



Effect of chitosan content on gel content of epoxidized natural rubber grafted with chitosan in latex form

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ABSTRACT

The epoxidized natural rubber (ENR) latex-g-chitosan (ENR-g-chitosan) was prepared in latex form using potassium persulphate as an initiator. Firstly, the reduction in molecular weight of chitosan was subjected to the addition of $K_2S_2O_8$ at 70 °C for 15 min. The structure of the modified chitosan was characterized by ATR-FTIR. Secondly, the influence of chitosan contents, reaction time, and temperature and $K_2S_2O_8$ concentrations on the gel content of the modified ENR was investigated. The chemical structure of the ENR-g-chitosan was confirmed by 1H -NMR and ATR-FTIR. The ether linkage of the ENR-g-chitosan was confirmed at 1154 and 1089 cm^{-1} by ATR-FTIR and 3.60 ppm by 1H -NMR. The gel content of ENR-g-chitosan at 5% chitosan showed the highest value compared with other samples. But when chitosan increased from 5% to 10% or 20%, the gel content of ENR-g-chitosan dramatically decreased. The ENR-g-chitosan showed good thermal resistance due to incorporation of chitosan. The morphology of ENR-g-chitosan particle showed the core-shell structure observed by TEM. The optimum condition of grafting ENR with chitosan was found at 65 °C for 3 h of reaction time, ratio of ENR/chitosan at 9:1.

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1. Introduction

Considering the properties of natural rubber (NR), the benefits of NR are excellent physical properties (i.e., high mechanical strength, low heat build up, excellent flexibility, and resistance to impact and tear and a renewable resource) [1,2]. But, it has also some drawbacks such as low flame resistance, sensitivity to chemicals and solvents (ozone and weathering), mainly due to its unsaturated hydrocarbon chain structure and its non-polar character, which causes limitations in a variety of applications. In addition, it is difficult to degrade in nature due to its high molecular weight [3]. In the past few years, the chemical modifications of NR have been studied widely, to find the new applications. Various types of well-known modified NR products were thus prepared such as epoxidized natural rubbers (ENR) [3,4], it is derived from the partial epoxidation of the NR molecule, resulting in a totally new type of elastomer. Moreover, the epoxide groups are randomly distributed along the NR molecule. When % level of epoxidation in ENR increased, ENR exhibits an increase in damping [5]; a reduction in swelling in hydrocarbon oils [3]; a decrease in gas permeability [5]; an increase in silica reinforcement [5]; improved compatibility with polar polymers like polyvinyl chloride [6]; reduced rolling resistance [7] and increased wet grip [7] as well as glass transition temperature [4]. However, the weak properties of ENR have been improved by the blending with biopolymer including starch [3], cellulose [8,9], chitosan [10–13] and gelatin

[14] there is also a growing environmental awareness regarding the disposal of these materials at the end of their useful life. Thus, the chitosan was used for this purpose. Chitosan consists of a linear polymer of α (1 → 4)-linked 2-amino-2-deoxy- β -D-glucopyranose derived from the N-deacetylation of chitin, a common structural polymer found in exoskeletons [14]. The raw source of chitin and chitosan are crustaceans such as crabs, shrimp and lobsters, which are highly abundant biomasses due to the food and beverage and canning industries. Due to its physical and chemical properties, chitosan has received much attention as a functional biopolymer and is being used in a wide range of applications ranging from biomedical engineering, pharmaceutical and cosmetic products to water treatment and plant protection [15,16]. In our previous work, the chitosan was used to blend with NR to improve degradation in nature and reinforced filler in rubber compounds [17,18], electric properties [10], organic solvent resistance [16] and natural fiber [18]. For example, after ENR was blended with chitosan and the slight changes in curing time (t_{90}), and scorch time (t_{S2}) of the compounds with the incorporation of chitosan were noticed [17,18]. In addition, the maximum torque, tensile modulus and durometer hardness of the compounds was enhanced but tensile strength and elongation at break decrease with chitosan loading. The vulcanized NR/chitosan blends were prepared by using dicumyl peroxide as a cross-linking agent [18]. In the case of tensile properties, peroxide vulcanized blends show higher tensile strength and hardness (Shore A) than the unvulcanized blend. The improved solvent resistance and thermal resistance for peroxide vulcanized blends proved the formation of crosslinks in the rubber phase. The blends showed reduced swelling rate due to the tortuosity

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of the path and the reduced transport area in blended samples. The ENR composite obtained chitosan fiber was prepared by electro-spinning method to apply in copper ion absorptivity [19]. Results showed that the rubber composite exhibited good ion absorption observed by SEM metal ion mapping mode. Until now, we have not found the ENR molecule grafting with chitosan in literature review. After chemical modification of ENR, it was found that their advantages are a new medical material, easy degradability in nature and a renewable resource leading to new applications in the future. We attempted to modify the hydrophobic property of ENR to become more hydrophilic properties by grafting it with chitosan. Firstly, the reduction of molecular weight of chitosan was achieved by the addition of potassium persulphate under heating. The chemical structure was revealed by ATR-FTIR. Then, the modified chitosan was grafted with ENR molecule in latex form by using potassium persulphate as a catalyst. The effects of chitosan concentration, reaction time, temperature and catalyst concentration on the gel content of ENR-g-chitosan were investigated in this work. The chemical structure of modified ENR was characterized by ATR-FTIR and $^1\text{H-NMR}$. The morphology and thermal stability of the ENR-g-chitosan was also characterized by SEM and TGA, respectively.

