



Robust and biodegradable polymer of cassava starch and modified natural rubber



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ABSTRACT

The application of starch based materials for packaging purposes has attracted significant interest because they are both cheap and renewable resources. The study investigated the preparation and properties of a novel biopolymer sheet produced from a blend of maleated epoxidized natural rubber (MENR) and natural rubber-g-cassava starch (NR-g-CSt). The water resistance, toluene resistance and elongation at break of the polymer blend were enhanced after the addition of the MENR compared to pristine NR-g-CSt. The maximum tensile strength and thermal stability of the NR-g-CSt/MENR blend were found in the 100:50 NR-g-CSt:MENR blend. The novel films demonstrated good biodegradability in soil.

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1. Introduction

Cassava starch (CSt) is a well-known biopolymer which is now widely cultivated in tropical and subtropical regions of Asia, Africa, and Latin America (Zhu, 2015). To date, starch has been widely used as a food (Wright, Bembridge, Picot, & Premel, 2015), as well as in packaging material (Teodoro, Mali, Romero, & Carvalho, 2015) and in the production of paper (Petersen, Radosta, Vorweg, & Kießler, 2013) because it is a low-cost, renewable resource. However, the drawbacks of native starch are that it has poor mechanical properties and low water resistance. Therefore, it is usually modified to diversify the structure and functionality to suit different applications. For example, the properties of starch for the packaging industry can be improved by the addition of plasticizers (Zhu, Li, Huang, Chen, & Lin Li, 2014) and fillers (Huang, Qian, Li, Lou, & Shen, 2015). In previously reported work, we focused on the modified properties of CSt by grafting it with natural rubber (NR) (Riyajan, Sasithornsonti, & Phinyocheep, 2012) and then blending it with maleated epoxidized natural rubber (MENR) (Riyapan, Riyajan, & Agnieszka, 2015). NR is a natural unsaturated elastomer with some good properties such as high strength, outstanding resilience and high elongation at break (Riyajan, Jitdaphon, &

Leejarkpa, 2014). However, after it is cured with sulfur (Milani, Leroy, Milani, & Deterre, 2013) and peroxide (Benmesli & Riah, 2014), it does not biodegrade easily due to its natural chemical structure and high molecular weight. However, this drawback can be improved by the incorporation of biopolymers (Riyajan, Intharit, & Tangboriboonrat, 2012). In previous work, many researchers have studied the properties of blends between NR and starch (Afiq & Azura, 2013; Carvalho, Job, Alves, Curvelo, & Gandini, 2003; Rajisha, Maria, Pothan, Ahmad, & Thomas, 2014; Riyajan, Tanbunrung, & Pinyocheep, 2010; Shey, Imam, Glenn, & Orts, 2006; Senna et al., 2012) and, there is growing interest in the development of starch-based products because of their biodegradability and because they are environmentally friendly forms of plastic and rubber. Starches have been widely used in blends with various polymers such as polymer ethylene (Sabetzadeh, Bagheri, & Masoomi, 2015), sodium alginate (Wu, He, Chen, Han, & Li, 2014), hydroxypropyl methylcellulose (Ortega-Toro, Jiménez, Talens, & Chiralt, 2014), gluen (Homer, Kelly, & Day, 2014), ethylene-co-vinyl alcohol (Susano, Leonor, Reis, & Azevedo, 2014), polylic acid (Jariyasakoolroj & Chirachanchai, 2014), poly(vinyl alcohol) (Riyajan, Chaiponban, & Tanbunrung, 2009), and polyester (Olivato, Müller, Carvalho, Yamashita, & Grossmann, 2014). In Afiq and Azura (2013), the incorporation of sago starch at ratios of between 0 and 25 phr in natural rubber latex (NRL) affected the physical properties of the film produced using the blends, particularly at high levels of sago starch loading. However, the optimum physical properties in that study

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were achieved by using a blend containing 10 phr of sago starch. In (Rajisha et al., 2014), potato starch was modified with sulfuric acid to produce nanocrystals through hydrolysis, which were then used as an effective reinforcing agent for NR. The results showed that the tensile strength and modulus of the composites improved tremendously with an increasing nanocrystal content due to the formation of a starch nanocrystal network. In Valodkar and Thakore (2011) NR was blended with starch modified with isocyanate. However, the tensile strength of the NR/starch blend was low and the tensile strength of the sample in the presence of 30 phr of starch was only around 4 MPa.

The preparation of graft copolymers of NR with cassava starch (NR-g-CSt) has been an area of great interest and there have been many studies of the reactive blending of rubber and starch using various types of rubber, for example, natural rubber (Afiq & Azura, 2013), maleated natural rubber (Riyajan, Khiatdet, & Leejarkpai, 2014; Riyajan, Riyapan, & Tangboriboonrat, 2014), epoxidized natural rubber (Riyajan et al., 2015) and natural rubber-g-poly (methyl methacrylate) (Nakason, Kaesaman, & Eardrod, 2005).

In the work, reported in this paper, maleated epoxidized natural rubber (MENR) was used to prepare reactive blends of NR-g-CSt. Evidence for the formation of a graft copolymer was found at 1790 cm^{-1} due to a chemical reaction between the ENR and the maleic anhydride (MA) carbon atom. With an increase in the MA content, the particle size and zeta potential of the maleated ENR particles increased due to a change in the chemical composition of the surface of the ENR particles. The swelling ratio decreased with an increase in the MA content due to both cross-linking and the hydrophilic group formed in the grafting between the ENR and the MA. However, the percentage grafting decreased with an increase of the MA content. This was due to the many side reactions such as chain scission and chain transfer reactions.

