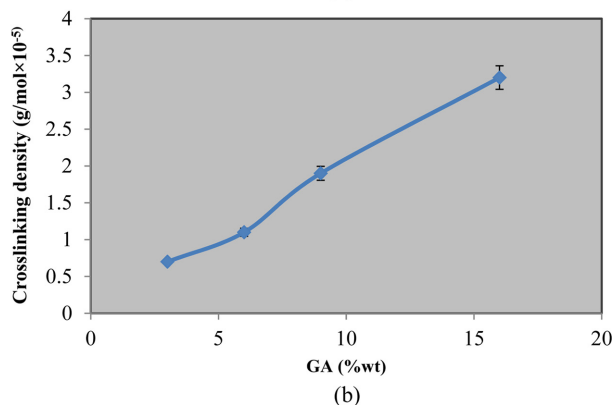
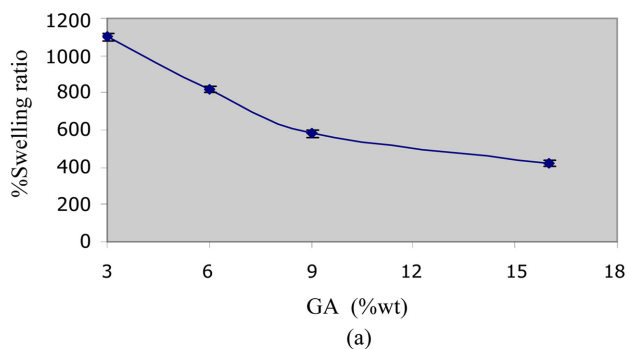
**Figure 1.** Possible reaction of crosslinked ENR with GA.



**Figure 2.** ATR-FTIR spectra of ENR and crosslinked ENR with GA with different immersion times.

when compared to that of pure PVA.

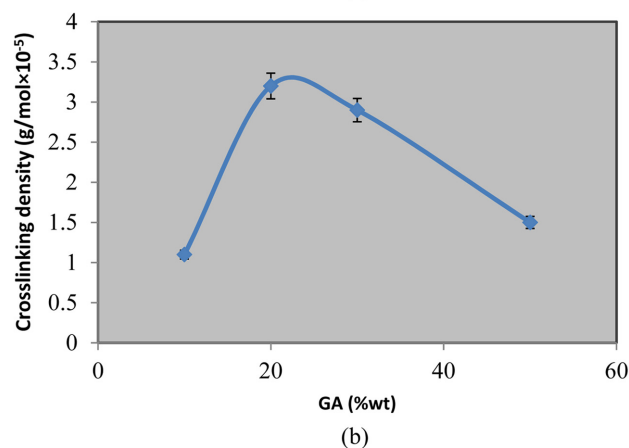
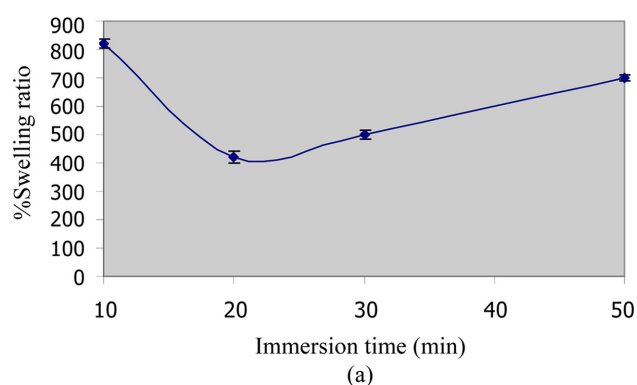
**Swelling Ratio of Cured ENR. Effect of GA Content:** The influence of GA content on the swelling ratio which is practically used to evaluate the crosslinking density of cured



**Figure 3.** Effects of GA on (a) the swelling ratio; (b) crosslinking density of crosslinked ENR with GA for 20 min of immersion time.