2. Experimental

2.1. Materials

The NR latex was manufactured by Thai Rubber Latex (Thailand). The percentage of dry rubber content (DRC) was about 60%. The potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) as a water soluble initiator was manufactured by RFCL Ltd (India). ENR was obtained from our work [3]. General Starch Co. (Thailand). The surfactant used for 10% Terric16A16 was manufactured by Lucky four. Co. Ltd. (Thailand). Chitosan was prepared from Local Company in Thailand and the degree of deacetylation of chitosan was found to be 87%.

2.2. Epoxidation of natural rubber latex

ENR latex was prepared from NR latex (60% DRC). The latex was first diluted with liquor water 100 g and stabilized with a non-ionic surfactant (10% Terric16A16) at 4 wt.% of dry rubber content. The NR latex was stirred for 30 min at room temperature to eliminate ammonia. The mixture was heated to 50 °C. Formic acid was then added drop by drop for 50 min, and then 50% w/w hydrogen peroxide was then added drop by drop for 30 min. The reaction mixture was stirred for 2 h. The amount of 50% w/w hydrogen peroxide used was calculated in order to obtain a theoretical epoxidation level of 20 unit%. 36% w/w formic acid was used in equimolar quantity by comparison with hydrogen peroxide. To characterize the structure of the ENR contained in the ENR latex and to confirm the level of epoxidation, a sample of ENR latex was taken off and the ENR isolated after coagulation in methanol and drying under vacuum, was analyzed by $^1\text{H NMR}$ (Varian Unity Inova 500 MHz).

2.3. Grafting procedure

The chitosan sample obtained was dried in an oven at 60 °C for 48 h. The chitosan solution was prepared by dissolving chitosan in distilled water containing 2% (v/v) of acetic acid. The blends were prepared by mixing chitosan solution and ENR latex to get a homogeneous solution in the presence of $\text{K}_2\text{S}_2\text{O}_8$ at 65 °C for 3 h. Then the mixture was cast on a petri dish at 30 °C. The ungrafted ENR was also extracted by toluene and water. After that, it was dried in an oven at 50 °C for 24 h and kept it in desiccator before characterization in next step.

2.4. Measurements

The chemical structure of modified ENR was analyzed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Bruker EQUINOK 55 measuring in the range of 4000–500 cm^{-1} . In addition, ENR-g-chitosan was also analyzed by $^1\text{H-NMR}$ (Varian Unity Inova 500 MHz).

The gel content of the grafted samples was determined by the extraction of samples in boiling toluene for 24 h and the extraction of samples in boiling water for 24 h using Soxhlet apparatus. The extracted samples were dried in an oven at 50 °C till constant weight. The gel fraction was calculated by Eq. (1).

$$\% \text{Gel content} = \frac{(W_0 - W_1) * 100}{W_0} \quad (1)$$

where W_1 and W_0 are the weights of the dried samples after extraction and before extraction, respectively.

Thermo Gravimetric Analyses (TGA) were performed using a TGA7, PERKIN ELMER Instrument. A 10–20 mg sample was placed in a platinum pan. Analyses were carried out under nitrogen and oxygen atmospheres, respectively (gas flow = 100 ml min^{-1}), at a heating rate of 10 °C min^{-1} , on a temperature range of 50–1300 °C.

The morphology of the modified ENR was also investigated by AFM OCA15EC data physic. Transmission Electron Microscopy (TEM) was used on JEOL JEM-2010 to study the morphology of the graft copolymer. The polymer-grafted natural rubber latex was diluted approximately 400 times of its original concentration with distilled water. An aqueous solution (2 wt.%) of OsO_4 was added to stain natural rubber macromolecules. The stained latex was then placed on a 400 mesh grid, and dried overnight in a desiccators before characterization.

3. Results and discussions

3.1. Degradation of chitosan with potassium persulphate

After adding KPS into the chitosan solution at 70 °C for 3 h, the degradation of chitosan by KPS was very fast and almost complete within 15 min, observing from in the viscosity changes and color change. KPS, when heated, would decompose into two anionic free radicals as shown in Fig. 1(1). The anionic free radical react cationic amino groups (NH_3^+) at the C-2 carbon of the chitosan ring because of the electrostatic attraction under heating [20]. Then, the anionic radical attacked the C-4 carbon and transferred the radical to the C-4 carbon by subtracting the hydrogen from it. The presence of a free radical at the C-4 carbon weakened and homolytically broke the next C–O bond at the C-1 carbon and transferred to the free radical to the C-1 carbon. Finally, the chitosan chain was degraded into two shorter chains. One had a free radical on the C-1 carbon at the end, and the other had a carbonyl group at the C-4 carbon in the terminal ring as show in Fig. 1(2). The ATR-FTIR was used to investigate the structure of the degraded chitosan as shown in Fig. 2.

The ATR-FTIR absorption peak of the C-1 carbon shifted from 1650 to 1652 cm^{-1} . Though, it is possible that the KPS free radical would attack the C-1 carbon and turned the two shorter chains the other way around [20]. If this were true, then the terminal C-1 carbon would become a carbonyl group and would have a higher chemical shift value. Yet, this was not supported by the NMR results. Nevertheless, the chitosan chain was getting shorter and shorter through the scission of C–O–C bonds in the main chain.

3.2. Synthesis of the graft copolymers (ENR-g-chitosan) observed by ATR-FTIR and NMR

Grafting of chitosan on ENR may be initiated by different free radicals. Chitin or chitosan molecule contains two reactive groups at C-2

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