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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):

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

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

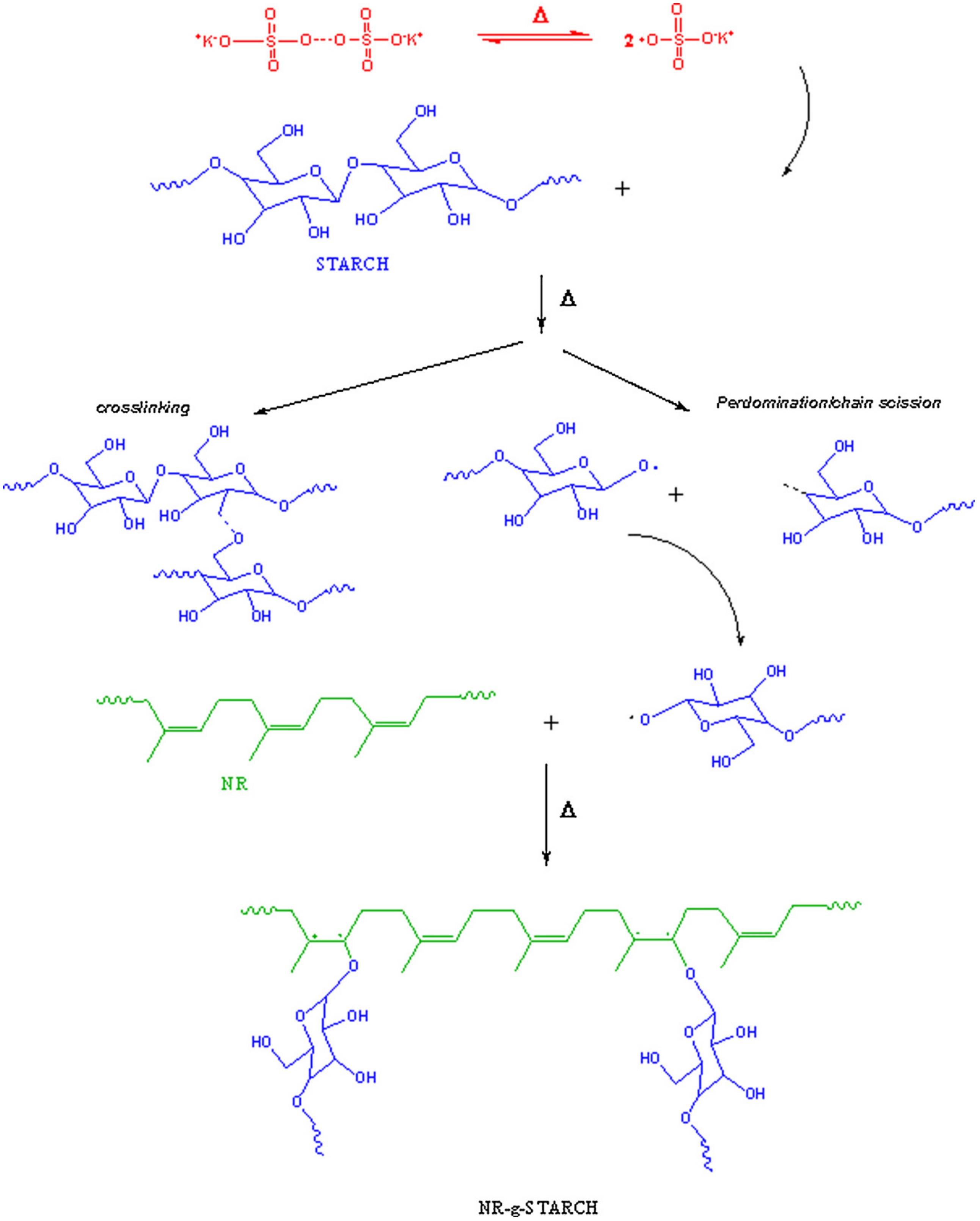

Fig. 1. The possible chemical reaction of NR-g-ST by using potassium persulfate as a catalyst.

the initiator concentration on graft copolymerization was studied at various $K_2S_2O_8$ concentrations by keeping other reaction conditions constant. It was found that the $K_2S_2O_8$ would destroy the structure of NR molecules. This result supports the previous work (Riyajan, 2007).

