

Reinforcement of Natural Rubber with Bacterial Cellulose via Latex Solution Process

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Abstract—Preparation of natural rubber (NR) composites reinforced with cellulose to enhance Young's modulus and tensile strength of the rubber has attracted much interest in recent years. Focusing on green material development, NR and cellulose represent major biopolymers and renewable materials that are highly available in Southeast Asia. Nevertheless, the development of this composite material is limited by nonhomogeneous dispersion of cellulose particle in rubber matrix due to the difference of polarity between NR and cellulose. In this study, in order to modify the properties of rubber composite films, we focus on NR reinforced with bacterial cellulose (BC) via one-step solution processing. The chemical structure of the natural rubber- bacterial cellulose composite (NRBC) was investigated by Fourier transforms infrared (FTIR) spectroscopy. The film morphology was assessed by Scanning electron microscope (SEM) and the mechanical properties were characterized by tensile testing. The mechanical properties, such as Young's modulus and tensile strength were found to increase by an increased load of BC, while elongation at break was decreased.

Keywords—Natural rubber, Bacterial cellulose, Reinforcement, Composites

I. INTRODUCTION

Thailand is the world's largest natural rubber producer and exporter. NR is a processed plant product produced in various regions of Thailand. However, the price of NR is unstable. Currently, the NR price continuously declines due to the oversupply in the world market. The development of NR composites can enhance its applications and thus, increase market size of NR.

NR is a flexible polymer that has the ability to regain its original shape after being deformed and therefore, NR is used as a raw material in elastomer industry, including automotive and truck tires, the major NR market [1]. The most common procedures of the production process have a modification step of the mechanical properties of NR in order to improve their properties for suitable applications. Due to low strength and abrasion resistance of NR, reinforcement is the most important step in a production process. The reinforcement of NR considerably depends on reinforcing reagents, typically in forms of fibers and nanoparticles [2]. In the past, nanoscopic additives such as carbon black and silica nanoparticle were main reagents for polymer reinforcement [3]-[4]. Silica-reinforced NR prepared via the sol-gel process is one of the

reinforcing methods that have been widely used [5]-[7]. Research studies for reinforcing additives are incessantly conducted, for instance, polyester, aramide, nylon, kenaf, glass fiber, graphene, nanoclays, as well as cellulose [8]-[14]. Cellulose nanofiber is applied as a reinforcing reagent such as carbon nanotubes and microfibrillated cellulose (MFC) [15]-[17]. BC has also been studied for the use in both natural and synthetic polymer reinforcing. BC is inexpensive and it is considered as a green polymer, renewable and biodegradable material [18]-[22]. However, without pretreatment, only low concentration of cellulose can be added in natural rubber matrix because of the difference of polarity between NR and cellulose. Effective methods for reducing this problem have been concerned. It has been reported that the preparation of NR composites via solution system instead of rubber melt blending could decrease the hydrophilicity and polarity of the nanofibers, and hence increase their adhesion to the rubber matrix [23].

In this work, we focus on preparation of NRBC composite films via solution method by adding slurry of BC into natural rubber latex as reinforcement fibers of NR composite films. The characteristics of the composite films were then determined. The main object of this work is to develop novo NRBC composite films, which can be further applied in the fields of packaging and biomaterials.

II. MATERIALS AND METHODS

A. Materials

NR Latex 60 Dry rubber content (DRC) were purchased from the Rubber Research Institute of Thailand. BC (98-99% water content in wet weight) was kindly provided by Pramote Thamarat (Institute of Research and Development of Food Product, Kasetsart University). All other chemical reagents were purchased from Sigma-Aldrich.

B. BC preparation

The cubes of BC (in form cubic centimeter) were purified by washing with deionized (DI) water, then were soaked with 1 wt % NaOH for 48h to remove bacterial cells, and were rinsed with DI water until the pH was 7. To prepare BC slurry, BC was thoroughly blended by a blender.

C. Preparation of NRBC composites

BC slurry was added into natural rubber latex (NRL) and the mixture was mechanically stirred for 5 minutes at room temperature. The mixtures were prepared with the compositions of BC/NR at 20/80 (NRBC20), 40/60

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(NRBC40), 60/40 (NRBC60) and 80/20 (NRBC80). NRBC composite films were prepared by pouring BC/NR mixtures into a tray or plastic culture dish and then aging at room temperature.

D. Characterization of the composite films

Fourier transform infrared (FTIR) spectra of the films were measured at wave numbers ranging from 4000 cm^{-1} to 400 cm^{-1} at a resolution of 4 cm^{-1} with a Nicolet (US) SX-170 FTIR spectrometer.

Scanning electron microscopy (SEM) micrographs were taken with a scanning electron microscope (model JSM-5410LV, JOEL, Tokyo, Japan). The NRBC film was frozen in liquid nitrogen, immediately snapped, and then vacuum-dried. The free surfaces were sputtered with gold and photo-graphed. SEM was obtained at 15 kV.

