XXXX-XXX

Curing characteristics and mechanical properties of nanocomposites based on acrylonitrile-butadiene rubber/natural rubber blends: Effect of cellulose nanocrystal loading

Punyarat Jantachum[1,2], Bualan Khumpaitool[1,2] and Songkot Utara[1,2*]

[1] Functional Materials and Composites Research Group, Faculty of Science, Udon Thani Rajabhat University, Udon Thani 41000, Thailand

[2] Division of Chemistry, Faculty of Science, Udon Thani Rajabhat University, Udon Thani 41000, Thailand

*E-Mail: songkot@udru.ac.th; songkot_u@hotmail.com

Abstract

This study examined the effect of cellulose nanocrystal (CNC) loading on curing characteristics and mechanical properties of acrylonitrile-butadiene rubber (NBR)/natural rubber (NR) nanocomposites. The blend ratio of NBR and NR was kept constant at 50/50, excluding the raw NBR (NBR100). Four distinct samples with different CNC loadings, in parts per hundred rubber (phr), including NBR-C0 (0 phr), NBR-C1 (1 phr), NBRC-3 (3 phr), and NBRC-5 (5 phr), were prepared using an internal mixer at 70 ℃ and a rotor speed of 15 rpm. The cure characteristics of the nanocomposites were studied using a moving die rheometer (MDR), while the mechanical properties of the vulcanizates were measured in accordance with ASTM standards. The results showed that scorch time, cure time and delta torque of rubber composites tended to increase with the CNC content, while NBR100 showed higher delta torque than those properties. Moreover, hardness, as well as the 100% and 300% modulus of rubber vulcanizates slightly increased with the CNC content. Furthermore, a NBR50-C1 composite containing CNCs at 1 phr showed an optimal value for tensile strength.

Keywords: Cellulose nanocrystals, nitrile rubber, natural rubber, nanocomposites, curing characteristics

1. Introduction

Polymer nanocomposites (PNCs) are well-known advanced engineering materials that currently receive wide interest among researchers. PNCs are based on the idea of developing a very large interface between nanoscale heterogeneities (inorganic materials) and neat polymer macromolecules (organic polymers) [1]. Therefore, they combine the benefits of inorganic materials (such as rigidity and thermal stability) with those of organic polymers (*e.g.*, flexibility, dielectric performance, ductility, and processability) [2]. PNCs' unique properties allow them to be used in a wide range of technologies, including advanced materials and goods, medicines, energy devices, and sensors [3].

It is usually accepted that the objective of elastomer blending is to produce the greatest number of suitable combinations, physical properties, and processability at an optimal cost. Natural rubber (NR) provides a number of advantages, including superior tensile and tear strengths as well as dynamic qualities. However, NR has low resistance to deterioration caused by solvents, oils, and ozone [4]. To overcome these limitations, NR is frequently blended with other elastomers that are more resistant to solvents, oils, and ozone. Acrylonitrile-butadiene rubber (NBR) is an oil-resistant rubber that has been applied in a wide range of applications as a stand-alone rubber or in combination with other rubbers [5]. Therefore, a combination of NR with NBR is designed to produce a vulcanizate with the best properties of each component [6].

In this work, cellulose nanocrystals (CNCs) are selected and used to improve the mechanical properties of NBR/NR blends. CNCs are used to create new nanoscale materials and this approach is becoming increasingly

popular. They are obtained from plants and are produced through an acid hydrolysis of cellulose [7]. During this process, disordered domains are eliminated from cellulose fibers. The final product consists of highly crystalline nanorods [8]. Moreover, CNCs have a high tensile strength (7500 MPa) and Young's modulus (100–140 GPa), suggesting that they have much potential as an ecofriendly filler for polymer reinforcement [9]. As a result, many researchers found that embedding CNCs in polymer matrices produces polymer-based nanocomposite materials with improved mechanical and barrier properties in comparison to neat polymers or traditional composites [4, 7, 10]. To the best of our knowledge, little research has been reported on the effect of cellulose nanocrystal loading on the curing characteristics and mechanical properties of NBR/NR blends. The aim of this study is to explore the effect of CNC content on the curing characteristics and mechanical properties of NBR/NR nanocomposites. Furthermore, scanning electron microscopy (SEM) was used to examine the morphology of the nanocomposites.