The synthesized copolymers were characterized by the functional groups using ATR-FTIR technique. ATR-FTIR spectra of unmodified ST and modified ST are presented in Fig. 2(A). The absorbent band of hydroxyl group was observed at 3340 cm^{-1}. The absorption at 879 cm^{-1} was referred to a methane vibration and

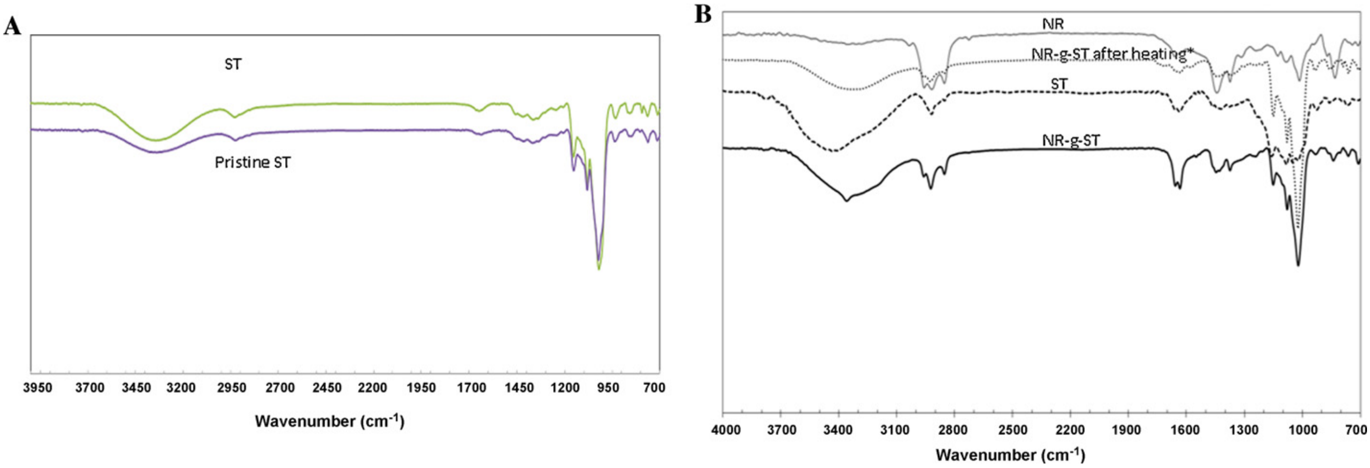

Fig. 2. ATR-FTIR spectra of ST and modified ST (B) NR, ST, NR-g-ST before and after THF extractions for 48 h and NR-g-ST after heating from 50 to 300 °C by TGA.

absorption at 1638 cm^{-1} is C—O vibrations in ST. The vibrations of unsymmetry C—O—C bond and C—O bond in ST are at 1154 cm^{-1} and 1045 cm^{-1}, respectively (Rouilly et al., 2004). After chemical modification of the ST with $K_2S_2O_8$, the FTIR peak band was slightly altered as shown Fig. 2(A). The FTIR spectra for ST, NR-g-ST before and after THF extractions for 48 h are presented in Fig. 2(B). The results showed that the main FTIR band of ST was observed at 3550–3200, 2933 cm^{-1} and the two band of 1155, and 1080 cm^{-1} for hydroxyl group, the C—H stretching and the C—O—C stretching (a triplet peak of ST), respectively. The C—H stretching at 2965, 2928 cm^{-1}, the C═CH stretching at 1659 cm^{-1}, the —CH_3 deformation at 1452 cm^{-1}, the —CH_2 deformation at 1379 cm^{-1} and the C═CH bending at 843 cm^{-1} of NR-g-ST appeared in the FTIR spectra (Fig. 2(B)). The chemical structure of NR-g-ST was confirmed again by both TGA and FTIR. After NR-g-ST was heated from 50 to 330 °C by TGA technique, then its chemical structure was continually characterized by FTIR. It was clear that the notable difference between the FTIR spectra of ST and NR-g-ST was that the strongest peak for NR-g-ST appeared at 1100 cm^{-1} (C—O—C) comparing to ST. This data indicated that NR was grafted with ST. In addition, the thermal stability of NR-g-ST was the highest comparing other samples (see in Section 3.4). These results agreed with works of Tanrattanakul and Chumeka (2010). They studied the preparation of thermoplastic starch foams from pristine cassava starch blended with NR latex by reactive blending and potassium persulfate as an initiator for graft copolymerization between the ST and NR during baking. The chemical structure of NR-g-ST was confirmed by ^1H NMR and FTIR characterization. In case of FTIR, it was found a trace of an NR component in NR-g-ST (this subtracted spectrum before and after Soxhlet extraction) as appeared at 2926–2854 cm^{-1}.