For tensile property testing, NRBC films were cut into strip-shaped specimens 10 mm wide and 10 cm long. The maximum tensile strength and break strain of NRBC films were determined with a Lloyd 2000R (Southampton, UK) universal testing machine. The test conditions followed ASTM D882. The tensile strength and break strain were the average values determined from 5 specimens.

III. RESULTS AND DISCUSSION

A. Fourier transform infrared spectroscopy (FTIR)

Fig. 1(A) shows the FTIR of NR, BC and NRBC20. Pure NR spectra adsorbed at 2916 and 2849 cm^{-1} are assigned to asymmetric stretching vibration of methyl ($-\text{CH}_3$). In addition, it is appeared a peak of symmetric stretching vibration of methylene ($-\text{CH}_2$) at 2963 cm^{-1} . The $\text{C}=\text{C}$ stretching is situated at 1664 cm^{-1} . In the case of pure BC, there are a peak of O-H stretching of hydroxyl group at $3000\text{-}3600\text{ cm}^{-1}$ and a peak of asymmetric stretching vibration of methyl ($-\text{CH}_3$) at 2896 cm^{-1} . The FTIR spectra of NRBC20 show peaks at 2963 cm^{-1} , 2913 cm^{-1} and 1664 cm^{-1} are assigned CH_2 , CH_3 and $\text{C}=\text{C}$ stretching respectively. Moreover, there is a peak of OH stretching at $3000\text{-}3600\text{ cm}^{-1}$. Observations have shown spectra peaks of NRBC composites slightly shifted from peaks of reactants, which implied some weak interactions without chemical reaction of NR and BC. Fig. 1(B) shows the effects of BC content on the patterns of functional groups in NRBC nanocomposites. Peak area of hydroxyl group was enhanced with the increase of BC fiber content, whereas peak areas of methyl and methylene groups were decreased.

B. Scanning electron microscopy (SEM)

SEM was employed to study the cross-section morphologies of NR (Fig. 2A), BC (Fig. 2F) and NRBC composites (Fig. 2B-E): NRBC20 (Fig. 2B), NRBC40 (Fig. 2C), NRBC60 (Fig. 2D) and NRBC80 (Fig. 2E). The NRBC20 composite film has the smoothest surface when compared with other NRBC composite films due to BC fibers dispersed homogeneously within the NR matrix. Homogeneous was reduced with the increase of BC concentration in NR matrix. NRBC40,

NRBC60 and NRBC80 composites which contained high concentration of BC had a rather rough surface; however, no phase separation was observed.

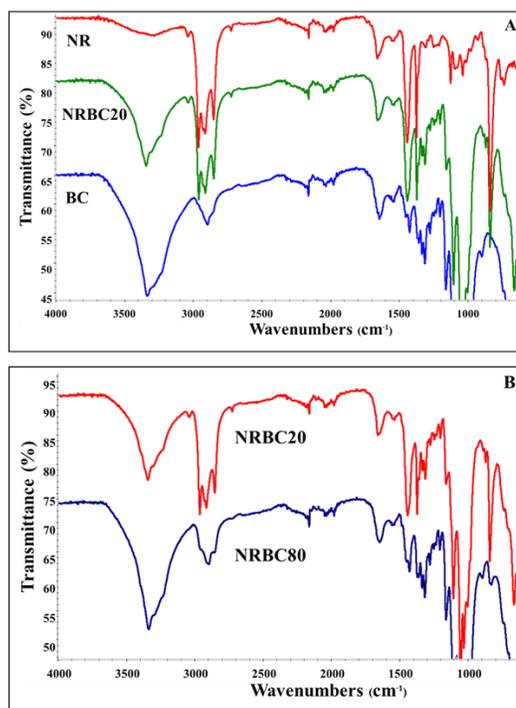


Fig. 1 FTIR spectra of NR, BC, NRBC films

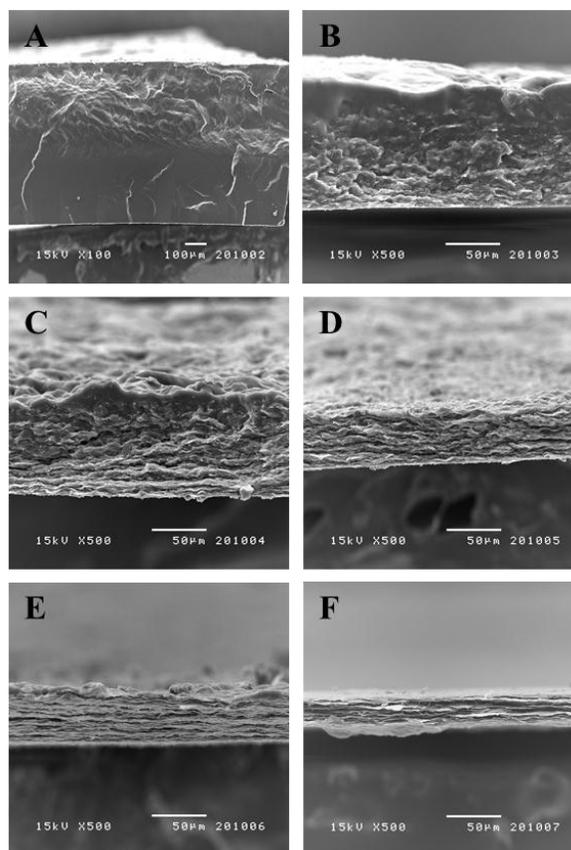


Fig. 2 SEM images of NR (A), NRBC (B-E) and BC (F)

