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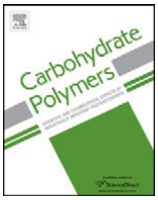

Green natural rubber-g-modified starch for controlling urea release

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ABSTRACT

The hydrophilicity of natural rubber (NR) was improved by grafting with modified cassava starch (ST) (NR-g-ST) by using potassium persulfate ($K_2S_2O_8$) as a catalyst. The modified ST was added to NR latex in the presence of Terric16A16 as a non-ionic surfactant at 60 °C for 3 h and cast film on a glass plate to obtain NR-g-ST. The chemical structure of NR-g-ST was confirmed by FTIR. The swelling ratio of NR-g-ST was investigated in water and results showed that the swelling ratio of the modified NR decreased as function of ST. In addition, the tensile strength of the modified NR in the presence of modified ST at 50 phr was the highest value. Also, the thermal stability modified NR-g-ST was higher than of NR/ST blend confirmed by TGA. Finally, the NR-g-ST was used a polymer membrane for controlling urea fertilizer and it easily degraded in soil. This product with good controlled-release and water-retention could be especially useful in agricultural and horticultural applications.

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1. Introduction

Natural rubber (NR) containing 93–95% *cis*-1,4-polyisoprene is an elastomeric material, which produces from latex of the rubber tree. NR, as a renewable natural resource, has many excellent comprehensive properties such as outstanding resilience, and high strength. However, as an unsaturated polymer, NR will gradually degrade at a high temperature or when exposed to oxygen, ozone or ultraviolet, leading to a portentous negative effect on its special application (Agarwal, Setua, & Sekha, 2005; Chaikumpollert et al., 2011; Pasquini, Teixeira, Curvelo, Belgacem, & Dufresne, 2010; Zou et al., 2001). To overcome these limitations of NR, the modification of NR is crucial. Various methods can be employed to modify the properties of NR. One way is chemical modification, in which other groups or atoms are introduced onto the NR molecular chains, for example, epoxidized NR (Gan & Hamid, 1997; Yu, Zeng, Lu, & Wang, 2008), hydrogenated NR (Mahittikul, Prasassarakich, & Rempel, 2009), and grafted NR (Abu Bakar, Ismail, & Abu Bakar, 2010; Derouet, Intharapat, Tran, Gohier, & Nakason, 2009; Kongparakul, Prasassarakich, & Rempel 2008).

From previous work, the NR was modified by grafting with dimethylaminoethyl methacrylate (DMAEMA) to form a latex with cationic water-soluble polymeric 'hairs' of polyDMAEMA. They acted as filler in the starch (ST) films, but with modified NR, the mechanical properties of the films were significantly altered (Rouilly, Rigal, & Gilbert, 2004). The elastic modulus was greatly decreased but strain at break greatly increased. Freeze-fracture TEM micrographs indicate strong interactions between the surface of the modified NR and ST. The polyDMAEMA chains are more hydrophilic than the ST, and the addition of grafted latex results in a 20° drop of the water contact angle of the formed film and a 25% increase of the water absorption compared to the native ST; with unmodified NR, causes the opposite effect. Moreover, the properties of NR were improved by blending with ST. For example, thermoplastic ST/NR polymer blends were obtained using NR latex and cornstarch and an intensive batch mixer at 150 °C, with NR content varying from 2.5 to 20% (Carvalhoa, Jobb, Alvesb, Curveloa, & Gandini, 2003). The results revealed a reduction in the modulus and in tensile strength; the blends became less brittle than thermoplastic starch alone. Increasing plasticizer content made higher amounts of rubber possible. The addition of rubber was, however, limited by phase separation the appearance of which depended on the glycerol content. After ST paste (MST) modified with polybutylacrylate (PBA), it was used as a reinforcing filler of rubber through mixing and co-coagulating with NR latex (Liu, Shao, & Jia, 2008). MST is much superior to unmodified ST paste because unmodified ST paste acts as an essential inert filler causing a decrease in tensile strength, tear strength and elongation at break. MST shows an obvious reinforcement for NR matrix observed from increasing mechanical properties. Moreover, fine ST dispersion and strong interfacial interaction are achieved in NR/MST composites (Liu et al., 2008). Recently, NR was used to improve the properties of ST foam by potassium persulfate as an initiator (Tanrattanakul & Chumeka, 2010). In this work, NR was grafted with modified cassava

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starch (ST) as a natural polymer available in large amounts from several renewable plant sources for encapsulation of urea fertilizer. Control release fertilizers were made to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant. This urea capsule can be physically prepared by coating granules of conventional fertilizers with various materials that reduce their dissolution rate. The release and dissolution rates of water-soluble fertilizers depend on the coating materials. At present, the degradability of natural polymer's coating was an important focus of research in this field because of the renewed attention towards environmental protection issues (Chen, Xie, Zhuang, Chen, & Jing, 2008; Chiu & Lai, 2010; Kim, Mukerjea, & Robyt, 2010; Valodkar & Thakore, 2011). Recently, ST and their derivatives with different functional groups have been used in biodegradable polymer due to its ability to biodegrade in soil and enhance in hydrophilic ability (Wang et al., 2009; Zou et al., 2012; Antoine, Luc, & Gilbert, 2004; Bhatt et al., 2003; Lanthong, Nuisin, & Kiatkamjornwong, 2006; Zhi-Fen et al., 2009). There have been many attempts to make NR become easily degradable. Therefore, we attempted to modify the hydrophobic property of NR to contain more hydrophopilic properties by grafting with modified ST to get a NR-g-ST. This present paper is the first study of its kind showing the NR latex grafting with of modified ST, which was modified with $K_2S_2O_8$ as a catalyst to use a polymer membrane for encapsulating fertilizer. Effects of modified ST content on the properties, i.e., swelling behavior, mechanical strength and thermal behavior of NR-g-ST were investigated. Theirs chemical structure and morphology were studied by using attenuated total reflection-Fourier transform infrared spectrophotometer (ATR-FTIR) and scanning electron microscope (SEM), respectively. In addition, the biodegradation of the NR-g-ST was evaluated in soil. After chemical modification of NR, we applied its use in encapsulation of urea fertilizers.

