



Material Properties

Physical property testing of a novel hybrid natural rubber-graft-cassava starch/sodium alginate bead for encapsulating herbicide



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ABSTRACT

A novel bead of modified starch for encapsulating 2,4-dichlorophenoxy acetate (2,4 DA) was made from natural rubber-graft-cassava starch (NS) and sodium alginate (SA) in a water-based system. The particle size and zeta potential of pristine NS, the NS/SA blend and the NS/SA blend containing 2,4 DA were evaluated. The swelling ratio in water of the beads was investigated and found to be enhanced as a function of the SA portion in the hydrogel due to an increase in the hydrophilic groups in the beads. In addition, the chemical interaction between 2,4 DA and the polymer matrix was investigated by FTIR and XRD. The results suggest that an NS/SA matrix is a good polymer membrane for encapsulating 2,4 DA in a water medium and the beads are also easily decomposed in the natural environment after use.

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1. Introduction

Starch is a polysaccharide polymer which is increasingly used in many branches of industry because of its physicochemical properties and because it is cheap, readily available and can be easily biodegraded. However, because native starch has various drawbacks, notably, poor mechanical properties, low water resistance and high hydrophilicity, hence it is often subjected to various modifications before use. The most common methods of making significant improvements in starch properties are chemical [1], physical [2] and enzymatic [3] modifications. In the study reported in this paper, the starch was modified by blending [4] and grafting [5] with natural rubber (NR). NR is a hydrophobic polymer which is widely used in many applications such as packaging films [6]. In our previous work, the improvement in the hydrophobicity of starch achieved by grafting with NR was studied [7]. It has also been used as a polymer matrix for encapsulating urea fertilizer, and the starch foam produced demonstrated greater ductility at higher relative humidity due to the addition of NR [8] using super cell (SC) as a blowing agent. Further, starch-graft-epoxidized natural rubber has been used as a compatibilizing agent to improve the elongation at break of a biodegradable polymer [9].

Many works have studied blending between cassava starch (CSt) and alginate [10–12]. In the work reported in this paper, natural

rubber grafted with CSt (NS) was used as a polymer matrix for the encapsulation of 2,4 trichlorophenoxyacetic acid (2,4 DA). In previous work, guayule resin which is a plant-based material was used as a polymer matrix for encapsulating bioactive volatiles by inverse gelation and oil emulsion entrapment [13]. The formulations used for entrapping volatile compounds (linalool or carvone) consisted of blends of alginate and starch with or without the addition of guayule resin at 1%. Guayule resin improved the loading of linalool from 5.4% to 13.7% in the capsules, but a similar improvement was not observed for beads, and the interaction of guayule resin with the matrices was studied in order to investigate the use of this new material in the encapsulation process. In another study, a natural rubber latex (NRL) membrane was used as a polymer matrix for the encapsulation of metronidazole (MET), a powerful antiprotozoal agent [14]. X-ray diffraction and FTIR spectroscopy data indicated that the MET retained its structural and spectroscopic properties after encapsulation in the NRL membrane, with no molecular-level interaction that could alter the antibacterial activity of the MET. The kinetics of the drug release were able to be fitted to a double exponential function with two characteristic times of 3.6 and 29.9 h, demonstrating that the induced angiogenesis known to be provided by NRL membranes can be combined with the controlled release of drugs, whose kinetics can be tailored by modifying experimental conditions of the membrane fabrication for specific applications. NR was blended with sodium alginate (SA) solution, and coconut waste used as a cofiber, to form a material for the absorption of lead ions (Pb^{2+}) [15]. After being cross-linked by

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calcium chloride, the beads were highly stable, flexible and easily used in the environment. The cofiber increased the porosity and contact area and, hence, the efficiency of the composite beads to adsorb up to 99.6% of the Pb^{2+} . The researchers concluded that the beads prepared are a promising material for use in the effective and economical removal of Pb^{2+} from water. Also, in Ref. [16], telechelic liquid natural rubber was used to create a thin coating ($<1 \mu\text{m}$) for the absorption of lead. The nature of the cross-linking reaction was elucidated by using FTIR spectroscopy. The study investigated the optimization of the cross-linking reaction (curing temperature and time) through kinetic studies. Modification of the physical properties (i.e. morphology and mechanical) during the cross-linking was followed by atomic force microscopy (AFM). It was concluded that, because of its physical properties as well as its processing conditions, the new material was a good candidate for the encapsulation of microelectronic systems. In other work, the properties of 19% mole epoxidized natural rubber (ENR) cross-linked with glutaraldehyde (GA) were studied and its application in the encapsulation of carbendazim (CAD) investigated [17]. A blend of cured ENR with SA which was then cross-linked by Ca^{2+} or GA/Ca^{2+} was successfully used for the encapsulation of CAD. The results showed that the release rate of the CAD was controlled by the GA/Ca^{2+} and ENR/SA ratios.

However, up to now, no study has investigated the preparation of 2,4 DA beads in a blend of NS and SA. In the present work, the effect of the NS/SA ratio on the particle size, morphology and swelling ratio of NS/SA beads was investigated. In addition, the chemical structure of the resulting beads was observed by FTIR and XRD. The release kinetics of 2,4 DA from beads with different ratios of NS/SA and their biodegradation in nature soil were studied.