ENR was investigated. The swelling ratio and crosslinking density of crosslinked ENR in toluene as a function of GA content is presented in Figure 3(a) and 3(b), respectively. It was found that the swelling ratio decreased from 1200, 800, 600 to 400% and the crosslinking density reduced from 0.7, 1.1, 1.9 and  $3.2 \times 10^{-5}$  g/mol with increasing GA content from 3, 6, 9 to 16% w/w, respectively. The swelling result agreed with the crosslinking density data. The results correlated well with the previous work<sup>12</sup> which studied the effect of GA on the degree of swelling of cured PVA. The more compact structure of polymeric chains resulted in less chain mobility and swelling results.<sup>23,24</sup>

**Effect of Immersion Time:** The effect of time for immersion of ENR in 9% w/w GA solution on the swelling ratio of crosslinked ENR is presented in Figure 4(a). After immersion in toluene for 10 min, the swelling ratio of cured ENR was ca. 800%. The lowest swelling ratio of sample was found at 20 min of immersion time due to the crosslinking between hydroxyl group of the ENR and aldehyde group from GA. With increasing the immersion time from 20 to 50 min, the swelling ratio of cured ENR increased from 400 to 500%. This

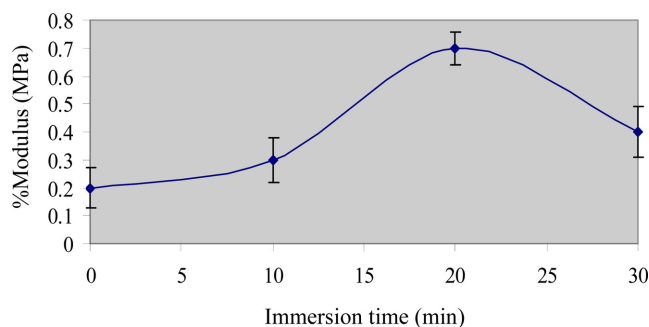


**Figure 4.** Effects of immersion time on (a) the swelling ratio; (b) crosslinking density of crosslinked ENR with 9% w/w GA.

was caused from the chain scission of the ENR chains which could be degraded by an excess GA.<sup>25</sup> The influence of immersion time of ENR in 9% w/w GA solution on the crosslinking density of crosslinked ENR is illustrated in Figure 4(b). It is clear that the crosslinking density of crosslinked ENR result supported with their swelling ratio data. The crosslinking density of crosslinked ENR containing 10, 20, 30 and 40% GA was 1.1, 3.2, 2.9 and  $1.5 \times 10^{-5}$  g/mol, respectively.

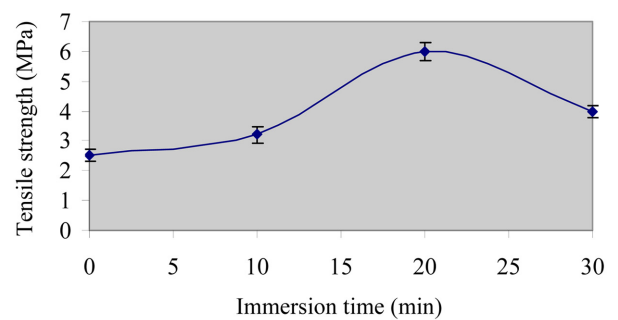
**Mechanical Properties of the Cured ENR:** The modulus of the cured ENR as a function of immersion time of ENR in GA solution is displayed in Figure 5. Similar to the swelling ratio, the modulus slightly increased in the beginning and rapidly increased to attain the maximum value of 0.7 MPa within 20 min of immersion. After that period, the modulus decreased to 0.4 MPa due to the chain scission of polymer as a mentioned above. The tensile strength and elongation at break of the cured ENR as a function of immersion time are presented in Figure 6(a) and 6(b), respectively. The highest tensile strength (5.3 MPa) was obtained within 20 min of immersion time which was due to the strengthened forces, by which the aldehyde groups covalently bonded with hydroxyl groups from ENR molecules.<sup>26</sup> The high crosslinking density of the cured ENR also led to the decrease of elongation at break from 680 to 550% when increasing immersion time from 10 to 20 min respectively, as observed in Figure 6(b).

