

Preparation and Mechanical Properties of Pre-vulcanized Natural Rubber Latex/Chitosan/Poly (3-hydroxybutyrate) Blends

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Abstract—In order to obtain natural rubber (NR) latex-based biomaterial, the NR latex concentrate was prepared into pre-vulcanized natural rubber latex (SNRL) and then blended with a water dispersion of chitosan (CS) and poly(3-hydroxybutyrate) (PHB) together, with the total amount of CS and PHB is of 1, 3, 5, 10 parts per hundred rubber (phr), and CS and PHB is of a ratio of 1:1; the SNRL was also blended with a water dispersion of CS or PHB only in the same amount for properties comparison. The mechanical properties including the tensile strength, elongation at break, 300% modulus, tear strength and hardness of the 24h water-leached SNRL/CS/PHB, SNRL/CS or SNRL/PHB films were tested. The results indicated that, the tensile strength first increased with increase in CS/PHB, CS or PHB content up to 1.0 phr then decreased, the elongation at break decreased, the 300% modulus, tear strength and Shore A hardness increased, with increase in CS/PHB, CS or PHB content, whereas most of the tensile strength and elasticity of the films can be retained when the content of CS/PHB, CS or PHB was less than 5.0 phr.

Keywords-natural rubber latex; chitosan; poly(3-hydroxybutyrate); blend; mechanical properties.

I. INTRODUCTION

Natural rubber (NR) latex is widely used in the production of many daily-used and medical products, due to its good comprehensive properties such as excellent wet-gel strength, film-forming ability, elasticity and flexibility. However, there still a few problems concerning

the use of NR latex and its products, for example, the allergy of protein, the potential carcinogen of nitrosamines, the poorer of NR latex-made products in tear strength, aging-resistance, and bio-compatibility such as blood compatibility and cytotoxicity comparing with such bio-compatible silicone and polyurethane products, which has limited its further application.

Chitosan (CS) is a cationic biopolymer and polysaccharide of natural origin. It has many useful features such as nontoxicity, biocompatibility, good mechanical strength and antimicrobial properties, and can be used in many areas from health care to agriculture and dyes for fabrics. By blending with CS or CS derivatives, the properties of NR latex films can be improved [1-7]. However, there are such shortcomings for CS as the easy adhesion of cell, low strength, easy to collapse and mismatching of degradation rate with the new tissue; and CS can also cause blood-clotting and accelerate the formation of thrombosis. The blood compatibility of CS can be increased by chemical derivation such as sulfated modification to significantly improve the anti-clotting property [8]. However, the process for sulfated modification of CS is not easy to control, low in yield, high in production cost and there is the problem of chemical residues as well.

Poly(3-hydroxybutyrate) (PHB) is obtained from microorganisms growing in imbalance condition. PHB possesses such properties as excellent bio-compatibility and biodegradability, and has become a new kind of

medical material. PHB is beneficial to the adsorption and differentiation of cell, and it has also such properties as piezoelectricity, non-toxicity, and non-irritating and blood anticoagulant property. It has been reported that the blending of CS with PHB can produce an effect similar to the sulfated modification of CS, resulting in significantly improvement in the blood anticoagulant property for CS. The CS/PHB blends have better biological properties than those of either CS or PHB, and a best blood anticoagulant activity is obtained by blending the CS and PHB in a ratio of 1:1[9, 10].

In order to find a process suitable for the manufacturing of NR latex-based medical products, the CS and PHB together was prepared into a water dispersion and then blended with the sulfur prevulcanized NR latex (SNRL); for property comparison, each of CS or PHB only was also used to prepare a water dispersion and then blended with SNRL, respectively. The SNRL/CS/PHB, SNRL/CS or SNRL/PHB films were immersed into distilled water for 24h and then dried, before the testing for mechanical properties such as tensile strength, elongation at break, 300% modulus, tear strength and Shore A hardness were carried out.

II. EXPERIMENTAL

A. Materials

The ammonia-preserved NR latex concentrate with a total solid content of 61.69% was obtained from a local rubber plantation; the chitosan (CS) with a deacetylation degree not less than 80%, biochemical reagent (BR), was supplied by Sinopharm Chemical Reagents Co., Ltd (China); the poly(3-hydroxybutyrate) (PHB) was purchased from TianAn Biologic Materials Co., Ltd (Ningbo, China); the remaining chemicals including sulfur, zinc oxide, zinc diethyl dithiocarbamate were all commercial products.

