PAPER • OPEN ACCESS

New Slow Release Fertilizer from ENR-50/RH/Urea Composites: Effect of Sodium **Chloride Concentration**

To cite this article: Marwa N Al-Samarrai et al 2018 J. Phys.: Conf. Ser. 1019 012062

View the article online for updates and enhancements.

You may also like

- Green natural rubber-based membrane for drug release Wichitraphon Prathumsuk, Atitsa Petchsuk, Mantana Opaprakasit et al.
- Effective non-retarded method as a tool for the design of tunable nanoparticle composite absorbers Guillermo Ortiz, Marina Inchaussandague, Diana Skigin et al.
- Comparison of epoxidised natural rubber (enr) 37.5 and enr 25/ enr 50 physical blend: Specialty polymer for 'green tyre' application N Y Wan, K P Chin and C S Mt Saad





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.147.89.47 on 12/05/2024 at 05:32

New Slow Release Fertilizer from ENR-50/RH/Urea **Composites: Effect of Sodium Chloride Concentration**

Marwa N Al-Samarrai, R Hamzah¹, S T Sam², N Z Noriman¹, Omar S Dahham¹, S Z Syed Idrus³, S Sudin⁴

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 School of Computer and Communication Engineering (SCCE), Green Advanced Computing and Technology (GREAT) Research Group - CEGeoGTech, Universiti Malaysia Perlis (UniMAP)

E-mail: rosnizahamzah@unimap.edu.my

Abstract. A green and renewable slow release material (SRM) was developed using combination of urea, epoxidized natural rubber (ENR-50), NaCl and rice husk (RH). The RH was used as a support to store urea within its fibrous structure after chemical modification with 7% sodium hydroxide (NaOH). ENR-50/NaCl was used as a coating material for RH/urea beads. Two different content of salt (5% and 10% NaCl) was used to study the effect of pore formation on the composites. FTIR spectroscopy reveals that urea was successfully absorbed into RH and the recorded peaks were overlapped with the main components of RH such as cellulose, hemicellulose and lignin. UV-Vis reveals that at 10% salt loading releases urea higher than 5% salt loading. This is due to the formation of many pores in this ENR-50 composite.

1. Introduction

Natural rubber is commercially accessible as latex from tropical tree Havea brasiliences. Epoxidized natural rubber-50 (ENR-50) contains 50% epoxidation mole of natural rubber. The physical properties of ENR-50 are higher mechanical strength such as tensile, elongation, hardness and compression set. It also has higher density, higher viscosity and lower refractive index. ENR-50 has higher oil and solvent resistivity. It is more resistant to non-polar solvent or hydrocarbon and reduces its resistivity in polar solvent. It also has lower air and oxygen permeability across the ENR membrane because of the simple diffusion of oxygen than air into the ENR membrane. The glass transition temperature (T_{e}) of ENR-50 is at -18 °C. The physical and chemical properties of ENR, for example heat and swelling resistance, can change as per the epoxide content. ENR likewise has higher polarity than virgin NR due to the presence of epoxide groups in its structure [1,2].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

1st International Conference on Green and Sustainable Computing (ICoGeS) 2017IOP PublishingIOP Conf. Series: Journal of Physics: Conf. Series 1019 (2018) 012062doi:10.1088/1742-6596/1019/1/012062

Rice husk (RH) are major agricultural wastes from paddy rice. Raw RH commonly made up of 35 % cellulose, 25 % hemicellulose, 20 % lignin, 17 % ash from a total of 94 % silica and 3 % moisture by weight [3,4]. The composition of RH is 23 % of the total paddy weight. The physical properties of RH are biodegradable, cheap, low density, abundant and easy to obtain [5]. Rice straw is an organic material, which commonly used and it contains many mineral nutrients. There are 0.5–1.5% N, 0.2–1.0% P, 0.8–1.0% K, and Si [6]. RS contains easily decomposable C and has a relatively wide C/N ratio compared with RS compost. RS is an economical soil revision to enhance fertilizer recovery efficiencies [7].

The fertilizers are applied to the soil in terms of slow release for market efficiency, economic cultivation and biomass production increment. The coated RH and RS are considered as a suitable candidate for development of slow release material in agriculture. This slow release coating technology supplies consistent nitrogen to the plants and reduce loss and contamination impacts. The coating technology intended for slow release of nutritional content of fertilizer to the plants. It additionally synchronizes the discharge rate with the nutritious request of the plants [8].