3.2. Swelling behavior and mechanical strength

The swelling ratio of the modified NR is shown in Fig. 3(A). The swelling ratio of NR/ST blend without $K_2S_2O_8$ showed the highest value compared to other samples due to the absence of chemical interaction between ST and NR. When NR/ST blend was immersed in water for 2 days, the swelling ratio of the NR/ST increased from 160 to 180%.

But after 2 days, the swelling ratio of NR/ST decreased as a function time due to solubility of ST in NR/ST. After adding $K_2S_2O_8$ in polymer blend, the swelling ratio of NR-g-ST was dramatically decreased due to grafting with ST on molecule of NR. When over 50 phr ST was added, the swelling ratio of NR-g-ST increased with increasing ST contents due to its hydrophilic ST. The highest swelling ratio was observed in sample in the presence of 150 phr ST. This explains that excess ST exhibits good water solubility and leads to excellent swelling ratio in water.

The effect of modified ST on the tensile strength of NR-g-ST is presented in Fig. 3(B). The tensile strength of NR-g-ST increased as a function of modified ST contents in sample at range from 25 to 50 phr of ST. The highest tensile strength of the modified ST was found to be in sample in the presence of 50 phr ST and its tensile strength was about 6.8 MPa. But when the amount of ST was increased from 50 to 100 or 150 phr, tensile strength of modified ST decreased from 6.8 to 4.5 (3.5) MPa, respectively. Fig. 3(C) shows the elongation at break of the modified NR. Results showed that the elongation at break of the NR was about 900% while the elongation at break of modified ST in the presence of 25 phr was 950%. When ST was over 25 phr, the elongation at break the modified NR was dramatically decreased due to difference in polarity between NR and ST (Rouilly et al., 2004).

3.3. Morphology

SEM was used to change the morphology of NR/ST blend and NR-g-ST by $K_2S_2O_8$ as a catalyst as shown in Fig. 4. It was observed that the polymer blend (Fig. 4(A)) showed the poor adhesion between NR and ST. The larger ST part (light-gray areas) was poor dispersed in NR/ST matrix (dark-gray areas). In addition, the ST part phase was separated from the polymer matrix because NR is hydrophobic while the ST is hydrophilic. In the case of NR-g-ST, the good distribution of light-gray color on the surface of polymer blend (Fig. 4(B)) revealed that NR-g-ST. However, some ST part was poor dispersed in polymer matrix (Fig. 4(B)) indicated the weak interfacial interaction between the polymer matrix (NR-g-ST) and ST. Therefore, NR-g-ST should be selected for coating membrane in encapsulated fertilizer.

3.4. Thermal behavior of NR-g-ST

TGA thermograms of plain NR, plain ST, NR/ST blend and NR-g-ST are presented in Fig. 5. The weight loss of all samples started at 100 °C, which was indicated in the moisture content. A three-stage thermal degradation profile was observed for all samples, the first stage of degradation in plain NR, plain ST, NR/ST blend and NR-g-ST specimens was negligible. The first weight loss stage varied with no specific trend for different compositions. This may be attributed to their residual water content in the network and the remaining acetate functional groups, which are more susceptible for cleavage than the OH functional group (Charoenkul, Uttapap, Pathipanawat, & Takeda, 2011;