2. Materials and methods

2.1 Materials

Cellulose nanocrystals (CNCs) (diameter < 20 nm and length ~ 100-300 nm) were extracted from *Luffa cylindrica (L.) Rox*. in our laboratory, using the same conditions reported in the doctoral thesis of Punyarat Jantachum [11]. Acrylonitrile-butadiene rubber (NBR), natural rubber latex (NR) and curing agents including zinc oxide (ZnO), stearic acid, N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and sulfur were purchased from GSP Products Co., Ltd. (Bangkok, Thailand).

2.2 Preparation of NR/CNC masterbatches

CNCs at 1, 3 and 5 parts per hundred rubber (phr) were added to NR latex. The ratio of fiber to distilled water was 1:30 (g/mL). The pre-dispersed CNCs were stirred at room temperature for 15 min. Then, the mixture was sonicated at 20 kHz in an ultrasonic bath at 30 ºC for 30 min. After that, pre-dispersed CNCs were added into the NR latex and stirred at room temperature for 30 min. The mixture was poured onto a glass plate and dried at room temperature. Then, the NR/CNC masterbatch was dried at 80 ºC for 3 h.

2.3 Preparation of CNC filled NBR/NR compounds

Formulations of CNC filled NBR/NR compounds are shown in **Table 1**. The NBR/NR ratio was fixed at 50/50 phr and the amounts of CNCs were varied from 0 to 5 phr. The amounts of other rubber chemicals were identical for all formulations. The rubber compounds were mixed in an internal mixer at 70 ºC and a rotor speed of 15 rpm. The mixing time of all rubber compounds was kept constant at 12 min, as shown in **Table 2.**

Table 1. Formulations of rubber compounds

Ingredients	Amount (phr)				
	NBR100	NBR50-C0	NBR50-C1	NBR50-C3	NBR50-C5
NBR/NR	100/0	50/50	50/50	50/50	50/50
CNCs	0	0	1	3	5
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
CBS	1	1	1	1	1
Sulfur	2	2	2	2	2

Table 2. Mixing procedure of rubber compounds

Steps	Ingredients	Time (min)
1	NBR + NR/CNCs masterbatch	0-5
2	ZnO + Stearic acid	5-7
3	CBS + Sulfur	7-12

2.4 Preparation of CNC filled NBR/NR vulcanizates

The specimens were shaped at 160 ºC *via* compression molding. Cure characteristics of rubber compounds were determined using a moving die rheometer (MonTech/MDR-3000). The maximum torque (M_H), minimum torque (M_L), scorch time (t_{s2}) and cure time (t_{c90}) were determined from the cure curve.

2.5 Testing of CNC filled NBR/NR vulcanizates

XXXX-XXX

Tensile properties were measured using an Instron universal tester (Instron/3366) with a crosshead speed of 500 mm/min, in accordance with ASTM D412. The results of tensile property testing were revealed in terms of the 100% and 300% modulus, %elongation at break and tensile strength.

Morphology of rubber vulcanizates was examined using scanning electron microscopy (Hitachi-SEM-SU3800). Fractured surfaces were prepared by cutting a rubber sheet. Then, each rubber piece was immersed in liquid nitrogen. The fracture surfaces of the vulcanizates were coated with Au and microscopically examined at an accelerating voltage of 5 kV.

3. Results and discussions

Cure characteristics of CNC filled NBR/NR composites are shown in **Table 3**. It was found that the scorch and cure times of NBR/NR blends filled with CNCs tend to increase with increasing CNC content. These results indicate that the adsorption of accelerators on CNC surfaces increased with the CNC content, resulting in a slowing of the vulcanization process [12]. NBR100 had higher scorch and cure times than NBR/NR blends filled with CNCs. This may have been due to the degree of unsaturation of NBR, which is less than NR [13, 14]. Moreover, delta torque values of the NBR/NR blends filled with CNCs were lower than that of NBR100. A possible explanation for this is that the addition of NR into NBR can reduce the viscosity of rubber compounds. Furthermore, the delta torque values of NBR/NR blends tended to increase with the CNC content, indicating increased stiffness of the vulcanized compounds. This may have been due to CNC restricting the mobility of the rubber molecules.