2. Methodology

2.1. Purification of ENR-50

About 20g of ENR-50 was swelled in 400 mL of chloroform and stirred for 24 hours at room temperature. The solution undergoes filtration process through a pack of cotton gauze to separate the high molecular weight from the low molecular weight of ENR-50 [9]. The latter precipitated in *n*-hexane while stirring using a glass rod. The white precipitate stuck to the glass rod transferred to a Petri dish and dried in a vacuum oven at 50 °C for two days. The purified sample was recorded every day until a constant reading is attained. The sample was then characterized by FTIR technique.

2.2. Cellulose pretreatment

The RH fibers were washed, cleaned, shredded and dried in a convection oven at temperature of 60 °C. The dried RH fibers were grinded using lab grinder with a 250 μ m screen mesh to achieve a uniform particle size. The cellulose pretreatment involved the process of soaking the mesh RH in 7 wt% sodium hydroxide (NaOH) for 24 hours. The 7 wt% of NaOH prepared by dissolve 7 g of NaOH solution in 100 mL of distilled water. The cellulose filtered using centrifugal method to separate the cellulose/NaOH mixture. After that, the pH value of the sample checked by using pH paper. If the pH value is higher, the sample washed using distilled water until neutral to remove all the NaOH solution. Then, the sample dried on a white paper under sunlight. The sample dried in a vacuum oven at 50 °C for 48 hours. After that, the sample analyzed using FTIR technique [10].

2.3. Preparation of RH/urea beads

The solvent prepared by dissolving 60 g of urea fertilizer in 500 mL of distilled water to produce 12 wt% urea. The prepared sample from cellulose pretreatment was dissolved in 12 wt% urea solution for 24 hours at room temperature. Then, the sample was filtered using centrifugal method to separate the RH/urea composite and solution mixture. Then, the sample was dried on a white paper under sunlight. The sample was further dried in a vacuum oven at 50 °C for 48 hours. After that, the RH/urea beads were characterized by FTIR technique [10].

2.4. Preparation of ENR-50/salt composites

About 10 mg of sodium chloride was dissolved in 10 mL of tetrahydrofuran. Another sample was prepared using 20 mg of sodium chloride dissolved in 10 mL of tetrahydrofuran. About 200 mg of purified ENR-50 was dissolved in 40 mL of chloroform. The different sodium chloride solutions and ENR-50 solution were dissolved together to form ENR-50/5% salt composite and ENR-50/10% salt composite respectively. The solution was then stirred for 24 hours at room temperature. This solution does not need to undergo drying process.

1st International Conference on Green and Sustainable Computing (ICoGeS) 2017IOP PublishingIOP Conf. Series: Journal of Physics: Conf. Series 1019 (2018) 012062doi:10.1088/1742-6596/1019/1/012062

2.5. Preparation of RH/urea beads coated ENR-50/salt composite

About 20 mg of RH/urea beads was dissolved into 50 mL of ENR-50/5% salt composite and 50 mL of ENR-50/10% salt composite separately (0.08 wt% ENR-50). Then, the mixtures were stirred for 24 hours at room temperature until homogenous solution occurred. The mixtures was dried in fume cupboard at 50 °C for 24 hours.

2.6. Formation of pores on RH/urea beads coated ENR-50/salt composite

The mixtures was dissolved in 200 mL distilled water. Then, the mixtures was filtered using filter paper and funnel. After that, the samples were dried using vacuum drier. The RH/urea beads coated ENR-50/5% salt composite and RH/urea beads coated ENR-50/10% salt composite were characterized using FTIR technique.

2.7. Release study

The slow release study of the beads was conducted in distilled water; the following experiments were carried out. About 5 g of dry samples of 5% salt loading and 10% salt loading were added to the conical flask containing 200 mL of distilled water. Then the conical flask put into incubators with the temperature 25 °C. Each day, 2 mL solution sampled for urea contents, and additional of 2 mL distilled water was added to the flask to maintain a constant amount of solvent. This experiment was carried out for 30 days. Then, it was characterized using UV-vis spectrometer [11].