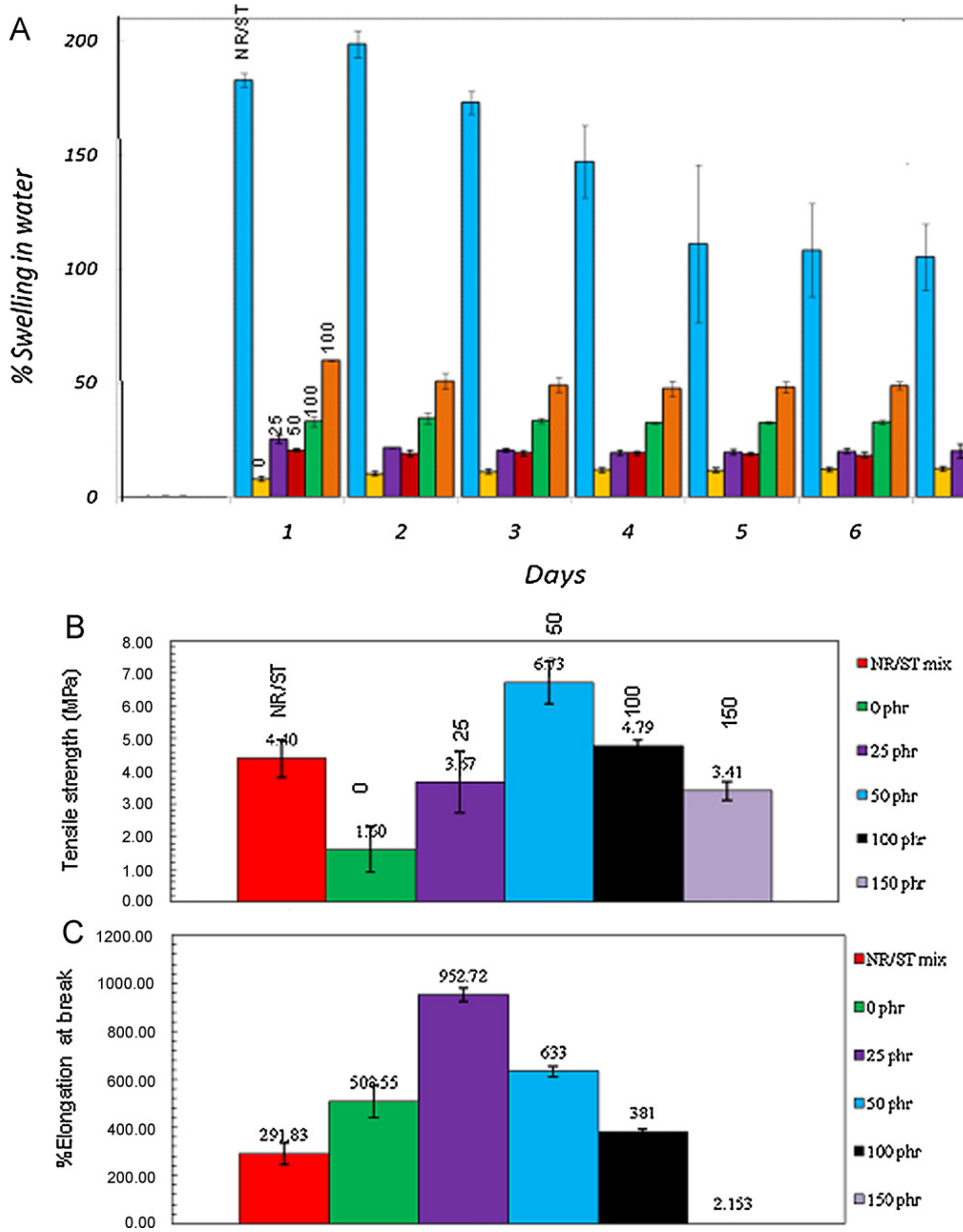

Fig. 3. Influence of ST on (A) swelling ratio in water, (B) tensile strength and (C) elongation at break of the NR/ST blend or NR-g-ST.

