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Cure and mechanical properties of natural rubber filled bacterial cellulose

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Abstract. Natural rubber (NR) containing the *nata de coco* fiber or Bacterial cellulose (BC) was prepared by co-coagulation of BC and concentrated NR latex with $CaCl_2$ and compounded by two roll mill. The effect of BC content was the important factor in this study. It was that found tensile strength and elongation at break of NR filled BC (NR/BC) decreased with increasing BC content. The addition of BC into NR affect Mooney viscosity of NR/BC masterbatch, with increasing BC content, scorch time and cure time of their compound decreased.

Introduction

Rubbers can't be used in pure form due to their low mechanical properties. Therefore, additives such as vulcanizing agent and filler are generally used in rubber compounds in order to improve the mechanical properties of rubber. The filler used in rubber compounds such as carbon black and silica are characterized by their reinforcing properties, depending on surface activity (filler surface chemistry) and size of the fillers (or specific surface area). However, carbon black is relatively expensive owing to its dependence on petroleum, while silica are quite difficult to be disperse in rubber matrix due to the polar silica surface, which results in a low interfacial compatibility with hydrophobic rubber matrix. Nowadays, recent researches point out the potential-value in using natural cellulose fibers as reinforcing filler in rubbers such as jute, pineapple, coir, sisal, rubber wood, coconut, oil palm and bamboo. The advantages of natural fibers compared with other filler are renewable nature, low cost, low density, ease of chemical modification and biodegradability.

Bacterial cellulose fiber (BC) is cellulose produced by bacteria of genus *Acetobacter*. It has molecular structure like plant cellulose but posse an ultrafine nanofiber network [1]. BC has many excellent properties such as high crystallinity, high tensile strength and biodegradability [8]. It was already introduced in various polymer systems and proved to be an effective reinforcement in many polymers. In this work, the using of BC as filler in natural rubber (NR) was investigated. The objective of this work was to study the cure and mechanical properties of NR filled BC with various amounts of BC. Their cure and mechanical properties were characterized by Oscillating Disk Rheometer (ODR) and mechanical tests.

Materials and Experiment

Materials

The high ammonia NR latex containing ca. 60% DRC was obtained from Muang Mai Gutherie Co., Ltd (Surachthani; Thailand). Bacterial cellulose fiber (BC) was obtained from Cocojelly shop (Kanchanaburi; Thailand). Calcium chloride ($CaCl_2$) was obtained from Photo Chemicals Co., Ltd (Thailand). Sulphur and Wing stay L (3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionate) were obtained Siam Chemicals Co., Ltd (Samutprakarn; Thailand). N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) and Zinc oxide (ZnO) were obtained from Global Chemical Co., Ltd (Thailand). Oleic acid was received from Fischer Scientific (Leicestershire, UK). Stearic acid was purchased from Imperial Chemical Co., Ltd (Thailand).

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NR filled BC masterbatch and compounding

Bacterial cellulose fiber (BC) was crushed by electrical crusher. Different amounts of BC (10, 15, 20 and 25 phr) were dispersed to the high ammonia NR latex while stirring for 30 min at room temperature, in order to obtain the mixtures (dry weight BC in relation to the 100 part per hundred of rubber). The homogeneously mixtures were coagulated by 2 wt% $CaCl_2$ solution. The coagulum was thoroughly washed with water and then dried in an oven at 60 ◦C until the weight of that constant. The NR filled BC masterbatchs (NR/BC masterbatch) were masticated on a two-roll mill for 3 min. The Mooney viscosity of that determined by using EKTRON Mooney Viscometer at 100°C. The testing procedure was conducted according to the method described in ASTM D 1646.

The masticated NR/BC masterbatchs were compounding on two-roll mill, which using friction ratio of 1:1.21. The additives such as ZnO, stearic acid, CBS, anti-oxidant agent as wing stay L and finally agent as sulphur were used and added while mixing. The standard recipe used for compounding is shown in Table 1. The rubber compound sheets were kept in a closed container at room temperature for 24 h before determined vulcanizing characteristics. The maximum torque, minimum torque, scorch time (ts_2) and cure time (tc_{90}) were also determined by EKTRON Oscillating Disk Rheometer (ODR) as described in ASTM 2084.