Previously, the effect of MENR on the physical properties of NR-g-CSt has not been reported in the literature. In this study, the effect of the MENR concentration on the physical properties of the NR-g-CSt blend, including the swelling ratio in toluene and water, the tensile strength, and the thermal stability were investigated. The chemical structure of the NR-g-CSt/MENR blend was characterized by ATR-FTIR and XRD, and its morphology and thermal stability were characterized by SEM and TGA, respectively. The biodegradation in soil of the blend was also reported.

2. Experimental

2.1. Materials

Natural rubber latex 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. The potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) used as a water soluble initiator, was manufactured by RFCL Ltd. (India). The surfactant used, 10% Triton X100, was manufactured by Sigma-Aldrich (Germany). The Formic acid and hydrogen peroxide used were manufactured by a local Company in Thailand and the CSt used, containing 32% amylose, was purchased from the General Starch Co., Bangkok, Thailand. The MA used was manufactured by Fluka (Germany), Merck Schuchardt OHG (Seelze, Germany) as well as by Kitpi boon Chemical Ltd. (Thailand). All the chemicals were used as received. The MENR obtained was as reported in our previous study (Riyajan, Riyapan, & Agnieszka, 2015).

2.2. Preparation of the NR-g-CSt

The NR-g-CSt was prepared following the method outlined in our previous work (Riyajan, Intharit et al., 2012). Before use, the CSt sample obtained was dried in an oven at 50°C for 48 h. A CSt

solution was prepared by dissolving CSt in distilled water containing 2% (v/v) of $\text{K}_2\text{S}_2\text{O}_8$ at $85 \pm 3^\circ\text{C}$ for 1 h. After cooling, the gelatinized CSt was mixed with 10 g of 0.5% w/w $\text{K}_2\text{S}_2\text{O}_8$ solution, and stirred at 60°C for 45 min to obtain a modified CSt. Then 86 g of 60% dry rubber content NR latex was mixed with 500 g of the 10% modified CSt in the presence of Triton X-100 and stirred at 60°C for 3 h.

2.3. Preparation of NR-g-CSt/MENR blend

A quantity of 100 g of 10% w/w NR-g-CSt was mixed evenly with MENR latex in different blend ratios (20:100, 50:100, and 100:100 NR-g-CSt:MENR) at $28\text{--}30^\circ\text{C}$ under stirring for 3 h. The resulting mixtures were poured into glass plates ($12 \times 12 \times 5\text{ cm}$) and allowed to dry at ambient temperature for 3 days. They were then allowed to continue drying at 50°C for 24 h and were kept in a desiccator prior to being characterized.

2.4. Measurements

The chemical structure of the NR-g-CSt and NR-g-CSt/MENR blends was analyzed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) using a Bruker EQUINOX 55 measuring in the range of $4000\text{--}500\text{ cm}^{-1}$. The chemical structure of the NR-g-CSt/MENR blend was elucidated by CP/MAS solid state ^{13}C NMR (Chemagenetics CMX 100). Measurement was conducted under a static field strength of 2.3 T (100 MHz, 1 H) at $20 \pm 1^\circ\text{C}$. The contact time for CP was 1 ms with a proton 90° pulse of $5.5\ \mu\text{s}$ and a decoupling power of 75 kHz. The MAS speed was 3 kHz and the delay time after acquisition of the FID signal was 4 s. The chemical shifts were calibrated by using an external hexamethyl benzene standard. In addition, the NR-g-CSt and NR-g-CSt/MENR blends were also analyzed by X-ray diffractometry (XRD) using a WI-RES-XRD-001, Philips X'Pert MPD under the following conditions: Nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$) at a current of 25 mA and a voltage of 35 kV. The scanning rate was $4^\circ/\text{min}$ in an angle range of $5\text{--}90^\circ$ (2). The molecular weights of the NR and NR-g-CSt were determined using a Waters liquid chromatography apparatus with UV and IR detectors. Tetrahydrofuran was employed as the eluant and a flow rate of $10\text{ cm}^3/\text{min}$ was used. The apparatus was calibrated by mono-dispersed polystyrene (PS) calibration standards. Thermo Gravimetric Analyses (TGA) was performed using a TGA7, PerkinElmer instrument. A 10–20 mg sample was placed in a platinum pan and analyses were carried out under nitrogen and oxygen atmospheres (gas flow = 100 ml/min), at a heating rate of $10^\circ\text{C}/\text{min}^{-1}$, in a temperature range of $50\text{--}1300^\circ\text{C}$. Friction force imaging and friction force measurements were conducted in contact mode with a scanning angle of 90° to the long axis of the cantilever beam at a scanning velocity of 1 Hz. A standard V-shape silicon nitride cantilever with a square-pyramidal tip (Veeco Probes, Inc.) was used. The manufacturer's nominal values for the cantilever length and spring constant were 125 mm and 0.38 N/m, respectively. The particle sizes of the three samples (MENR, NR-g-CSt and NR-g-CSt/MENR blend latex) were also determined using a micro-electrophoresis apparatus (Zetasizer 4, Malvern) at 25°C , in a pH 7 medium. A known weight of the graft copolymer film of specific dimensions ($2.5\text{ cm} \times 2.5\text{ cm} \times 0.5\text{ mm}$) was immersed in toluene, benzene oil and water for a period of 5 days at 32°C . The sample was dried in an oven at 50°C for 24 h and then weighed until a constant weight was achieved. The swelling ratio was calculated from Eq. (2) as follows:

$$\text{Swelling ratio} = (W_2 - W_1)/W_1 \quad (2)$$

where W_1 = original weight of the sample, W_2 = weight of the swollen sample.

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