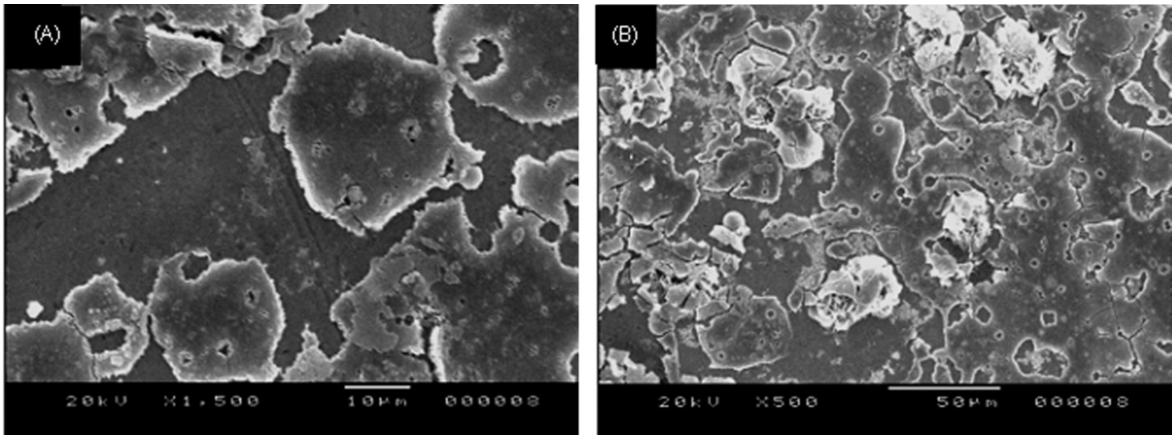

Fig. 4. SEM images of (A) NR/ST blend and (B) NR-g-ST.

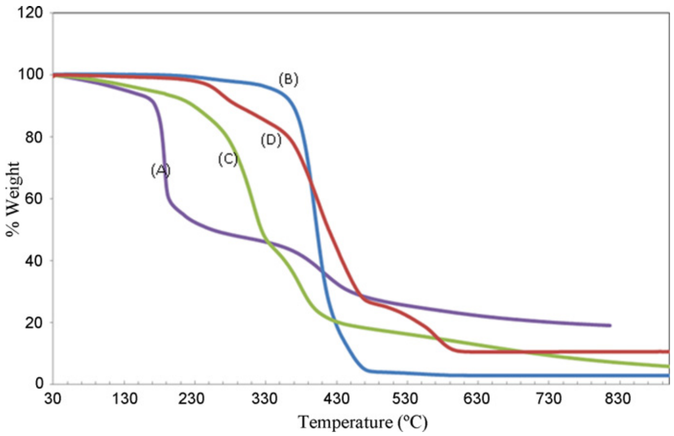

Fig. 5. TGA thermograms of (A) NR, (B) NR/ST blend, (C) NR/$K_2S_2O_8$ and (D) NR-g-ST.

Demiate, Dupuy, Huvenne, Cereda, & Wosiacki, 2000; Parra, Tadini, Ponce, & Lugão, 2004; Sriburi, Hill, & Barclay, 1999). Each sample showed its own temperature range for each stage according to the composition. The overall temperature range for first stage was up to 200 °C, the second stage from 200 to 400 °C and the third stage from 400 up to 600 °C. The thermal degradation process of NR and NR-g-ST were very similar, and there were only one turn in the TG curve (Fig. 5), indicating that the thermal degradation of NR. The thermal degradation curve of modified ST/NR blend, compared to the pristine NR, shifts towards low temperatures, while that of the NR-g-ST moves to higher temperatures at 450–550 °C. The thermal stability of NR was improved significantly after grafting with modified ST (Liu et al., 2008). The enhanced thermal stability and mechanical properties of NR-g-ST were mainly expected due to the improved phase interface interactions between rubber and ST.

3.5. *Encapsulation of urea fertilizer*

The urea fertilizer granule was surrounded by different walls and released through diffusion in water medium. The amphiphilic NR-g-ST has a core–shell structure with a hydrophobic NR as a core and a hydrophilic grafted ST as a shell. The hydrophobic NR core formed a wall-like barrier inside, while the hydrophilic starch part and the urea particles were encapsulated inside the matrix as shown in as shown in Fig. 6. Urea fertilizer contents