2.8. Kinetic study

A standard urea concentration was prepared by using 100 ml aqueous solution having concentration between 0.2 and 1.0 mg/ml. 20 mg of urea was dissolved in 100 ml of distilled water to obtain 0.2 mg/ml. UV-vis spectrometer 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. Microsoft Excel was used to draw the equation of the graph (Eq. 1.). 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.

$$A = \epsilon C \ell$$

$$C = \frac{A}{I \, x \, \epsilon}$$
(1)

3. Results and Discussion

3.1. Characterization of purified ENR-50 and ENR-50/salt composite

The FTIR spectrum of purified ENR-50 is shown in Figure 1(a) and compared with FTIR spectra of ENR-50/salt at both 5% and 10% salt loadings (Figure 1(b,c)). Generally, 5% and 10% salt loading showed approximately similar FTIR spectra. Both showed broad OH absorption band at range 3433-3420 cm⁻¹. For both salt loading, CH₃ peaks occurred at range 2966-2963 cm⁻¹ and 2857-2850 cm⁻¹. The CH₂ peaks at 2924-2921 cm⁻¹ and 1448 cm⁻¹. The C-H peak remains similar like purified ENR-50 at 1378 cm⁻¹. The present of the epoxide group at 878-875 cm⁻¹ and C=C at 838 cm⁻¹ indicated that the chemical structure of purified ENR-50 didn't affect by the salt loading. The salt only dispersed amongst the polymeric chains of purified ENR-50 and not causing the ring opening reaction of the epoxide group [12].



Figure 1: FTIR spectra of (a) purified ENR-50, (b) ENR-50/5% salt composite and (c) ENR-50/10% salt composite

3.2. Characterization of RHRS/urea beads

The FTIR spectrum of pretreated RH is shown in Fig. 2(a) and compared with FTIR spectra of RH/urea beads in Fig. 2(b). Generally, the peaks of RH/urea beads are similar to pretreated RH. The most characteristics peaks of urea at 1667 and 1629 cm⁻¹ are assigned to carbonyl (C=O) and N-H bending vibration respectively. In the region 3200-3500 cm⁻¹, there are also peaks, which may be attributed to urea compounds, like 3425 cm⁻¹ assigned to symmetric stretching vibration of NH₂. Also peak at 2917 cm⁻¹ can be assigned to C-H stretching vibration of absorbed water. However, this region is overlapped with RH spectrum. It shows that no chemical interaction involves between RH and urea but it just involves physical interaction. Therefore, more evident and reliable data related to increasing amount of urea in extruded sample are in region between 1629-1667 cm⁻¹ [13].

3.3. Characterization of RH/urea beads coated with ENR-50/Salt composite

The FTIR spectra of both RH/urea beads with ENR-50/5% and ENR-50/10% salt composite are shown in Fig. 2(c) and 2(d) respectively. Generally, both of the spectra are almost similar based on its characteristics peaks. The peaks observed at 3357 cm⁻¹ and 3434 cm⁻¹ are assigned to OH of groups [14,15]. This OH groups was due to the hydroscopic nature of salt that exist in the composites. At high loading of salt, the OH peaks are more broad and intense as compare to low loading of salt. The peaks at 2917 cm⁻¹ and 1464 cm⁻¹ are attributed to the C-H stretching vibrations. The peaks at ranges 2846-2850 cm⁻¹ are assigned to CH₃ symmetry stretching. In addition, the peaks at 1031-1063 cm⁻¹ could be suggested as C-O stretching vibration. The peak at 1645 cm⁻¹ at 10% salt loading which is not detected earlier in 5% salt loading is due to the C=C aromatic which is dominant in this composite than 5% salt. At high salt loading, aromatic group of lignin plays a crucial role to more space for urea to be absorbed into cellulose fibers. The peak at 1319 cm⁻¹ was due to C-O vibration. The C-O-C asymmetric stretching is shown at 1118-1163 cm⁻¹. In addition, the peak at 895 cm⁻¹ is assigned to C-H deformation vibration [12, 16-19].



