

BAGASSE FIBER-CHLOROACETATED NATURAL RUBBER COMPOSITES: ESTERIFICATION CROSSLINKING

Ploenpit Boochathum*, Kanjanabha Sratongmao, Anusara Hirsansri

Chemistry Department, Faculty of Science,

King Mongkut's University of Technology Thonburi

Contact E-mail ploenpit.boo@kmutt.ac.th

ABSTRACT

In this work, the fiber-rubber composites were prepared by adding the bagasse fiber with different loading of 1 % w/w and 3 % w/w into the functionalized natural rubber latex. Bagasse fiber was extracted from ground sugarcane bagasse agricultural waste with 0.5 cm in length by using alkaline solution of 0.5M NaOH. The natural rubber molecules were chemically modified to add the chloroacetate groups by reacting chloroacetic acid with the epoxy group in the epoxidized natural rubber latex that was prepared by adding performic acid at the reaction temperature of 40°C. The main aim is to improve the performance of the natural rubber by the expected bonding and the molecular interaction with bagasse fiber. The occurring of the ester bonds and the hydrogen bonds between chloroacetate groups present on the rubber molecules and hydroxyl groups of the celluloses of the bagasse fibers was confirmed by FTIR measurements. These bonds between chloroacetated natural rubber (CNR) molecules and the bagasse fibers formed networking in the composites. This esterification crosslinking resulted in the enhanced rigidity of the rubber molecules. Furthermore, the rigidity of rubber molecules in the composites was found to remarkably increase respectively to the bagasse fiber loading. DSC measurement showed the increase of the glass transition temperature of rubber from -37.64°C for CNR to -26.76°C for 1% w/w bagasse-CNR composite and -12.53°C for 3% w/w bagasse-CNR composite. On the other hand, the elastic property of rubber was also found to be enhanced from the result of the storage modulus of the composites measured using Rubber Process Analyzer (RPA). The storage modulus of the bagasse-CNR composites considerably increased with the bagasse fiber loading too. As a result, the addition of the chloroacetate groups on the natural rubber molecules could induce the chemical bonds with the bagasse fibers resulting in the better performance of rubber.

1. INTRODUCTION

It is well known that one of the main sources of air pollution in many countries comes from the burning large quantities of natural fibers such as rice straw, bagasse and wood flour. Recently, the interest in composite polymers that were reinforced with natural fibers has increased such as bagasse fiber-polypropylene composites (Vazquez & Dominguez, 1999 and Cerqueira, et al., 2011). The composites of natural rubber and natural fibers including bamboo fiber (Ismail, et al., 2002), cotton (Chuayjuljit, et al., 2008) and jute fiber (Pantamanatsopa, et al., 2014) were studied to aim the enhancement of natural rubber mechanical properties as well as the reduction of the environmental pollution. The potential of bagasse as filler in natural rubber products has been considerably investigated. It was found that the tensile strength and abrasion resistance of the natural rubber product increased with the carbonized bagasse loading (Osarenmwinda & Abode, 2010). Biodegradable nanocomposites were prepared by casting a mixture of natural rubber latex and bagasse fiber that was isolated from sugar cane bagasse by the acid hydrolysis reaction using sulfuric acid (Bras, et al., 2010). It was claimed that the incorporation of bagasse cellulose into natural rubber resulted in the enhanced thermomechanical properties as well as biodegradability of the rubber product. However, bagasse fiber loading decreased the resistance to water vapor permeation of the bagasse fiber-rubber composite due to the hydrophilic property of bagasse.

This work aims to prepare the composite based on the addition of the bagasse fiber into the chemically modified natural rubber. Addition of the chloroacetate functional group on the rubber molecules (CNR) is believed to enhance the rubber properties due to the crosslinks and/or interfacial interaction between the hydroxyl group of bagasse fiber and the chloroacetate group of rubber molecules. The molecular structural analysis of the

composites was investigated by using FTIR measurement. The rigidity of the rubber molecules due to the bonding as well as the bagasse fiber-CNR interaction was studied through the glass transition temperature and storage modulus of the composites with variable bagasse fiber loading.

2. EXPERIMENT

2.1 Experimental Apparatus

Optical microscopy, SZX 9 Olympus

Fourier Transform Infrared Spectrophotometer (FTIR), Nicolet 6700.

Rubber Process Analyzer (RPA 2000), Alpha Technology.

2.2 Extraction of sugarcane bagasse

20 g of ground sugarcane bagasse about 0.5 cm in length was added with 400 mL of 0.5 M NaOH solution and continuously stirred at 60-70°C by using bath shaker for 8 hr. Sugarcane bagasse was washed till the pH of washing water is 7 and then dried at 60°C for 16 hr.



Fig. 1 Bagasse (a) before extraction and (b) after extraction.