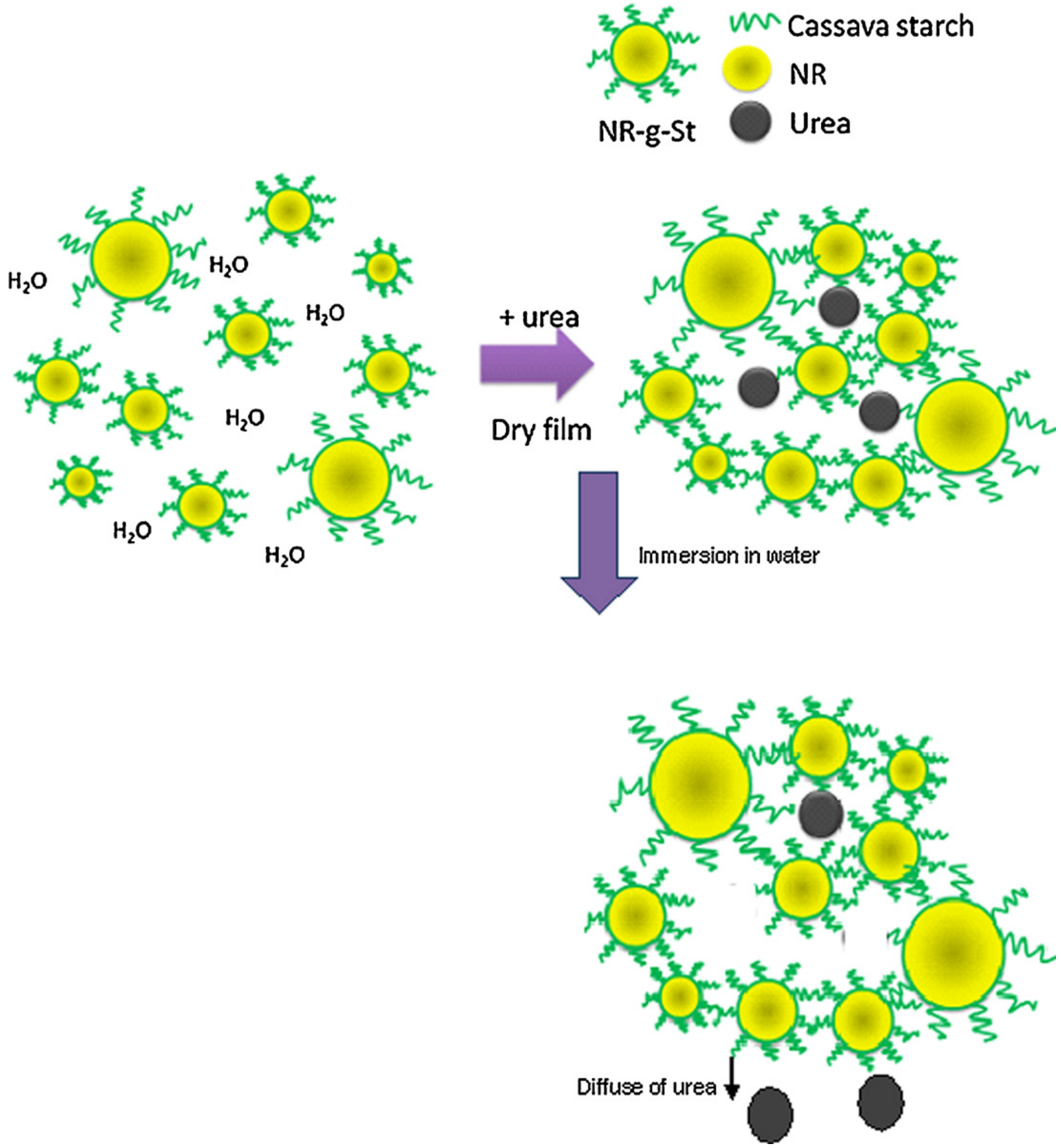

Fig. 6. Possible mechanism of the urea encapsulation film formed by the NR modified with ST.

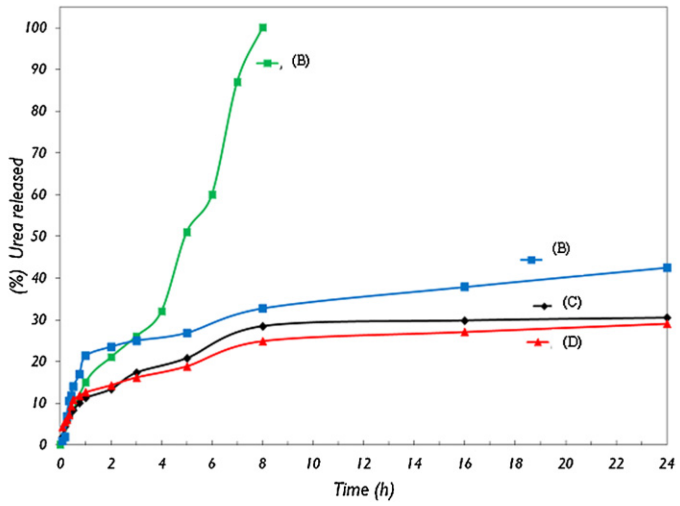

Fig. 7. Urea fertilizer release curves from capsule with coating (A) ST, (B) NR, (C) NR/ST blending and (D) NR-g-ST.

may be released by swelling it under particular conditions, as in the case of an enteric fertilizer coating. In other systems, the wall is broken by solvent action and hydrolysis as shown in Fig. 6.