2. Experimental

2.1. Materials

For the encapsulation of 2,4 DA, CSt was purchased from Tantanawan company (Bangkok, Thailand). The SA and $\text{K}_2\text{S}_2\text{O}_8$ were from Central Drug House (Delhi, India) and the calcium chloride and all other reagents of analytical grade were purchased from Ranbaxy Fine Chemical Ltd. (Delhi, India). Other analytical grade chemicals were purchased from Sigma-Aldrich (Mumbai, India). Triton™ X-100 was purchased from Sigma-Aldrich (Munich, Germany). NRL with an average molecular weight of $\sim 1 \times 10^6 \text{ g/mol}$ (Chana Latex Co., Ltd., Songkhla, Thailand) was used for the present study and 2,4-DA was purchased from P. Chemitech. Co., Ltd (Bangkok, Thailand). The NR was grafted with CSt according to our previous work (Riyajan et al., 2012). The gelatinization was performed by stirring 20 g of CSt in distilled water at $85 \pm 3 \text{ }^\circ\text{C}$ for 1 h. After cooling, the gelatinized CSt was mixed with $\text{K}_2\text{S}_2\text{O}_8$ solution and stirred at $60 \text{ }^\circ\text{C}$ for 45 min to obtain modified CSt. The 17 g of NR latex having 60% dry rubber content in the presence of Terric® 16A16 was mixed with 100 g of 10 % wt modified CSt (1/1 NR/CSt) and stirred at $60 \text{ }^\circ\text{C}$ for 3 h.

2.2. Preparation of beads

SA solution was prepared in distilled water by homogenization at 1500 rpm for 30 min 2,4-DA was added to the solution at a concentration of 10 mg/ml. A 4% w/v cross-linking medium was prepared by dispersing calcium chloride in distilled water and stirring at 600 rpm using a mechanical stirrer (Remi Motors, Mumbai). The 20% NS solution was blended with 10% SA solution to obtain mixtures at ratios of 0.0:1.0, 0.1:1.0, 0.2:1.0, 0.3:1.0, 0.5:1.0, 0.7:1.0 and 1.0:1.0, NS:SA (dry weight). The homogenized solution was extruded through a syringe with a no. 24 needle into the cross-

linking medium. The beads were cured for 10 min to produce rigid discrete particles. The beads were collected by decantation and the product then washed with distilled water. Finally, the beads were hardened by washing in acetone and dried at $40 \text{ }^\circ\text{C}$ under vacuum for 8 h. The particle size and zeta potential of NR, NS and NS/SA blend were evaluated using an optical laser scattering particle size analyzer (Malvern, UK).

2.3. Dynamic viscosity determination

Rheological measurements were carried out using a Brookfield R/S + Portable rheometer and analyzed with RHEO3000 software. The samples were prepared by dissolving in deionized water. The flow curves were obtained by registering the viscosity and shear stress at a shear rate which was increased from 0 to 500 s^{-1} . All the measurements were performed twice, at a temperature of $25 \pm 0.1 \text{ }^\circ\text{C}$. The viscosity was expressed in mPa s.

2.4. Characterization of the beads

A sample bead was deposited on a brass holder and sputtered with gold. SEM photographs were taken with a JSM 6400 scanning microscope (Japan) at the required magnification at room temperature.

Five samples of the completely dried beads from the different formulations were selected and their sizes were measured using a micrometer screw gauge (Sargent, USA) with an accuracy of $\pm 0.01 \text{ mm}$.

Infrared spectra were taken using the KBr pellet technique in a Shimadzu FT-IR 8300 spectrophotometer (Shimadzu, Tokyo, Japan) at a wave length of $4000\text{--}400 \text{ cm}^{-1}$. The sample was placed in the light path and scanning was performed at a resolution of 4 cm^{-1} at a speed of 2 mm/s.

The X-ray diffractograms of the bead samples were obtained using an X-ray diffractometer with a Cu–NF filter and Cu K α radiation (XRD) (X'Pert MPD, PHILIPS, Netherlands). Thermogravimetric Analyses (TGA) was performed using an STA 449 F3 Jupiter thermal analyzer. A 10–20 mg sample was placed in a platinum pan. Analysis was carried out under nitrogen flushing (gas flow = 100 ml/min), at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$, over a temperature range of $30\text{--}800 \text{ }^\circ\text{C}$.

The swelling ratio in distilled water was determined. A sample of the beads was weighed before being immersed in 25 ml of distilled water at room temperature for 7 h. After that, the sample was reweighed after removing excess water from the surface of the beads with tissue paper. The swelling ratio was calculated by equation (1).

$$\% \text{Swelling ratio} = (W_2 - W_1) / W_1 \times 100 \quad (1)$$

where W_1 is the initial dry weight of the sample (g) and W_2 is the weight of the swollen sample (g).

2.5. Entrapment efficiency and 2,4 DA release

The beads were crushed using a mortar and pestle and screened through an 80 mesh sieve to obtain a fine powder. A quantity of 100 mg of powder was accurately weighed and transferred, with 50 ml of 0.1 M hydrochloric acid (pH 1.2), into a 100 ml flask. The resulting mixture was shaken on a mechanical shaker for 24 h. The solution was filtered with Whatman filter paper no. 5 and analyzed spectrophotometrically at 274 nm using a UV–Vis spectrophotometer (Hitachi, U-2001, Japan). The entrapment efficiency was calculated as the ratio between the initial mass of 2,4 DA to be encapsulated and its mass in the final product. A quantity of 20 mg

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