**Biodegradability of the Cured ENR:** The effect of time for the immersion of the ENR in 9% w/w GA solution on the decomposition of cured ENR buried in soil is investigated. Figure 7 displays that %weight loss of cured ENR dramatically decreased with increasing the immersion time. The rate of biodegradability of cured ENR at 15 min of immersion time in Figure 7(a) was faster than that of ENR immersed for 20 and 30 min in Figure 7(b) and 7(c), respectively. It was explained that the higher crosslinking density of cured ENR in the latter

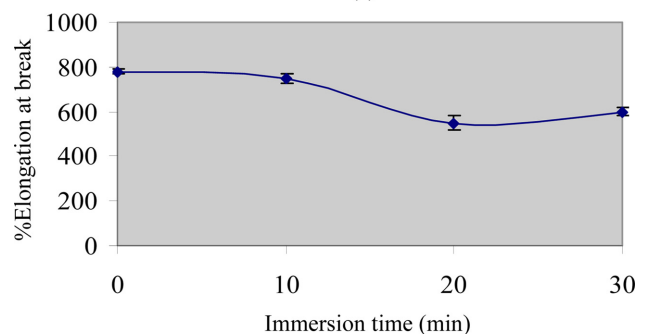


**Figure 5.** Effect of GA on modulus of crosslinked ENR with GA at different immersion time of cured ENR in 9% GA solution.

cases impeded the penetration of bacteria into the sample. It is well known that NR containing high molecular weight ( $\sim 10^6$ ) *cis*-1,4-polyisoprene was responsible for the more difficult biodegradation compared to starch.<sup>1</sup> NR can be slowly degraded in nature by specific microorganisms i.e., *Streptomyces* 31 strains, *Micromonospora* 5, *Actinoplanes* 3, *Nocardia* 2, *Dactylosporangium* 1, and fungi.<sup>1,25,26</sup> The total aerobic activity started from the decomposition of polymer chain, followed by the metabolization of the depolymerization products by the mixed microbial populations and their eventual mineralization.<sup>27</sup> Certainly, the biodegradability of cured rubber by

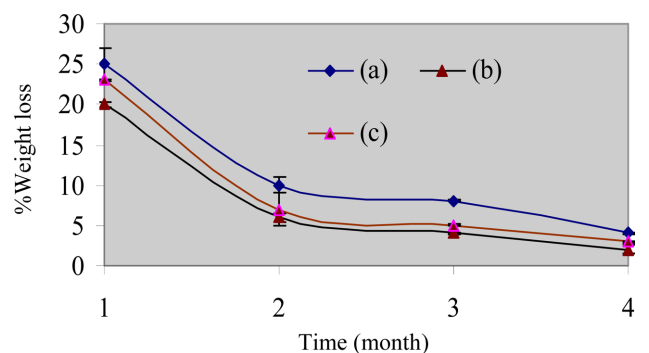


(a)



(b)

**Figure 6.** (a) Tensile strength; (b) elongation at break of crosslinked ENR with GA.

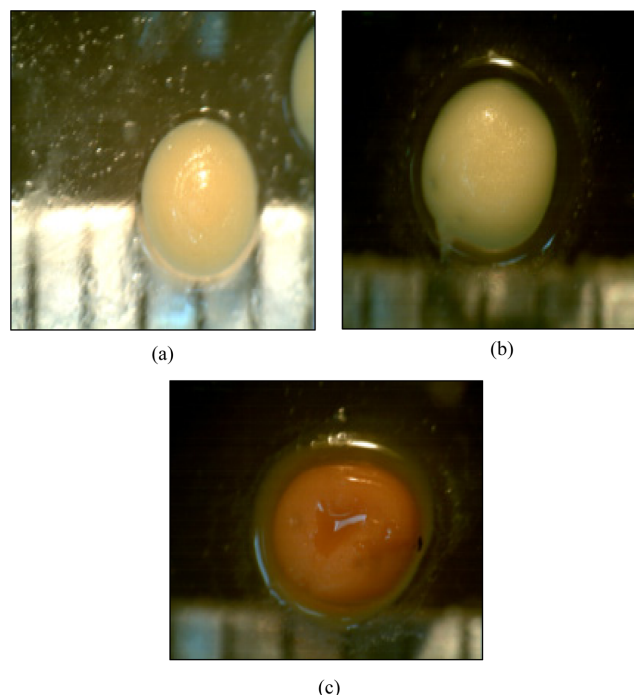


**Figure 7.** Biodegradation of crosslinked ENR with 9% GA at (a) 10; (b) 20; (c) 30 min of immersion time in soil.

microorganisms is slower.<sup>28</sup> Due to ester linkage between ENR and GA, ENR cured with GA would be decomposed easier by microorganisms in soil compared with that cured with sulphur. In addition, the oxirane groups of ENR played an important role in enhancing the biodegradability.<sup>29</sup>