Figure. 2: FTIR spectra of (a) pretreated RH, (b)RH/urea beads, (c)RH/urea beads coated with ENR-50/5% salt composite and (d)RH/urea beads coated with ENR-50/10% salt composite

3.4. Release study

The UV-Vis spectra of slow release study of the RH/urea beads coated with ENR-50/salt at 5% and 10% salt loadings are shown in Fig. 3. Generally, the absorbance value for 10% salt loading is higher than 5% salt loading. This indicated that the composites at10% salt loading released more urea than the composites at 5% salt loading. At 10% salt loading represented high amount of salt of as compared to 5% salt loading. Thus more pores are available to release urea at 10% salt loading as compared to 5% salt loading.



Fig. 3: The release study curve of the composites at different salt loading

1st International Conference on Green and Sustainable Computing (ICoGeS) 2017IOP PublishingIOP Conf. Series: Journal of Physics: Conf. Series 1019 (2018) 012062doi:10.1088/1742-6596/1019/1/012062

3.5. Kinetic study

The slow release mechanism can be divided into three stages. First stage is a lag period in which water penetrated the ENR-50 coating without urea release. Then, a constant release period followed when urea dissolved and flowed through the coating which can be said as burst effect. Finally, there came a stage of decline until the release of urea ultimately ended [20].

4. Conclusion

In conclusion, FTIR spectroscopy showed that the urea was successfully absorbed into RH and the recorded peaks were overlapped with the main components of RH i.e. cellulose, hemicellulose and lignin. UV-Vis showed that the composite at 10% salt loading releasesed urea higher than composite at 5% salt loading. This was due to number of pores formation in this composite.

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. A. Kumar, B. Sengupta, D. Dasgupta, T. Mandal, and S. Datta, *Reviews in Environmental Science and Bio/Technology* 15, 47-65 (2016).
- 4. M. A. Fuad, Z. Ismail, Z. M. Ishak and A. M. Omar, European Polymer Journal, **31**, 885-893 (1995)
- 5. M. Suzeren Jamil, I. Ahmad and I. Abdullah, *Journal of Polymer Research* **13**, 315-321 (2006).
- 6. A. Polthanee, V. Tre-loges and K. Promsena, *Paddy and Water Environment* **6**, 237-241 (2008).
- 7. P. J. A. Van Asten, P. M. Van Bodegom, L. M. Mulder and M. J. Kropff, *Nutrient Cycling in Agroecosystems* **72**, 255-266 (2005).
- 8. M. Y. Naz, and S. A. Sulaiman, *Journal of Controlled Release* 225, 109-120 (2016).
- 9. O. S. Dahham, R. Hamzah, M. A. Bakar, N. N. Zulkepli, S. S. Dahham and S. S. Ting, Polym. Test. **59**, 55-66 (2017).
- 10. J. W. Dormanns, J. Schuermann, J. Müssig, B. J. Duchemin and M. P. Staiger, *Composites Part A: Applied Science and Manufacturing* **82**, 130-140 (2016).
- 11. G. Z. Zhao, Y. Q. Liu, Y. Tian, Y. Y. Sun and Y. Cao, *Journal of Polymer Research* 17, 119-125 (2010).
- 12. W. L. Tan and M. A. Bakar, Journal of Alloys and Compounds 561, 40-47 (2013).
- 13. P. Rychter, M. Kot, K. Bajer, D. Rogacz, A. Siskova, and J. Kapusniak, *Carbohydrate polymers* **137**, 127-138 (2016).
- 14. N. N. Zulkepli and H. Ismail, Polymer-Plastics Technology and Engineering, **51**, 350-357 (2012).
- 15. N. Z. Noriman, H. Ismail and A. A. Rashid, A. A. Journal of Applied Polymer Science, **126** (2012).
- 16. K. Jantanasakulwong, N. Leksawasdi, P. Seesuriyachan, S. Wongsuriyasak, C. Techapun, and T. Ougizawa, *European Polymer Journal* **84**, 292-299 (2016).
- 17. T. Xu, Z. Jia, Y. Luo, D. Jia and Z. Peng, Applied Surface Science 328, 306-313 (2015).
- 18. W. A. K. Mahmood and M. H. Azarian, *Current Applied Physics* 15, 599-607 (2015).
- 19. W. A. K. Mahmood, M. M. R. Khan and M. H. Azarian, *Journal of Non-Crystalline Solids* 378, 152-157 (2013).
- 20. L. Wu, M. Liu and R. Liang, *Bioresource Technology* 99, 547-554 (2008).