The tensile properties of vulcanized rubber were measured by using Hounsfield Tester machine, model H 10KS followed ASTM D412-2005 with cross-head speed of 500 ± 50 mm/min.

The morphology of tensile fracture surface of vulcanized rubber obtained from the tensile properties test was investigated using a JEOL model JSM-6400 scanning electron microscopy at 15 kV. The specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was coated with gold.

Table 1. The standard recipe used for compounding

Ingredients	Content (phr)
NR	100.0
ZnO	5.0
Stearic acid	2.0
Wingstay L	2.0
Aromatic oil	5.0
CBS	1.5
Sulphur	1.5
BC	10.0 - 25.0

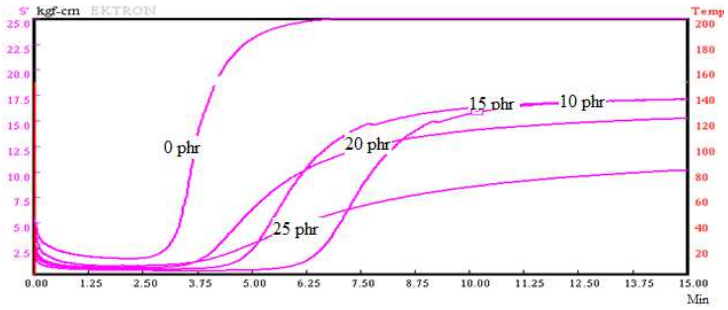


Fig. 1. Vulcanized curve of NR/BC compound

Results and discussion

The effect of BC loading on Mooney viscosity and vulcanization properties

The test temperature of Mooney viscosity of rubber compound was set at 100°C. Table 2 shows the effect of BC loading on Mooney viscosity of BC masterbatch of natural rubber measured with EKTRON Mooney Viscometer. The addition of BC increased Mooney viscosity of BC masterbatch of natural rubber due to the presence of filler in rubber matrix that can reduced the mobility of rubber chains. But the increasing of BC loading tented to decrease the Mooney viscosity of NR[4]. The reducing of Mooney viscosity of NR causes the incompatible and agglomeration of filler particles.

The influence of the BC loading on the vulcanization properties of NR/BC compounds was investigated. The results of the maximum torque (MH), minimum torque (ML), torque difference (ΔM), scorch time (ts_2) and cure time (tc_{90}) are shown in Table 2 and Fig 1. The addition of BC caused a decrease in ML value of NR compound due to the longer time of mastication and mixing step because NR/BC masterbatch at 10 and 15 phr has higher Mooney viscosity than neat NR. The

shearing force that applied to the rubber and additives during the compounding process results in a decrease in molecules weight and viscosity of rubber compound. The ML value of NR/BC compound was increased with increasing the BC contents. This result can be explained by the high compatibility between BC and NR molecules which affects to difficult mobility of rubber molecules. The cause of this opposite result of Mooney viscosity of NR/BC masterbatch and ML value of NR/BC compound arising from the ingredient of this research formula such as aromatic oil plasticizer which can improve compatibility of filler in rubber matrix.