**Encapsulation of Carbendazim:** The ratio between ENR and NaAlg and crosslinkers on encapsulation efficiency were investigated (Table 1). When the ratios of ENR and NaAlg increased from 2.5: 1, 5:1 and 8:1 ENR/NaAlg, the encapsulation efficiency was about 90, 95 and 96%, respectively. There are two models for encapsulation of reactive agent e.g. carbendazim such as encapsulation model and matrix model. The capsules consisting of a core and a permeable or non-permeable wall have been widely used in release and transfer control.<sup>30,31</sup> The model of encapsulation for this work is a matrix model in which carbendazim disperses in ENR/NaAlg matrix. Comparison between two crosslinkers, the encapsulation efficiency of 5:1 ENR/NaAlg which was cured with  $\text{Ca}^{2+}$  was lower than that of sample crosslinked with both GA and  $\text{Ca}^{2+}$ . These phenomena were due to a higher crosslinking density which results two crosslinkers. These data were correlated well with the swelling ratio results. It can't dissolve in epoxidized natural rubber/sodium alginate blend matrix and dispersion in the matrix. However, this occurs chemical interactions between the carbendazim and the matrix.

**Effect of Crosslinker.** The capsule embedding CAD into NaAlg blended with ENR and then crosslinked with  $\text{Ca}^{2+}$  and GA/ $\text{Ca}^{2+}$  was prepared for the controlled release purpose. The resulted capsule was spherical in shape and its average particle size was  $1.12 \pm 0.3$  mm as shown in Figure 8. When increasing immersion time of capsule, the color changed from yellow into brown due to more crosslinking reaction (Figure 8(a)-(c)). Jaiswal and co-worker<sup>32</sup> reported that NaAlg a bead, suspended in solution, crosslinked with GA was white and it changed in reddish brown after drying. The carboxylic acid



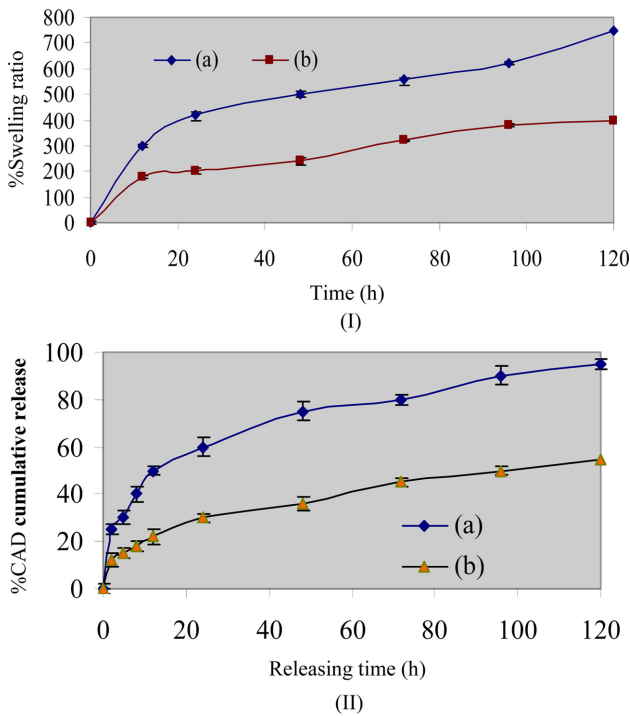
**Figure 8.** Photograph images of crosslinked ENR with 2% w/w  $\text{Ca}^{2+}$ /9% w/w GA at (a) 10; (b) 20; (c) 30 min of immersion time observing from digital camera.

from NaAlg reacted with GA/ $\text{Ca}^{2+}$ , while hydroxyl group of ENR reacted with aldehyde group of GA. The influence of  $\text{Ca}^{2+}$  and GA on the swelling ratio of the bead immersed in DMSO/ $\text{H}_2\text{O}$  medium is presented in Figure 9(I). Results show that the swelling ratio of beads crosslinked with GA/ $\text{Ca}^{2+}$  in Figure 9(I)(b) was lower than that of sample cured with  $\text{Ca}^{2+}$  in Figure 9(I)(a). The %swelling ratio of beads crosslinked with  $\text{Ca}^{2+}$  for 72 h was 600, while that of beads cured with GA/ $\text{Ca}^{2+}$  was 300. The higher  $\text{Ca}^{2+}$  or GA concentration was responsible for the formation of gels having higher crosslinking densities. These results supported the previous study concerning the decrease of swelling degree of all NaAlg/gelatin hydrogels when increasing concentration of both the crosslinking agents.<sup>26</sup>