2.3 Chemical modification of natural rubber

High concentrated natural rubber latex with 60 % DRC (dry rubber content) (NR), 100g, was initially stabilized by adding triton-x (14 % w/v, 75 mL) and then added with the mixture of formic (98 % v/v) acid and hydrogen peroxide (35 % w/w). The mole ratio of NR:H₂O₂:HCOOH was 1:0.5:0.5. Epoxidation reaction was carried out at 40°C for 3 hr, subsequently, cooled down to room temperature. The chloroacetic acid solution (100 % w/v), 12 % mol based on dry rubber content of NR, was added in the epoxidized NR latex and then the mixture was continuously stirred for 1 hr. The chloroacetated natural rubber (CNR) latex was obtained.

2.4 Preparation of bagasse-CNR composites

Two bagasse-CNR composites were prepared by mixing the extracted bagasse in CNR latex using the weight loading of 1 % w/w and 3% w/w based on dry rubber content at room temperature and the mixtures were continuously stirred for 1 hr and then let stand still for 48 hr until the composites coagulated and then separated from water. The bagasse-CNR composites obtained were washed with a plenty of water till the pH of washing water is 7 and then dried at 60°C by using vacuum oven.



Fig. 2 (a) 1 % w/w sugarcane bagasse-CNR composite and (b) 3 % w/w bagasse-CNR composite.

2.5 Study of interface interaction between bagasse and CNR

Molecular structure analyses of CNR and bagasse-CNR composites added with bagasse 1 % w/w and 3 % w/w were carried out using FTIR spectroscopy, Nicolet 6700, scanning from 4,000 cm⁻¹ to 500 cm⁻¹ with a resolution of 4 cm⁻¹.

Glass transition temperatures (T_g) of CNR and bagasse-CNR composites were determined by using Differential Scanning Calorimetry (DSC), Mettler Toledo DSC1. The measurements were done under the condition of the heating rate of 10°C/min scanning from -100°C to 25°C.

The Storage modulus (G') of bagasse-CNR composites was determined for comparison with that of CNR by using Rubber Process Analyzer (RPA 2000). The measurement condition was carried out at the temperature of 50°C, frequency of 0.1 Hz and variable %strain from 0.28 % to 999.94 % regarding to the testing method of ASTM D5289.

3. Results and Discussion

Purified bagasse cellulose

As know, sugarcane bagasse is the major by-product of the sugar cane industry. It composed of 45.5 % alphacellulose, 27 % hemicellulose, 21.1 % lignin and 6.9 % others. The extraction was performed to remove lignin and others. The purified cellulose after extraction that was believed to compose of the only remaining alphacellulose and hemicellulose is as shown in Fig 3. (b) in comparison with the cellulose before extraction as shown in Fig 3(a).



Fig. 3 Pictures x 200 taken by optical microscopy SZX 9 Olympus of (a) bagasse before extraction (b) bagasse after extraction.

It can be seen that cellulose fiber of bagasse after extraction is finer than those before extraction.

Bagasse-CNR composites

The bagasse-CNR composites prepared was aimed to produce the green composites from the renewable resources such as para rubber and bagasse. The addition of the bagasse in NR with the expectation that bagasse which is polar cellulose could be able to enhance the reinforcement to the NR when the chloroacetate group is added on NR molecules, i.e. CNR. Fig. 4 shows the pictures of bagasse-CNR composites added with bagasse of (a) 1 % w/w and (b) 3 % w/w as taken by the optical microscopy with 200 times enlargement. Almost all bagasse loading of 1 % w/w was found to incorporate in to CNR which was different from 3% w/w. From the picture, the excess of bagasse was obvious for the bagasse-CNR composite 3 % w/w.

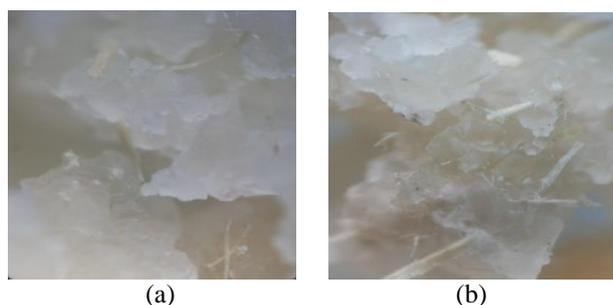


Fig. 4 Bagasse-CNR composites with loading of (a) 1 % w/w and (b) 3 % w/w (x 200 optical Microscopy)

In these composites, the reinforcement is believed to be resulted from both interfacial interaction and chemical bonding. The FTIR spectra of bagasse-CNR composites with loading of 1 % w/w and 3 % w/w and CNR are as shown in Fig. 5.