Table 2. Effect of BC content on the Mooney viscosity and vulcanization properties of NR

	BC Content (phr)	Mooney Viscosity (ML 1+4 100 ◦C)	ML (dN.m)	MH (dN.m)	ΔM (dN.m)	Ts_2 (min)	TC_{90} (min)
Gum	-	81.02±1.50	1.44±0.51	25.33±1.98	23.89±2.98	3.44±0.56	4.58±1.09
NR/BC	10	94.03±2.84	0.57±0.13	17.70±2.87	17.13±1.34	4.06±0.34	6.02±1.89
	15	85.94±3.54	1.24±0.23	18.18±3.02	16.94±2.22	3.29±0.78	5.39±0.87
	20	55.03±1.44	1.64±0.34	16.18±1.55	14.54±3.98	2.57±1.00	5.35±0.67
	25	37.14±1.32	2.79±0.11	13.79±2.21	11.00±1.00	2.58±0.89	5.49±0.56

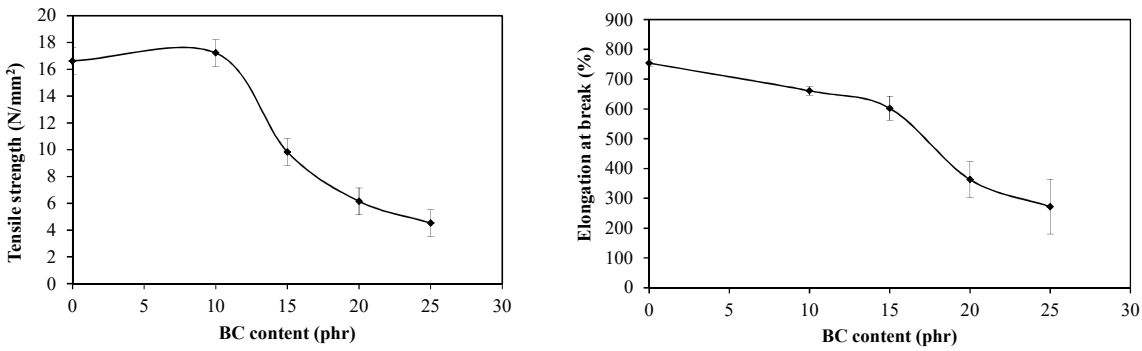
The scorch time (ts_2) value of NR/BC compound, which is measured of premature vulcanization of rubber compound are shown in Table 2. It indicate that the addition of BC will reduce ts_2 value because the increase of filler loading is associated with the increase of viscosity and mixing temperature. The addition of BC in NR compound was little increased in tc_{90} value of compound due to the interaction between BC functional group (-OH), moisture or activity surface of filler with the compounding additive [2-3]. H. Ismail et al. [4] reported that the cure enhancement was possibly attributed to the formation of bond due to interaction between –OH in chitosan and the compounding additives. However, the increasing of BC contents has not significantly affected value of TC_{90}.

The effect of BC loading on mechanical properties of vulcanizates

The influence of BC content on the mechanical properties of vulcanized natural rubber was investigated. The results of the Tensile strength of vulcanized natural rubber are shown in Fig 2(a). The tensile strength of vulcanized natural rubber filled BC (NR/BC) exhibited maximum value at 10 phr of BC content and the further addition of BC in vulcanized natural rubber tented to decrease the tensile strength of NR/BC. From Fig 2 (b), the elongations at break of NR/BC was decreased with increasing the BC content [4].

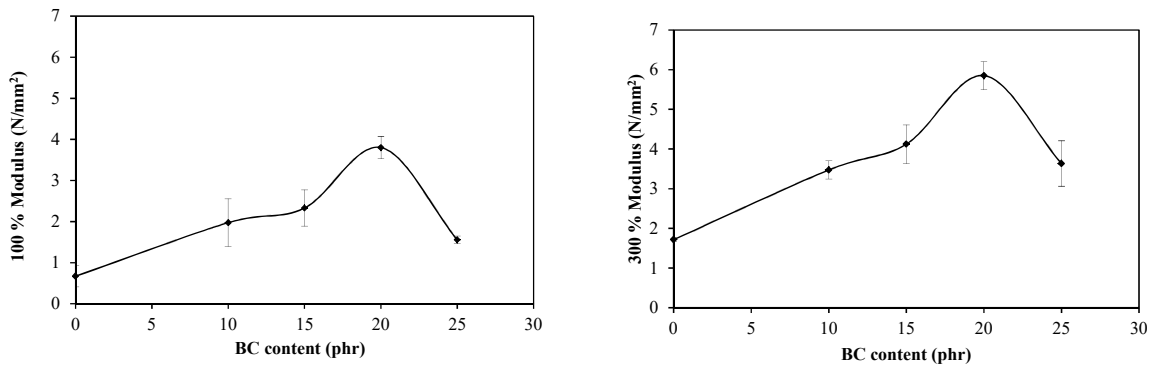
The tensile modulus at 100% and 300% of NR/BC showed in Fig 3. The tensile modulus of NR/BC increased with increasing BC content and reached to maximum value at 20 phr. While the tensile modulus of the vulcanized natural rubber was decreased when 25 phr of BC content was added. This could be explained that the better rubber-filler interaction resulted in higher crosslink density of the vulcanizated. Kuno and Ismail et. al [5] reported a similar observation, the tensile modulus 100% and 300% value decreased with decreasing crosslink density. This can be seen in Table 2 for MH and ΔM value.