2. Experimental

2.1. Materials

The main materials used for this work were 60% HA-latex (Chana company, Thailand), potassium persulfate 99%, RFCL Ltd (India) while ST containing 32% amylose was purchased from General Starch Co., Bangkok, Thailand. 10% Terric16A16 as a non-ionic surfactant and urea were obtained from Lucky Four.co.TLD and Ajax Finechem pty ltd, New Zealand, respectively.

2.2. Preparation of natural rubber grafted starch (NR-g-ST)

The gelatinization was performed by stirring 20 g of ST in distilled water at 85 ± 3 °C for 1 h. After cooling, the gelatinized ST was mixed with $K_2S_2O_8$ solution, stirred at 60 °C for 45 min modified ST was obtained. The 17 g of NR latex in the presence of Terric® 16A16 was mixed with modified ST and stirred at 60 °C for 3 h. The influence of ST at 0, 25, 50, 100 and 150 phr on the properties of the NR-g-ST was investigated. The mixture was cast on glass plate and then left at room temperature for 3–4 days. After that, it was baked in an oven at 50 °C for 24 h and kept it in desiccators before characterization.

2.3. Preparation of encapsulated urea fertilizer with NR-g-ST

The urea fertilizer granules were dipped to different coating materials such as the gelatinized ST, NR latex, NR/ST blend and NR-g-ST at 15 wt% concentration. Then, the coating capsules were dried at 30 °C for 72 h. The different capsules were characterized in Section 2.4.

2.4. Characterization of NR-g-ST

The chemical structure of polymer composite was investigated by using attenuated total reflection-Fourier transform infrared spectrophotometer (ATR-FTIR) (Equinox 55; Bruker) for 100 scans. The sample was then dried at 50 °C for 24 h and weighed until a constant weight was obtained. The degree of swelling ratio was estimated from Eq. (1):

$$\text{Swelling ratio} = \left(\frac{W_2 - W_1}{W_1}\right) \tag{1}$$

where W_1 is the original weight of the sample and W_2 is the weight of dried residual sample after immersion for 5 days. The tensile strength and elongation at break of dried polymer blend was analyzed by universal testing machine (LR10K, Lloy Instruments) based on ASTM D 412 at a rate of 500 mm/min using five dumbbell test pieces.

SEM (JMS-5800 LV, JEOL) was used for study of the morphology of cross-sectional sample at an accelerating voltage of 6 kV. After fracturing a specimen under liquid N_2, its cross-sectional area was coated with platinum under a 12 Pa vacuum.

For thermal analysis, 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 heating rate of 10 °C/min. In addition, TGA at heating from 50 to 300 °C was used to prepare the NR-g-ST to continue the chemical structure by ATR-FTIR. The amount of released urea from the NR-g-ST or starch matrix was measured at 191 nm by UV–vis spectrophotometer (UV-1601, Shimadzu). About 1 g of dried capsule sample was extracted in distilled water to form a homogeneous solution. The total urea in the solution was extracted for 72 h with a distilled H_2O and its mass was determined by UV–vis spectroscopy (Shimadzu UV-1601). At definite intervals of time, the conical flasks were shaken and a 10-mL aliquot was taken for analysis of urea using UV (Shimadzu UV-1601) at 191 nm. Experiments were performed in triplicate in order to minimize the variation error.

For the examination of biodegradation of NR, NR-g-ST and NR/ST blend, the specimen (2 cm × 2 cm) was buried under soil (100 g) at 7 cm from top soil (Hat Yai, Songkhla, Thailand) Water was added 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.

3. Results and discussion

3.1. Chemical structure of ST, modified ST and NR-g-ST analyzed by ATR-FTIR

The chemical modification of ST was carried out by the addition of $K_2S_2O_8$ under stirrer at 60 °C for 45 min. $K_2S_2O_8$ was activated by heat and it changes into $K_2S_2O_8$ free radical. Then, the $K_2S_2O_8$ free radical reacted with ST molecule. The degradation of ST was occurred as shown in Fig. 1. Finally, we acquired the short ST chain. The viscosity of ST dramatically decreased after addition of $K_2S_2O_8$ at 75 °C for 45 min to get the modified ST. The free radicals from ST attacked with carbon=carbon double bonds of NR, which was activated by $K_2S_2O_8$ leading to the NR-g-ST formation.

At the same time, free radical $K_2S_2O_8$ reacted with carbon double bond of NR.

Then, the ST free radical continued to react with NR molecules leading to the NR-g-ST formation as shown in Fig. 1. The chemical modification of NR was carried out in latex form (medium is a water). Therefore, the 10% Terric16A16 was used to stabilize the NR particles during NR-g-ST. If the concentration of Terric16A16 was less than that of 10%, the NR particle would coagulate. However, when the concentration of Terric16A16 increased more than 10%, the %grafting of modified ST decreased. To study the effect of