Table 3. Cure characteristics of CNC filled NBR/NR compounds

Property	NBR 100	NBR50 -C0	NBR50 -C1	NBR50 -C3	NBR50 -C5
M_H (dN.m)	10.98	8.78	8.89	8.54	9.47
M_L (dN.m)	0.49	0.63	0.75	0.65	0.74
M_H-M_L (dN.m)	10.49	8.15	8.14	7.89	8.73
t_{s2} (min)	2.97	1.83	2.16	2.09	2.31
t_{c90} (min)	22.47	5.38	6.05	5.43	6.11

Table 4 shows the tensile properties of CNC filled NBR/NR vulcanizates. The elasticity of NR in polymer blends and tensile strength of NBR/NR vulcanizates were found to be higher than that of NBR100 vulcanizate. One explanation for this is that NR has a higher tensile strength as a result of the strain-induced crystallization phenomenon of NR [6]. Interestingly, an NBR50-C1 composite containing CNCs at 1 phr shows an optimal tensile strength value. It is possible that good dispersion of CNCs in NBR/NR blends is the cause. As the content of CNCs increased, the tensile strength of vulcanizates tends to decrease. It is observed that aggregation of CNCs increases with their content, as evidenced by the SEM images of Figs. 1 (d and e). According to Balachandrakurup and Gopalakrishnan [15], cellulose nanofibers may agglomerate and disrupt load transfer, resulting in decreased tensile strength of rubber nanocomposites.

Table 4. Tensile properties of CNC filled NBR/NR vulcanizates

Property	NBR 100	NBR50 -C0	NBR50 -C1	NBR50 -C3	NBR50 -C5
Tensile strength (MPa)	4.2 ± 0.5	22.5 ± 0.5	24.5 ± 1.8	21.3 ± 1.8	14.7 ± 1.1
%EB	435 ± 15	638 ± 13	634 ± 14	633 ± 8	589 ± 12
100% Modulus (MPa)	1.22 ± 0.04	1.03 ± 0.01	1.12 ± 0.03	1.11 ± 0.03	1.25 ± 0.01

XXXX-XXX

300% Modulus (MPa)	2.38 ± 0.10	2.17 ± 0.03	2.52 ± 0.09	2.40 ± 0.07	2.76 ± 0.02

%Elongation at break (%EB) of the NBR/NR vulcanizates was the highest at 1 phr of CNCs. It tended to decrease with increasing CNC content. This is because as the level of CNCs in NBR/NR vulcanizates increases, the elasticity of the vulcanizates may decrease. However, %EB of NBR/NR vulcanizates was higher than that of the NBR100 vulcanizate.

It was found that the 100% and 300% modulus of the NBR/NR vulcanizates increase with CNC content. These findings suggest that increasing the CNC levels in NBR/NR vulcanizates increases stiffness. Additionally, the 300% modulus of NBR/NR vulcanizates is clearly higher than the 100% modulus.

SEM micrographs of tensile fractured surfaces of (a) NBR100, (b) NBR50-C0, (c) NBR50-C1, (d) NBR50-C3 and (e) NBR50-C5 with various contents of CNCs at 0, 1, 3, and 5 phr are show in **Fig. 1**. **Fig. 1 (a)** displays an SEM image of an unfilled NBR100 vulcanizate with a smooth surface. SEM images of fractured surfaces of NBR/NR blends at various CNC contents are shown in **Figs. 1 (b) – (e),** indicating aggregation of CNCs when the CNC content is increased. This may have been because the CNCs are difficult to disperse after drying due to hydrogen bonding interactions between the CNCs and fibers [16].
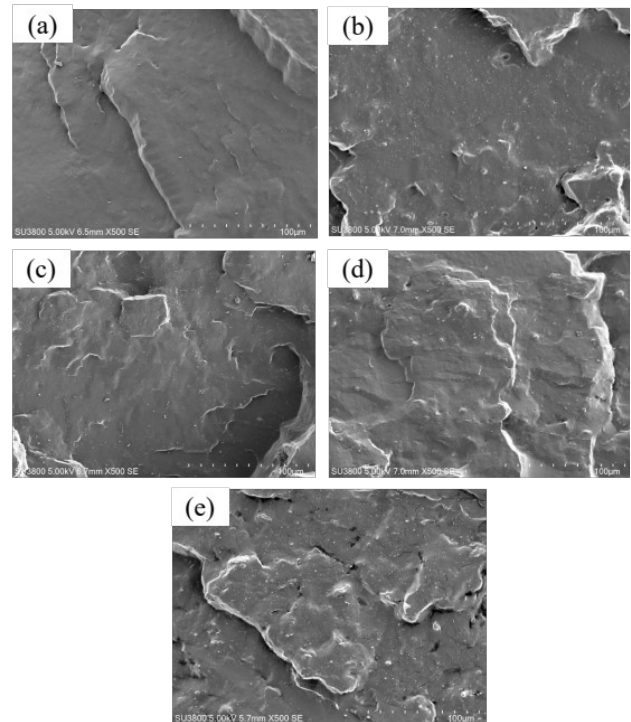