The SEM micrographs of Vulcanized NR and NR/BC filled with 10 phr of BC content shown in Fig (a) and (b) respectively. Large agglomerates of BC paricles dispersed in the rubber matrix showed in Fig 4(b) whereas Fig 4(a) shows much more uniform distribution of other additive in the rubber matrix.



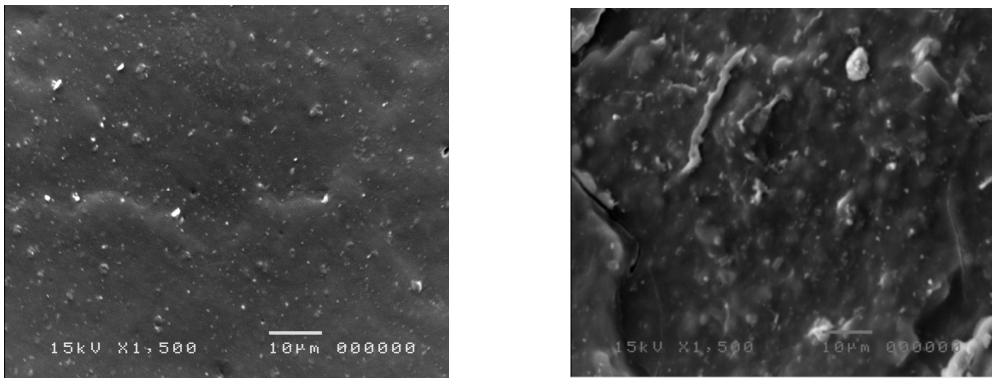
(a) (b)

Fig. 2. Effect of BC content on (a) tensile strength and (b) elongation at break of vulcanizates



(a) (b)

Fig. 3. Effect of BC content on (a) 100 % modulus and (b) 300 % modulus



(a) (b)

Fig. 4. SEM micrographs of the failure surface of (a) vulcanized NR and (b) NR/BC at 10 phr of BC content

Conclusion

Natural rubber containing Becteral cellulose (BC) was compounded on a two roll mill. The effect of BC content was the important factor in this study. It was found that tensile strength and elongation at break decreased with increasing BC content.

References

[1] S. Chen, Y. Zou, Z. Yan, W. Shen, S. Shi, X. Zhang and H. Wang. J Hazaedous Mater. 161 (2009) p.1355.

[2] P. Sae-oui, C. Sirisinha, K. Hatthapanit and U. Thepsuwan. Polym Test. 24 (2005) p.439.

[3] H. Ismail, H.D. Rozman, R. M. Jaffri and Z.A. Mohd Ishak. Eur Polym. J. 33 (10-12) (1997) p. 1627.

[4] H. Ismail, S. M. Shaari and N. Othman. Polym Test. 30 (2011) p.784.

[5] K. A. J. Dijkhuis, J. W. M. Noordermeer and W. K. Dierkes. Eur Polym J. 45 (2009) p. 3302.