Slow Release Material from Epoxidized Natural Rubber and Rice Husk Composites for Agriculture Applications

Marwa N Al-Samarrai¹, R Hamzah¹, S T Sam², N Z Noriman¹, Omar S Dahham¹, S Z Syed Idrus³, T Adam¹,⁴

¹ Center of Excellence Geopolymer and Green Technology (CEGeoGTech), Faculty of Engineering Technology (FETech), Universiti Malaysia Perlis (UniMAP), Level 1 Block S2, UniCITI Alam Campus, Sungai Chucuh, Padang Besar, 02100, Perlis, Malaysia.
² School of Bioprocess Engineering, Universiti Malaysia Perlis (UniMAP), Kompleks Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia.
³ School of Human Development and Techno-communication (iKOM), Green Advanced Computing and Technology (GREAT) Research Group – CEGeoGTech, Universiti Malaysia Perlis (UniMAP)
⁴ Institute of Nano Electronic Engineering (INEE), Universiti Malaysia Perlis (UniMAP), 01000 Kangar, Perlis, Malaysia
E-mail: rosnizahamzah@unimap.edu.my

Abstract. This synthesis and characterization of slow release material from epoxidized natural rubber (ENR) and rice husks (RH) composites was conducted. The alkali modification of rice husks was carried using different NaOH concentration. ENR-50 and RH composites were analyzed by FTIR. Furthermore, the release behavior of the composites was investigated using UV-visible spectroscopy. From the purified ENR-50, it can be characterized the peak epoxide group identified at 875 cm⁻¹ and for the isoprene at 835 cm⁻¹. For RH/urea beads, the CH₂ peak of cellulose was obtained at 1457 cm⁻¹. However, the CH₂ is overlapped with cellulose at 1741 cm⁻¹ and 1726 cm⁻¹ that resulted for the partial opening of epoxide ring from carbonyl peak for hemi-cellulose and lignin, there are C=C stretching from aromatic group can be obtained at 1512 cm⁻¹ and 1595 cm⁻¹. The release of the composite at 7% NaOH concentration was higher than the composite at 1% NaOH concentration.

1. Introduction
Natural rubber (NR) is a Malaysia’s commodity that obtained from latex tree Hvea Brasiliences. NR that contain 99% of cis-1,4-polyisoprene is an elastomeric material and contributes to high degree of crystallization as well as high mechanical properties for natural rubber. Epoxidized natural rubber (ENR) is a modified NR while epoxidized natural rubber-50 (ENR-50) is a modified natural rubber with 50 mole percentage of epoxidation and 50 mole percent of isoprene. There are various fields that used the ENR such as polymer blends, polymer modifications, polymer composites and advanced green materials [1,2]. Both NR and ENR are considered as green polymer and green materials due to non-toxic and non-hazardous properties [3].

Rice husk (RH) are one of the major by-product, which would always be removed during the rice-milling process [4]. The RH contains cellulose, hemicelluloses and lignin [5]. The exterior structure of rice husk is the silica coated with a thick cuticle and surface hairs. It provides with other special husk to form physical interaction matrix [6]. The chemical composition of rice husk is cellulose (40-50%),...
lignin (25-30%), ash (15-20%) and moisture (8-15%). The common organic fibers mostly contains the same composition like a rice husk [7]. Rice husk is suitable as filler in polymer composites due to the low cost, low density, high specific strength and modulus, and recyclability [8]. Slow release is a method that active ingredient is release as a function of time [9]. The release of the active ingredient may be controlled by microbial release or water and it is due to chemical properties of materials. Fertilizer is the important thing in the food security that might be as a input material for the sustainable development of the crop production [10]. The slow release fertilizer (SRF) is a fertilizer that been coated with another materials to release it active ingredient slowly to the soil for a period time. This method is suitable in agriculture and it consistently releases the nitrogen to the plants. It also improves the soil quality, property control and the germination rate [11]. Ultraviolet and visible spectroscopy is a technique to infrared spectroscopy and it will be used to analyze solutions of organic compound and complex metal ions. UV-Vis spectroscopy is used to determine the concentration of the solution. According to the Beer-Lambert law, the relationship of the absorbance of a solution with the concentration of the absorbing species in the solution and the path length is directly proportional. This law also is the principle behind absorbance spectroscopy [12]. The law may be written in terms of the absorption A for a single wavelength which is equation 2.

\[ A = abc \] (2.0)

Where \(a\) is the molar absorptivity of the compound or molecule solution (M\(^{-1}\)cm\(^{-1}\)), \(b\) is the path length of the cuvette or sample holder (usually 1 cm) and \(c\) is the concentration of the solution (M) [4].