Fig 1. SEM images of CNCs filled NBR/NR vulcanizates,

 (a)   NBR100, (b) NBR50-C0, (c) NBR50-C1,

 (d)   NBR50-C3, (e) NBR50-C5

4. Conclusions

The present study demonstrates the potential of cellulose nanocrystals as a reinforcing filler for NBR/NR nanocomposites. Addition of CNCs to NBR/NR blends increases scorch and cure times, indicating a reduction in the rate of the vulcanization process. The composite torque differences are lower than for NBR gum (NBR100), indicating that composite viscosities are decreased. Designed and controlled loading of CNCs into an NBR/NR matrix appreciably enhanced the mechanical properties of the composites in comparison to those of unfilled NBR gum (NBR100). Compared to other samples, the optimal CNCs level is 1 phr (NBR50-C1). This sample had a higher tensile strength and elongation at break, indicating good CNC dispersion in the NBR/NR blend. This finding is supported by SEM imagery.

XXXX-XXX

6. References

1. Pielichowski, K.; Pielichowska, K. *Elsevier Science B.V.* 2018, 6, 431-485.

2. Zou, H.; Wu, S.; Shen, J. *Chem. Rev.* 2008, 108 (9), 3893-3957.

3. Kato, M.; Usuki, A.; Hasegawa, N.; Okamoto, H.; Kawasumi, M. J. P. j. *Polym. J.* 2011, 43 (7), 583-593.

4. Nunes, R.C.R. *In Progress in Rubber Nanocomposites*, 2017, 463-494.

5. Sahakaro, K.; Pantupon, N. *Int. Polym. Process.* 2008, 23 (2), 140-145.

6. Ismail, H.; Tan, S.; Poh, B.T. *J. Elastomers Plast.* 2016, 33 (4), 251-262.

7. Jardin, J. M.; Zhang, Z.; Hu, G.; Tam, K. C.; Mekonnen, T. H. *Int. J. Biol. Macromol.* 2020, 152, 428-436.

8. Kontturi, E.; Laaksonen, P.; Linder, M. B.; Nonappa; Gröschel, A. H.; Rojas, O. J.; Ikkala, O. *Advanced Materials through Assembly of Nanocelluloses*. 2018, 30 (24), 1703779.

9. Tang, J.; Sisler, J.; Grishkewich, N.; Tam, K. C. *J. Colloid Interface Sci.* 2017, 494, 397-409.

10. Flauzino Neto, W. P.; Mariano, M.; da Silva, I. S. V.; Silverio, H. A.; Putaux, J. L.; Otaguro, H.; Pasquini, D.; Dufresne, A. *Carbohydr. Polym.* 2016, 153, 143-152.

11. Jantachum, P. Preparation and characterization of modified Luffa Cylindrica fibers applied for reinforcement of natural rubber. Ph.D. Thesis, Mahidol University, Bangkok, Thailand, 2020.

12. Jie H.; Fan Y.; Ke L.; Zhengqing K.; Jinli Q.; Yongxin D.; Jianming Z. *J. Polym. Sci*. 2021,1–11.

13. Ivanoska-Dacikj, A.; Bogoeva-Gaceva, G.; Wießner, S.; Heinrich, G. Mathematical and Biotechnical Sciences, (2017), 37(1).

14. Wijesinghe, H.G.I.M.; Etampawala T.N.B.; Edirisinghe, D.G.; Gamlath, G.R.V.S.; Wadugodapitiya, R.R.W.M.U.G.K.; Bandara, T.A.R.W.M.M.C.G. *J. Agric. Sci.* 2022, 17, 1, 1-18.

15. Balachandrakurup, V.; Gopalakrishnan, J. *Ind. Crops. Prod.* 2022, 183, 114935.

16. Roy, K.; Potiyaraj, P. *Cellulose*. 2017, 25(2), 1077-87.