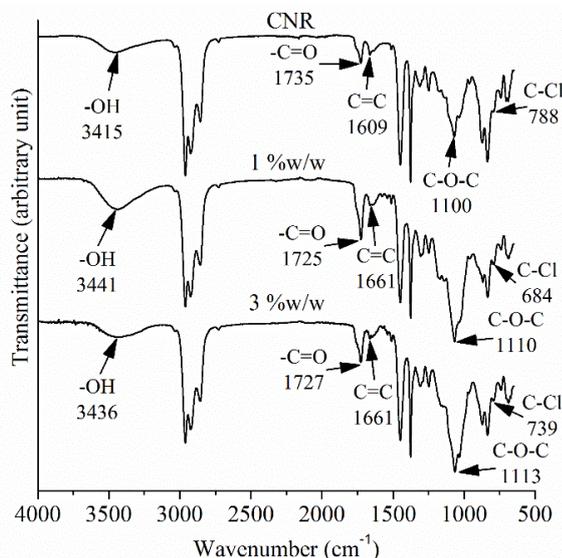


Fig. 5 FTIR spectra of CNR and bagasse-CNR composites.

From Fig. 5, the drastic increase of the intensity of $-C-O-C-$ and $-OH$ peaks of the composites showed the occurrence of the bagasse incorporation in to rubber matrix. The facial interaction between bagasse cellulose and CNR molecule is assumed to be due to the hydrogen

bond between $-C=O$ of acetated group added on the rubber molecules and hydrogen atom of $-OH$ present on the bagasse cellulose. This is confirmed by the shift of the FTIR peak of $-C=O$ from 1735 cm^{-1} to 1725 cm^{-1} and 1727 cm^{-1} for bagasse-CNR composites 1 % w/w and 3 % w/w, respectively. Moreover the chemical bond of $-C-O-C-$ formed between bagasse cellulose and CNR molecule in the composites was obvious at 1110 cm^{-1} and 1113 cm^{-1} for 1 % w/w and 3 % w/w, respectively.

As a result, the bagasse cellulose is clarified to be as a binder that is able to crosslink the rubber molecules. The schematics of the proposed (a) interfacial interaction and (b) chemical bond are as shown in Fig. 6.

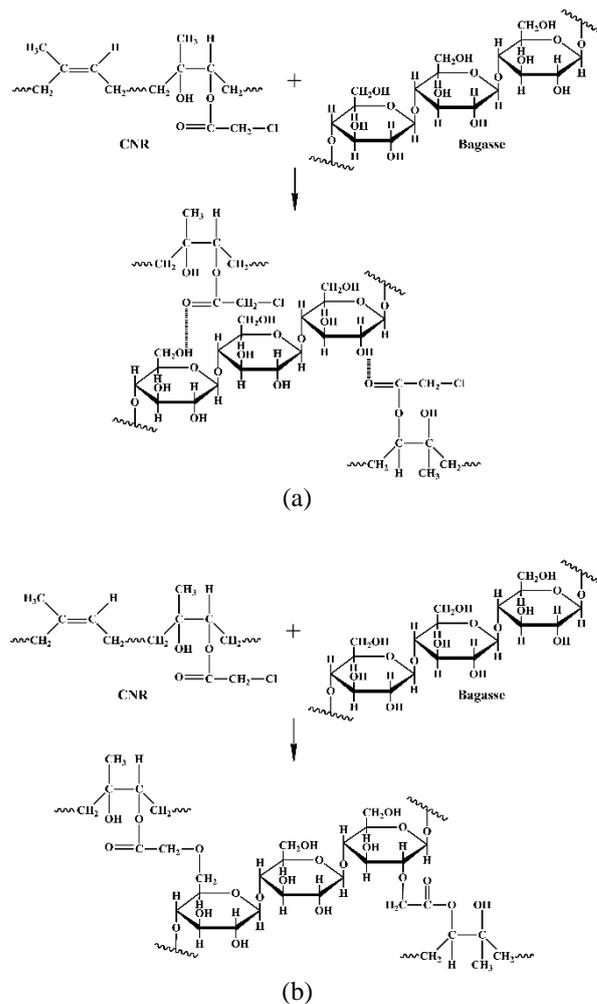


Fig. 6 Schematics of (a) interfacial interaction and (b) chemical bond between rubber molecule and bagasse fiber

The occurrence of both interfacial interaction and ester bond between the bagasse fiber and CNR molecule was believed to increase the rigidity of rubber molecules as well as result in the enhancement of the rubber properties. The rigidity of rubber molecules was confirmed by the drastic increase of T_g of the bagasse-CNR composites from -37.64°C (CNR) to -26.76°C (1 % w/w) and -12.53°C (3 % w/w). DSC thermograms of CNR and its composites are as shown in Fig 7.