B. Sample Preparation

The formula used for the prevulcanization of NR latex is as follows (based on dry mass): NR 100, sulfur 0.8, zinc diethyl dithiocarbamate 0.4, zinc oxide 0.4. The vulcanizing ingredients were first prepared into a water dispersion of about 50 wt% solid content and then added into the NR latex concentrate that had been stabilized by a suitable amount of 10% casein solution, 20% potassium hydroxide solution and 10% fatty alcohol polyoxyethylene ether (Peregal O). The mixture was heated at 60°C for 2.0h under continuous stirring, and quickly cooled down with tap water to obtain sulfur-prevulcanized NR latex (SNRL), and the SNRL was then filtered after a maturation of three days at ambient temperature.

The CS/PHB with a blending ratio of 1:1, and CS or PHB only were prepared respectively into a water dispersion of 5 wt% solid content using a high speed sand mill under continuously stirring, and then mixed thoroughly with the above-mentioned filtered SNRL to obtain homogeneous SNRL/CS/PHB, SNRL/CS or SNRL/PHB blends having the following contents of CS/PHB, CS or PHB (based on dry mass): 1, 3, 5 and 10 parts per hundred rubber (phr), respectively. After standing in room temperature for several hours to remove bubbles, the blends were cast in glass moulds, dried in air,

leached in running distilled water for 24 h and then dried in an oven of 50°C to obtain the SNRL/CS/PHB, SNRL/CS or SNRL/PHB films, respectively. Film obtained from the SNRL were used as control for properties comparison, and designated as sample with a CS/PHB, CS or PHB content of 0.

C. Testing

The tensile properties and tear strength of the SNRL/CS/PHB, SNRL/CS or SNRL/PHB films were tested on an UT-2080 universal testing machine (U-CAN DYNATEX INC, China) according to GB/T 528—2009 and GB/T 529—2008, with a crosshead speed of 500mm/min, respectively.

The Shore A hardness of SNRL/CS/PHB, SNRL/CS or SNRL/PHB films was determined according to GB/T 531.1—2008.

III. RESULTS AND DISCUSSION

A. Tensile Properties of SNRL/CS/PHB, SNRL/CS and SNRL/PHB films

The tensile strength, elongation at break and 300% modulus of the SNRL/CS/PHB, SNRL/CS and SNRL/PHB films are shown in Figs.1, 2 and 3, respectively.

It can be seen from Fig.1 that, the tensile strength of the SNRL/CS/PHB, SNRL/CS and SNRL/PHB films increased with the addition of 1.0 phr of CS/PHB, CS or PHB, then decreased, in which the SNRL/CS films showed the highest degree of reduction, followed by the SNRL/CS/PHB films, then by the SNRL/PHB films, and most of tensile strength can be retained for all these films when the addition of CS/PHB, CS or PHB was less than 5.0 phr, especially for the SNRL/CS/PHB and SNRL/PHB films.

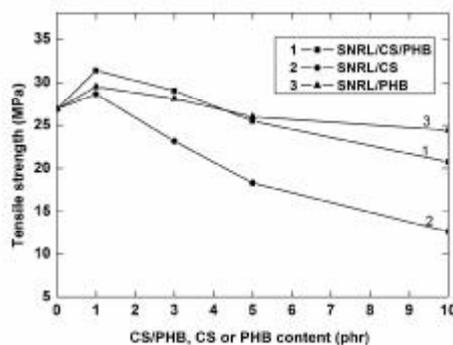


Figure 1. Tensile strength of blend films

The changes in elongation at break (an indication of elasticity) as shown by Fig.2 indicated that, the elongation at break of the SNRL/CS/PHB, SNRL/CS and SNRL/PHB films decreased with increase in CS/PHB, CS or PHB content, respectively, and the SNRL/CS films showed the highest degree of reduction, followed by the SNRL/CS/PHB films, then by the SNRL/PHB films. However, most of the elasticity be retained for these three kinds of films, when the addition of CS/PHB, CS or PHB

was less than 5.0 phr, especially for SNRL/PHB films, because the elongation at break is an indication of elasticity.

It is suggested that, when the CS/PHB, CS or PHB content was lower, the film forming ability of SNRL was not greatly damaged by the addition of these materials, but even showing enhancement in tensile strength especially for SNRL/CS/PHB and SNRL/PHB films because of interaction. However, when the content of CS/PHB, CS or PHB was higher, the amount of continuous phase of NR became less and more CS or PHB molecules might aggregate together, which would damage the film formed; and the great difference in shrinkage ratio between the elastic continuous phase of NR and the dispersive phase of plastic CS/PHB, CS or PHB that has a plastic behaviour during the drying process, would also break the continuity of the SNRL/CS films; the reduction in tensile strength and elongation at break with increase in CS/PHB content could also be attributed to decrease in strain-induced crystallization ability caused by the reduction of NR content in the blends.