2. Experimental Part

2.1. Materials and chemicals

All chemicals were obtained commercially and used without further purification unless otherwise mentioned as tabulated in Table 3.0. n-hexane were from Systerm, Malaysia. Epoxidized natural rubber of 50% epoxidation level (ENR-50) was purchased from the Rubber Research Institute, Malaysia. Rice Husk (RH) were from Merbuk MDF Sdn. Bhd., Kedah, Malaysia. Urea fertilizer was purchased from PETRONAS Fertilizer (Kedah) Sdn. Bhd., Kedah, Malaysia. Tetrahydrofuran (THF) from BASF Petronas Chemicals Sdn. Bhd., Selangor, Malaysia. Isopropanol (IPA) was obtained from Primechem Malaysia Sdn. Bhd., Johor, Malaysia. Chloroform was obtained from Octagon Chemicals Sdn. Bhd., Selangor, Malaysia. Sodium chloride (NaCl) was purchased from BIS Chemicals Sdn. Bhd., Selangor, Malaysia.

2.2. Purification of ENR-50

About 20.00 g of ENR-50 was swelled in 400 mL of chloroform and it stirred for 24 hours at room temperature [13]. The cotton gauze was used to separate the high molecular from the low molecular weight ENR-50. Next, the precipitate was obtained by stirring the low molecular weight ENR-50 in n-hexane by using glass rod. The white precipitate that form on the surface of glass rod was removed onto the Teflon Petri dish and dried in a vacuum oven at 50 °C for two days. The weight of purified ENR-50 was recorded daily until the constant weight of ENR-50 achieved. The dried sample was characterized using FTIR analysis.

2.3. Pretreatment of Cellulose

The rice husk was washed with tap water to remove excess of soil and dirt and finally with distilled water. Then, it was dried in a convection oven at temperature of 60 °C to remove excess moisture for 2 hours. The dried rice husk was stranded and through the grinder with 500 μm mesh screen to achieve a uniform particle size. The rice husk was soaked in the 7 wt% of sodium hydroxide (NaOH) solution for 24 hours and abbreviated as cellulose pre-treatment process. The 7 wt% of NaOH solution was prepared by dissolving 7.0 g of NaOH in 100 mL of distilled water. The filter funnel and filter paper were used to filter the mixture and to separate the cellulose from its NaOH mixture. Then, the pH value of the supernatant was measured using pH paper. The sample was washed repeatly using
distilled water until neutral was attained. Then, the sample was air dried under sunlight and later dried in a vacuum oven for 48 hours at 50 °C. This steps was repeated by soaking the rice husk in the 1 wt% of sodium hydroxide (NaOH) solution. The FTIR was used to analyze the sample [14].

2.4. Pretreatment of Cellulose /urea beads
A 60 g of urea fertilizer was dissolved in 500 mL of distilled water to prepare a thick mixture of 12 wt% of urea fertilizer solution [9]. The sample obtained from treated of rice husk was soaked in 12 wt% urea solution for 24 hours at room temperature. The sample was filtered to separate the cellulose/urea solution mixture by using filter funnel. Then, the sample was air dried under sunlight and later in a vacuum oven for 48 hours at 50 °C. The FTIR analysis was used to characterize the sample

2.5. Pretreatment of Cellulose/Urea Beads Coated with ENR-50/Salt Composite
The solution mixture was mixed with 20.0 mg of cellulose/urea beads. The homogenous solution was formed after stirring the mixture for 24 hours at room temperature. The mixture was air dried for 48 hours and then further dried using vacuum oven at 50 °C for 24 hours.

2.6. Release study
The distilled water was used to conduct the slow release of the SRM in this experiment. About 200 mL of distilled water was used to soak the composite obtained from the preparation of beads. About 5.0 g of dry sample were added into the conical flask that containing 200 mL of distilled water and it being placed in an incubator at 25 °C. About 5 mL of solution was taken daily to investigate the content of urea in the solution. Thus, 5 mL of distilled water was added to maintain the constant amount of solvent. The experiment has been carried out for 30 days and the UV-Vis spectrophotometer was used to characterize the samples.

2.7. Kinetic study
A standard urea fertilizer concentration was prepared for kinetic study reason. 100 mL aqueous solution was prepared having concentration between 0.2 mg/mL and 1.0 mg/mL. 20 mg of urea fertilizer dissolved in 100 mL of distilled water to obtain 0.2 mg/mL. UV-Vis spectrophotometer was used to record the UV-Visible absorbance spectrum of the prepared solution. The spectrum with absorbance on the y-axis (dependent variable) and concentration in mg/mL on the x-axis (independent variable) was plotted as the calibration curve. The gradient of the graph was used as molar absorptivity for Beer-Lambert equation. Then, the concentration was calculated to plot a graph of concentration versus time.