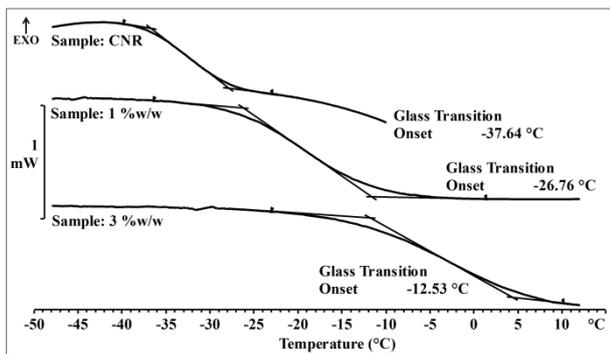


Fig. 7 DSC thermograms showing T_g of CNR and bagasse-CNR composites.

Moreover, the storage modulus (G') was investigated for the study on the difference of the molecular rigidity of the CNR molecules when the bagasse was added. It was remarkable that 3 %w/w bagasse-CNR composite gave much higher G' than 1 %w/w and CNR, respectively, as shown in Fig. 8. It clarified that the higher loading of bagasse, the increase of the rigidity of rubber molecules is obvious. This is due to the increase of the hydrogen bond and the ester bond as described above. This result of storage modulus is in agreement with the result from T_g measured by DSC.

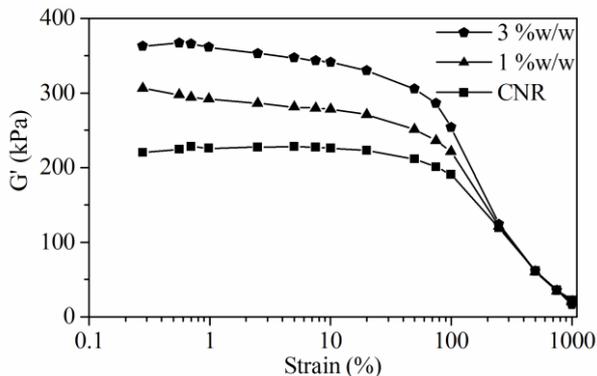


Fig. 8 Storage modulus of CNR, 1 %w/w bagasse-CNR composite and 3 %w/w bagasse-CNR composite

CONCLUSION

The addition of the chloroacetate functional group on the natural rubber molecules results in the occurrence of the interfacial interaction and ester bond between bagasse fiber and rubber molecules. The bonding causes more rigidity of rubber molecules that remarkably increases with bagasse loading as confirmed by the increase of T_g and G' . The mechanical property of his bagasse-CNR composites that is a new green polymer is believed to be considerably improved.

REFERENCES

Cerqueira, E.F., Baptista, C.A.R.P., and Mulinari, D.R., Mechanical Behaviour of Polypropylene Reinforced Sugarcane Bagasse Fibers Composites, *Procedia Eng.*, vol. 10, pp. 2046-2051, 2011.

Chuayjuljit, S., Su-Uthai, S., Tunwattanaseree, C., and Charuchinda, S., Preparation of Microcrystalline Cellulose from Waste-Cotton Fabric for Biodegradability Enhancement of Natural Rubber Sheets, *J. Reinf. Plast. Comp.*, vol. 28, no. 10, pp. 1245-1254, 2009.

Ismail, H., Edyham, M.R., and Wirjosejono, B., Bamboo fibre filled natural rubber composites the effects of filler loading and bonding agent, *Polym. Test.*, vol. 21, pp. 139-144, 2002.

Osarenmwinda, J.O., Mohammad, and Abode, S.I., Potential of Carbonized Bagasse Filler in Rubber Products, *J. Emerg. Trends Eng. Appl. Sci.*, vol. 1, no. 2, pp. 157-160, 2010.

Bras, J., Hassan, M.L., Bruzesse, C., Hassan, E.A., Elwakil, N.A., and Dufresne, A., Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites, *Ind. Crop Prod.*, vol. 32, pp. 627- 633, 2010.

Pantamanatsopa, P., Ariyawiriyanan, W., Meekeaw, T., Suthamyong, R., Arrub, K., and Hamada, H., Effect of Modified Jute Fiber on Mechanical Properties of Green Rubber Composites, *Energy Procedia*, vol. 56, pp. 641-647, 2014.

Vázquez, A., Domínguez, V.A., and Kenny, J.M., Bagasse Fiber-Polypropylene Based Composites, *J. Therm. Comp. Mat.*, vol. 12, no. 6, pp. 477-497, 1999.

NOMENCLATURE



Ploenpit Boochathum received the B.Sc. (1982), M.Sc. (1985), and D.Eng. (1993) degrees in Polymer from Tokyo University of Agriculture and Technology.

She is an Associate Professor, Department of Chemistry, King Mongkut's University of Technology Thonburi. Her Current interests include nanopolymer composites, chemical modification of natural rubber and its application.



Kanjanabha Sratongmao received the B.Sc. (2015)



Anusara Hiransri received the B.Sc (2015)