The CAD dispersed in bead matrix with different crosslinking densities was released into water medium. Before determining the released CAD by using UV-visible spectroscopy, the beads were washed with water to completely remove the CAD remained on their surface. The effect of  $\text{Ca}^{2+}$  or GA/ $\text{Ca}^{2+}$  used as a crosslinker on the CAD release is displayed in Figure 9(II). It was clear that %CAD released from the capsules crosslinked with only  $\text{Ca}^{2+}$  (as shown in Figure 9 II(a)) was faster than those crosslinked with GA/ $\text{Ca}^{2+}$  (as shown in Figure

**Table 1. Efficiency of Encapsulation Obtained at Different Ratios between ENR/NaAlg and Crosslinkers**

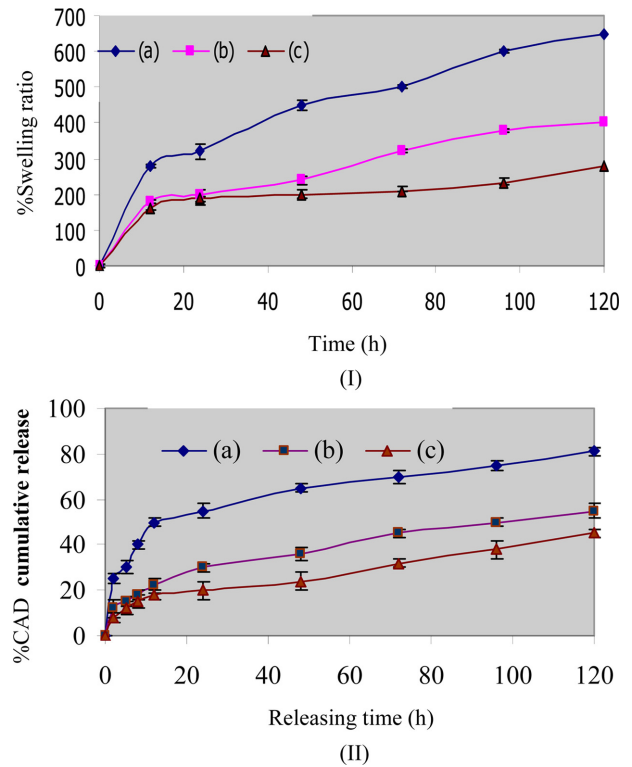
Condition	% Efficiency of encapsulation ( $\pm\%$ S.D.)
2 % w/w $\text{Ca}^{2+}$ / 9%w/w GA	90 (2.5)
2.5: 1 ENR/NaAlg	95 (5.0)
5:1 ENR/NaAlg	96 (3)
8:1 ENR/NaAlg	
2% w/w $\text{Ca}^{2+}$	91 (5)
5:1 ENR:NaAlg	



**Figure 9.** Effects of crosslinking with (a)  $\text{Ca}^{2+}$ ; (b) 2% w/w  $\text{Ca}^{2+}$  and 9%w/w GA at 20 min of immersion time in bead on (I) %swelling ratio in 50/50 DMSO/ $\text{H}_2\text{O}$  and (II) release of CAZ from bead (5:1 ENR:NaAlg).

9(II)(b)) having higher crosslinking density.<sup>23</sup> The cumulative CAD released from two capsules was very fast within 20 h. Then, the rate of cumulative CAD released from these capsules was slightly increased. The cumulative CAD released from beads crosslinked with  $\text{Ca}^{2+}$  and GA/ $\text{Ca}^{2+}$  stored at the same condition for 72 h were 80 and 45%, respectively. The capsule wall was broken by solvent action due to its dissolution and different osmotic pressures between capsule and medium. Then, the CAD diffuses from capsule.