3. Results and Discussion

3.1. FTIR of ENR-50 and ENR-50/Salt Composite
Figure 1(a) shows the FTIR spectrum of purified ENR-50. Generally, there are five types of peaks presented the CH, CH₂, CH, epoxide, and isoprene (C=C). The CH peaks are detected at 2863 cm⁻¹ and 2963 cm⁻¹ while CH₂ at 2927 cm⁻¹ and 1451 cm⁻¹ [13]. The CH peak at 1378 cm⁻¹. The evidence of epoxide group at 875 cm⁻¹ is the C-O epoxide half ring stretching [7]. The stability of isoprene group is shown by C=C peak at 838 cm⁻¹.

The FTIR spectrum of ENR-50/salt composite is shown in Figure 1(b). The OH peaks is broad as compared to purified ENR-50. This is due to the hydrosopic nature of NaCl. It is well known that most of the salt such as NaCl, MgCl₂ etc is easily trapped moisture contain its ionic structure. This explains the incorporation of moisture to ENR-50 matrix in the presence of salt. Thus, OH peak of ENR-50/salt composite is detected at 3427 cm⁻¹. The CH₃ peaks at 2963 cm⁻¹ and 2853 cm⁻¹. The CH₂ peaks at 2921 cm⁻¹ and 1448 cm⁻¹. The CH peak at 1378 cm⁻¹ [15]. The epoxide groups are remained at 875 cm⁻¹ and isoprene at 835 cm⁻¹. The rest of the peaks almost similar to the purified ENR-50 as and this suggest that the loading of salt does not change the chemical structure of purified ENR-50.
3.2. FTIR of pretreated RH and RH/urea beads

Figure 2 shows the FTIR spectra of treated RH with (a) 1% NaOH, (b) RH/urea beads with pretreated 1% NaOH, (c) 7% NaOH and (d) RH/urea beads with pretreated 7% NaOH. In general, RH contains cellulose, hemicellulose and lignin. The pretreated of RH with different concentration of NaOH is carried out to expand the volume of fibrous cellulose structure in RH. The expanded volume is necessary to occupy more urea into it. Thus, it is acceptance for RH to contain cellulose, hemicellulose and lignin after the pretreatment process.

Typically, there are several groups of peaks attributed to the structure of cellulose, hemicellulose and lignin. The OH stretching of cellulose is located at 3353 cm\(^{-1}\) in Figure 2(a) [15]. The CH\(_2\) peak of cellulose was obtained at 1457 cm\(^{-1}\) due to the C-H bending as shown in Figure 2(b). The broad and strong peak in Figure 2 were obtained between 1153 cm\(^{-1}\) to 1159 cm\(^{-1}\) due to the C-O stretching vibration from tertiary alcohol [16]. For the hemicellulose, The CH\(_2\) is overlapped with cellulose at 1741 cm\(^{-1}\) and 1726 cm\(^{-1}\) (Figure 2(a,c)) that can be seen as a result of partial opening of epoxide ring from carbonyl peak [17]. This peak also shows the carbonyl stretching vibration which is C=O stretching of carboxylic group [18]. For lignin, there are C=C stretching from aromatic group can be obtained at 1512 cm\(^{-1}\) and 1595 cm\(^{-1}\) (Figure 2(c,d)) due to the removal of lignin after alkali treatment [8].

The spectrum of rice husk after treatment with 1% NaOH and 7% NaOH shows the differences peak from 1058 cm\(^{-1}\) to 1043 cm\(^{-1}\) in Figure 2(a,c). The physical interaction between epoxy groups and cellulose groups might be occurred. After mesh urea, the new peaks in Figure 2(b,d) was observed at 3460 cm\(^{-1}\) and 3442 cm\(^{-1}\) for RH/urea beads with pretreated 1% NaOH and RH/urea beads with pretreated 7% NaOH. This is due to the hydroscopic nature of NaCl to trap moisture. Thus, most of the urea peaks overlapped with RH such as CH\(_3\), CH\(_2\) and CH types.
3.3. Evaluation of release study

The Figure 3 shows the release curve of absorbance versus time from RH/urea beads 1% NaOH coated with ENR-50/NaCl composite and RH/urea beads 7% NaOH coated with ENR-50/NaCl composite for 30 days.

The trending for both graph shows the release of urea fertilizer was gradually increased. This figure shows the amount of urea release from the RH/urea beads for 1% NaOH is higher than RH/urea beads for 7% NaOH. This is due to the formation of pores on the surface of RH/urea beads coated with ENR-50/NaCl composite that more available to release the urea fertilizer.

Figure 3. The release study of treated composites at different NaOH concentration.
3.4. Kinetic study of release rate

The standard curve was obtained from the absorbance values for different concentration of urea fertilizer. The standard urea concentrations were chosen between 0.2 to 1.0 mg/mL and the value of $a$ is obtained from gradient of the standard curve. Then, its values substituted into Beer-Lambert equation to find the concentration.