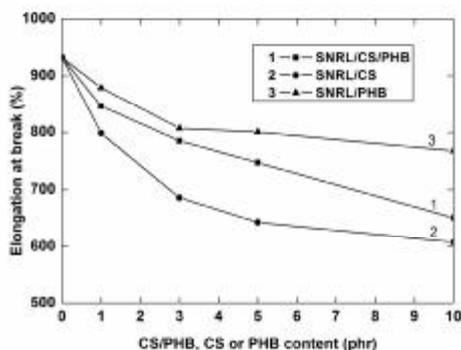


Figure 2. Elongation at break of blend films

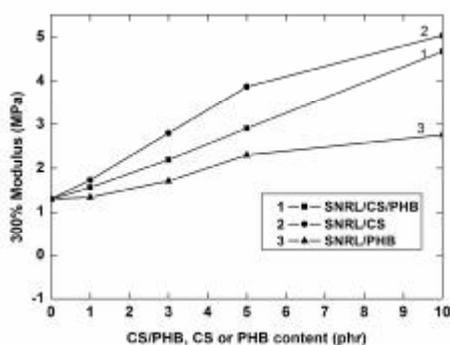


Figure 3. 300% Modulus of blend films

Fig. 3 shows that the 300% modulus of the SNRL/CS/PHB, SNRL/CS and SNRL/PHB films increased with increase in CS/PHB, CS or PHB content, respectively, and the SNRL/CS films showed the highest degree of increasing, followed by the SNRL/CS/PHB films, then by the SNRL/PHB films. The increase in 300% modulus could be the result of increase in elastic modulus

and crystallinity by the addition of CS/PHB, CS or PHB, respectively; and a higher 300% modulus for SNRL/CS than that for SNRL/PHB could be due to a higher elastic modulus of CS than that of PHB.

B. Tear Strength of SNRL/CS/PHB, SNRL/CS and SNRL/PHB films

The tear strength of SNRL/CS/PHB, SNRL/CS and SNRL/PHB films is shown in Fig.4. It can be seen from Fig. 4 that, the tear strength increased rapidly when their content was lower than 5.0 phr, then smoothly with increase in CS/PHB, CS or PHB content, respectively, and the SNRL/PHB films showed the highest degree of increasing, followed by the SNRL/CS/PHB films, then by the SNRL/CS films. This could be also caused by the increase in elastic modulus and crystallinity by the incorporation of CS/PHB, CS or PHB, respectively.

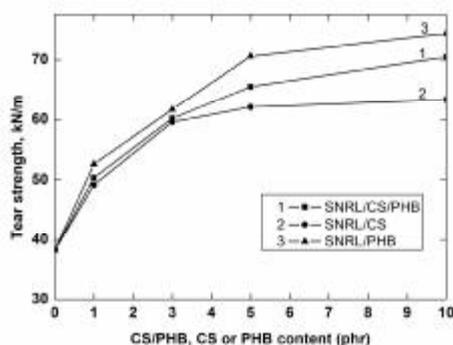


Figure 4. Tear strength of blend films

C. Hardness of SNRL/CS/PHB, SNRL/CS and SNRL/PHB films

Fig. 5 demonstrates that, the Shore A hardness of SNRL/CS/PHB, SNRL/CS and SNRL/PHB films increased with increase in CS/PHB, CS or PHB content, respectively. It can also be seen from Fig. 5 that, the hardness of the SNRL/CS films showed the highest degree of increasing, followed by the SNRL/CS/PHB films, then by the SNRL/PHB films. This is correlated with the change in modulus as mentioned-above.

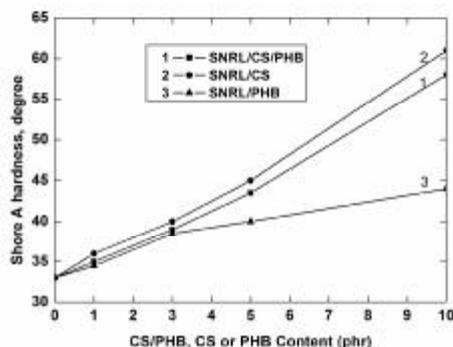


Figure 5. Shore A hardness of blend films

IV. CONCLUSIONS

Homogenous blends of SNRL/CS/PHB, SNRL/CS and SNRL/PHB were prepared by incorporation of the water dispersion of CS/PHB, CS or PHB into the SNRL, respectively. The tensile strength of the blend films first increased with increase in CS/PHB, CS or PHB up to 1.0 phr then decreased, the elongation at break decreased, the 300% modulus, tear strength and Shore A hardness increased, with increase in CS/PHB, CS or PHB content, whereas most of the tensile strength and elasticity of the films can be retained when the CS/PHB, CS or PHB content were less than 5.0 phr; and it seems that the each value of property for SNRL/CS/PHB film was between those for SNRL/CS and SNRL/PHB films, except for the tensile strength film when the CS/PHB content was low.

ACKNOWLEDGMENT

The research work was supported by the Natural Science Foundation of Hainan Province, P.R. China (with Contract Grant Number 513150).

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