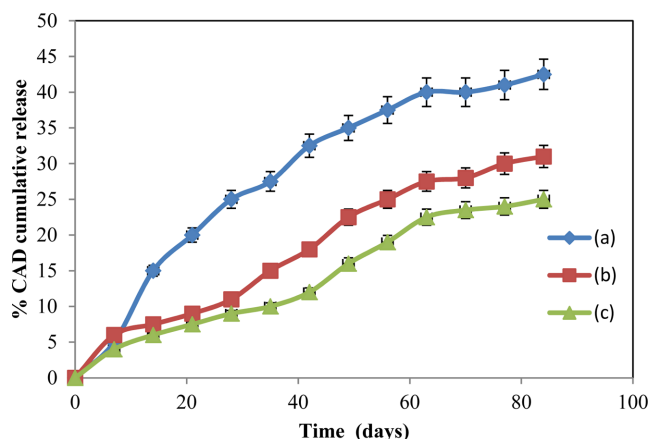
**Effect of ENR:NaAlg Ratio:** The swelling ratio of beads prepared from different ENR: NaAlg ratios, i.e., 2.5:1, 5:1 and 8:1 ENR:NaAlg matrix as a function of immersion time in 50:50 DMSO/water is displayed in Figure 10(I) (a), (b) and (c), respectively. Results showed that the swelling ratio of beads immersed for 72 h decreased from 500, 320 to 210 with increasing ENR content from 2.5, 5 to 8, respectively. When the immersion time increased from 72 to 120 h, the swelling ratio of beads at 2.5:1, 5:1 and 8:1 ENR:NaAlg was 650, 400 and 280%, respectively. The effect of ENR:NaAlg blend on the CAD release is presented in Figure 10(II). The CAD release rate was significantly reduced when increasing ENR content in the blend. This might be explained by the different



**Figure 10.** Effects of (a) 2.5:1; (b) 5:1; (c) 8:1 ENR:NaAlg in bead on (I) %swelling ratio in 50/50 DMSO/ $\text{H}_2\text{O}$  and (II) release of CAD from bead crosslinked with 2 % w/w  $\text{Ca}^{2+}$  and 9%w/w GA at 20 min of immersion time.

swell ability of ENR:NaAlg matrix which is the rate limiting step for swelling and CAD release. The beads having low ENR content were easily swollen by water, and, consequently, the CAD rapidly diffused through the swollen beads due to the weak interaction between CAD and polymer matrix membrane. The CAD contents cumulatively released from the beads containing 2.5:1, 5.0:1 and 8:1 ENR:NaAlg within 120 h were 76, 55 and 40%, respectively. This result correlated well with the previous study involving the effect of PVA/NaAlg ratio on the properties of neem capsule.<sup>12</sup> The neem capsule made from PVA/NaAlg absorbed smaller amount of water than those obtained from NaAlg. PVA had higher water resistance due to greater crystalline content.

In case of soil medium, the influence of ENR:NaAlg blend on the CAD release from bead was also evaluated comparing to water medium and data are illustrated in Figure 11. A slow and sustained release of CAD over a period more than 3 months was observed. In general, the CAD release from all beads increased as a function of time. The CAD release from bead in soil medium was correlated with water medium. The maximum CAD cumulative release from bead when using



**Figure 11.** Influence of (a) 2.5:1; (b) 5:1; (c) 8:1 ENR:NaAlg in bead on release of CAD from bead crosslinked with 2%w/w  $\text{Ca}^{2+}$  and 9%w/w GA at 20 min of immersion time.

2.5:1 ENR:NaAlg. The release behaviour observed with fertilizer composition is not as uniform as that observed for drug-release compositions. It was explained that the fluctuations in the physical environment of the soil compared to the relatively stable physical parameters present in a biological system.<sup>33</sup> In addition, the rate of CAD release in soil medium was very slower than that of water medium owing to different environments affecting on destroy of the matrix.

## Conclusions

GA could be effectively used as a crosslinker of ENR at 70 °C. The swelling ratio in toluene of cured ENR was lower than the uncured ENR. The highest modulus and tensile strength of cured ENR were obtained with using 20% GA w/w. The cured ENR was easily degraded in soil. The swelling ratio and elongation at break of cured ENR reduced with increasing dipping time in GA and the GA concentration. The optimal immersion time for curing ENR was 20 min. When ENR was blended with NaAlg and then cured with GA/ $\text{Ca}^{2+}$  for use for encapsulation of CAD, the rate of controlled release of CAD decreased with increasing NaAlg concentration. The cured ENR membrane which was biodegradable displayed a good barrier for controlling the release of CAD from capsule.

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