Figure 4 shows the amount of urea fertilizer released at RH/urea beads 1% NaOH coated with ENR-50/NaCl composite, about 49.14%, 62.99% and 100% (wt%) of urea fertilizer are released at day 1, 15 and 30 of water incubation respectively. At RH/urea beads 7% NaOH coated with ENR-50/NaCl composite, the urea fertilizer released 56.26%, 79.73% and 100% (wt%) at day 1, 15 and 30 respectively.

The release study was divided into three stage which are the water penetrated the ENR-50 coating at the first stage. For the second stage, the urea released is constant by following the period of time and its flowed through the coating. Then, the urea fertilizer released at a stage of deadline that finally ended.

The slow release mechanism involves the absorption of water by the coating material which cause it to swell and will transform into hydrogel. Thus, ENR-50 is cross-linked hydrophilic polymer which has an ability to absorb water and cannot discharged easily even under extended pressure. The core urea fertilizer then dissolves in the hydrogel water and diffuses slowly through a grid of the swollen hydrogel from within the hydrogel to water in the soil via mass transfer of water. Water was diffused through the coating on the surface then slowly penetrated the RH/urea beads layer to dissolve the urea fertilizer. The urea fertilizer will flow out gradually between hydrogel free water and soil moisture.

![Graph Concentration against Time (Days)](image)

Figure 4. The release study curve from the graph concentration against time

4. Summary

In conclusion, the peak of epoxide group in the composite was identified at 875 cm$^{-1}$ and for the isoprene at 835 cm$^{-1}$. The CH$_2$ peak of cellulose in the composite was obtained at 1457 cm$^{-1}$ due to the C-H bending. However, the CH$_2$ is overlapped with cellulose at 1741 cm$^{-1}$ and 1726 cm$^{-1}$. The release of urea from treated composite at 7% NaOH was higher than treated composite at 1% NaOH.

5. Acknowledgement

The authors would like to acknowledge UniMAP Short Term Grant Scheme (9001 - 00521). We would also appreciate Universiti Malaysia Perlis (UniMAP) for providing us all the facilities to make this research.
6. References
1. R. Hamzah, M. A. Bakar, O. S. Dahham, N. N. Zulkepli and S. S. Dahham, J. Appl. Polym. Sci., 133 (2016).
2. O. S. Dahham, R. Hamzah, M. A. Bakar, N. N. Zulkepli, S. S. Ting, M. F. Omar, K. Muhamad, and S. S. Dahham, Polymer Testing 65, 10-20 (2018).
3. I. S. A. Rahim and M. A. Ahmad 9, 64–69 (2015).
4. O. S. Dahham, N. Z. Noriman, S. T. Sam, N. M. Al-Samarrai, Z. Shayfull, A. M. Alakrach and S. A. Elnaid, MATEC Web of Conferences 78, 01075 (2016).
5. B. Ndazi, J. V. Tesha, S. Karlsson and E. T. N. Bisanda, Journal of Materials Science 41, 6978–6983 (2006).
6. S. Turmanova, S. Genieva and L. Vlaev, International Journal of Chemistry 4, 62–89 (2012).
7. G. Liu, L. Zotarelli, Y. Li, D. Dinkins and Q. Wang, Controlled-Release Fertilizers Slow-Release Fertilizers Controlled-Release Fertilizers, 1–7. (2014).
8. R. Syafri, I. Ahmad and I. Abdullah, Sains Malaysiana 40, 749–756 (2011).
9. L. C. Medina, J. B. Sartain and T. A. Obreza, Hort Technology 19, 13–15 (2009).
10. L. Xie, M. Liu, B. Ni, X. Zhang and Y. Wang, Chem. Eng. J. 167, 342–348 (2011).
11. B. Azeem, K. Kushaari, Z. B. Man, A. Basit and T. H. Thanh, J. Controlled Release 181, 11–21 (2014).
12. R. Gandhimathi, S. Vijayaraj and M. P. Jyothisarmaie, International Journal of Pharmaceutical Research & Analysis 2, 72–78 (2012).
13. O. S. Dahham, R. Hamzah, M. A. Bakar, N. N. Zulkepli, S. S. Dahham and S. S. Ting, Polym. Test. 59, 55-66 (2017).
14. N. A. Samad, R. Othaman and I. Abdullah, International Journal of Materials Engineering Innovation 5, 61-69 (2014).
15. N. Z. Noriman, H. Ismail and A. A. Rashid, Journal of Applied Polymer Science, 126, 56 (2012).
16. R. T. Conley, “Qualitative Analysis” in Infrared Spectroscopy, 2nd edition by Boston (Allyn and Bacon Inc., 1972), pp. 112-140
17. W. A. K. Mahmood, M. M. R. Khan and M. H. Azarian, J. of Non-Cryst. Solids 378, 152-157 (2013).
18. M. Taheridanak and H. Zilouei, Fuel 115, 714-719 (2014).