After water washing, the urea exposed on the surface of bead was removed completely. By measuring urea content in the water, the released urea from capsule was calculated by using UV–vis spectroscopy. The release profile of urea with ST coating was also shown for comparison. The urea release rate was reduced significantly by NR-g-ST coating, which is consistent with the results of the swelling study as shown in Fig. 7. The NR-g-ST membrane is very strong, rigid and hard to swell, thus the diffusion through this coating is the rate limiting step for swelling and urea release. These phenomena may be explained by different swell ability of NR-g-ST matrix because ST and NR/ST can easily be swollen by water. The urea in the swollen NR/ST blend or plain ST can diffuse rapidly and can be released quickly due to weak interaction between urea and polymer matrix membrane. The urea cumulatively release from capsule coating with plain ST was almost complete within 8 h. When NR, NR/ST blend and NR-g-ST coated on capsule, the urea cumulatively release of capsule stored at the same condition for 24 h was 24, 40 and 21%, respectively. With NR-g-ST coating, the capsule matrix becomes denser resulting in a decrease in the rate of diffusion of urea through the swollen beads due to chemical interaction between NR and ST through grafting interaction. This result is supported by Chen et al. (2008). They found that the ST-g-poly(L-lactide) (PLLA) is an effective material for encapsulating urea for controlled release (Chen et al., 2008).

3.6. Biodegradable

The reduction of weight of pristine NR, NR/ST blend and NR-g-ST decomposed in soil was investigated. Results in Fig. 8 display that after chemical modification of NR, the biodegradation of NR-g-ST dramatically increased with increasing the ST contents. The rate of biodegradable of NR-g-ST was faster than that of NR/ST and NR due to grafting between NR and ST. ST was greatly degraded by bacteria and fungi in soil activated by moisture and heat. In the case of NR containing high molecular weight (~10^6) a *cis*-1,4-polyisoprene were responsible for the more difficult biodegradation (Bhatt, Shah, Patel, & Trivedi, 2008). The previous work reported that NR can be slowly degraded in nature by specific microorganisms (Bhatt et al., 2008). The high rate of degradation of NR-g-ST within 3 weeks was due to the high amount of ST in the NR-g-ST.

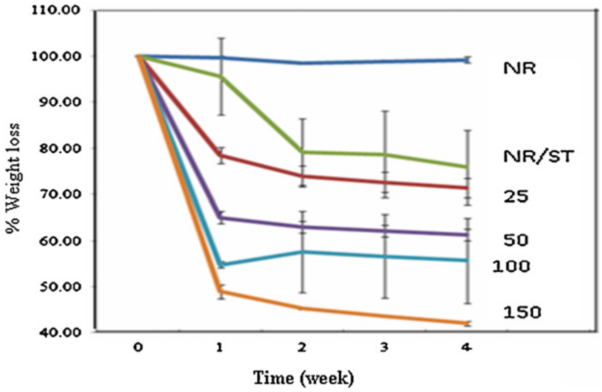

Fig. 8. Weight loss of pristine NR, NR/ST blend and NR-g-ST with different ST contents in soil.

4. Conclusions

The NR-g-ST was achieved to graft with modified ST and $K_2S_2O_8$ as a catalyst for coating the granular fertilizer to reduce solubility in water. The structure modified NR was confirmed by ATR-FTIR. In medium water, the swelling ratio of the modified NR decreased as function of ST due to hydrophilic behavior of ST incorporation in NR matrix. In addition, the tensile strength of modified NR in the presence of ST at 50 phr was the highest compared to other sample and the thermal stability modified NR-g-ST was higher than that of NR-g-ST, which was confirmed by TGA. After NR grafted with ST, it can lead the intermolecular linkage between ST and NR molecules therefore the hydrophobic groups of NR were reduced to control releasing urea fertilizer from capsule. The NR-g-ST membrane displays a good barrier for controlling release of urea fertilizer from capsule and 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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