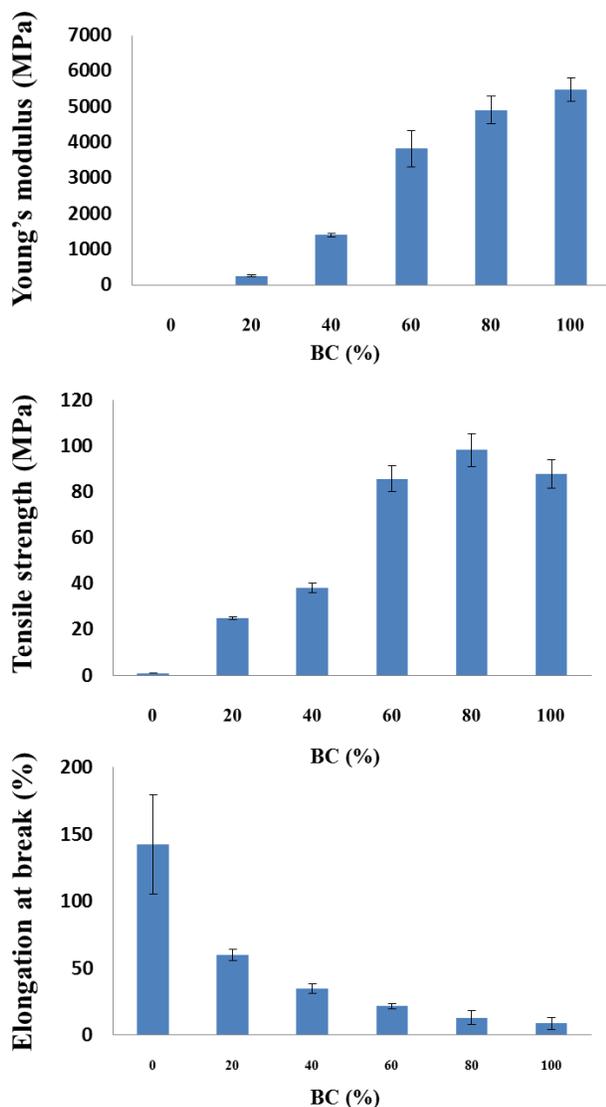


Fig. 3 Mechanical properties of NRBC composite films with different BC loading content; Young's modulus (A), tensile strength (B) and elongation at break (C)

C. Mechanical properties

The Young's modulus (Fig. 3A), tensile strength (Fig. 3B) and elongation at break (Fig. 3C) of dry films of NR, BC and NRBC at different BC loading content were determined. In general, pure NR has low Young's modulus, low tensile strength, but high elongation at break. On the other hand, BC has high Young's modulus, high tensile strength, but low elongation at break. Overall, it was shown that BC could be used as a reinforcing element in a NR matrix. Young's modulus and tensile strength of the NRBC films were enhanced with the increase of BC fiber contents. The maximal Young's modulus and tensile strength at 4910.4 and 98.4 MPa, respectively were obtained with BC loading at 80%. High modulus and high strength are advantages of reinforcing process which is controlled by fiber contents. However, there

are limitations of reinforcement such as elasticity decline. From Fig. 3C, the decrease of elongation at break of the composites was observed as BC loading content was increased. Moreover, compatibility and homogeneity of NR and BC in the composites might be reduced at high BC loading content. The NRBC20 had the highest elongation at break 59.9%, which was about 0.4 of that of NR. Generally, NR has a very high elasticity; however the preparation steps such as aging and drying could also make the materials become less elastic.

IV. CONCLUSION

The mechanical properties of NR composites were successfully enhanced via reinforcement by BC fibers. The NRBC composites could be prepared via latex solution process. Within composition studies, no aggregation of BC in the NR matrix was observed. Some weak interactions between BC fibrils and NR were illustrated via FTIR analysis. Young's modulus and tensile strength of the NRBC films were enhanced with the increase of BC fiber contents, while elongation at break was decreased. Compared to NR film, NRBC20 composite film showed significant improvements in the Young's modulus and tensile strength with smooth surface, homogeneous distribution of BC fibers in NR matrix and high elastic elongation. On the other hand, NRBC60 and NRBC 80 had very high Young's modulus and tensile strength with rather low elasticity.

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