Effect of Starch Nanocrystal on the Properties of Carbon Black-Natural Rubber Composites†

Y.J.S. Gao[1,2], L. Fang[1,2], S.D. Li[3], L.F. Li[1,2], S.Q. Liao[1,2,*] and Z.F. Wang[1,2,*]

[1]College of Materials and Chemical Engineering, Hainan University, Haikou 570228, P.R. China
[2]Hainan Engineering Research Center of Advanced National Rubber Composite Materials, Haikou 570228, P.R. China
[3]College of Science, Guangdong Ocean University, Zhanjiang 524088, P.R. China

*Corresponding authors: E-mail: lsqhnu@hainu.edu.cn; wangzhifen2005@163.com

Starch nanocrystals (SNC) is the representative of a new class of fillers. In our work SNC were prepared by acidolysis. The starch nanocrystal-carbon black-natural rubber (SNC/CB/NR) composites were obtained by blending CB/NR master batch with SNC/NR master batch in the open mill. The effect of SNC on the properties of CB/NR composites was investigated. The results showed that mechanical properties decreased with the increasing content of the SNC. The abrasion surface was observed by scanning electron microscopy and the abrasion surface of samples were much rougher. Thermal analysis presented that the glass transition temperature and the endothermal peak decreased gradually with the increment of SNC and the thermal degradation reaction of SNC/CB/NR composites was two-step reaction. The curves of G' and tan δ *versus* strain of vulcanization were presented by rubber process analyzer, respectively. Dynamic mechanical thermal analysis showed that the loss factor at 0 ℃, SNC increased and decreased at 60-80 ℃ by adding SNC.

Keywords: Starch nanocrystal, Composites, Mechanical properties, Viscoelastic properties.

INTRODUCTION

With excellent comprehensive performance, natural rubber (NR) was widely used in the tyre industry[1-3]. In general, the reinforcing agents such as carbon black (CB) and silicon need to be added into the NR for strengthening the mechanical properties to meet the application requirements. Even if CB is one of the most widely employed reinforcing agents[4], however, CB is derived from petroleum resources usually accompanied with serious environmental pollution. In addition, despite the silicon will not contaminate products, practical limitations arising from the potential safety issues resulting from electrostatic charge accumulation. Besides, kaolin and silicate are often used to fill in NR. Unfortunately, the reinforcing is worse than that enhanced by CB[5,6]. In recent years, as the growing depletion of oil resources and the improvement on environmental protection consciousness, people try to take advantage of starch, with the characteristics of abundance, renewability and biodegradability, to replace the CB[7,8].

However, the size of the starch particles is too big to disperse well in the rubber matrix. Thus, the large size limits to prepare higher performance starch/natural rubber composites. While, Goodyear tyre and Rubber Company addressed this issue by using maize SNC as rubber reinforces filler to replace CB, which significantly decreased the weight and cost of tyres. Meanwhile, it can also reduce rolling resistance, save fuel and reduce pollution, in the condition that the performance of the tyres was kept unchanged[9-11]. Angellier prepared waxy maize SNC/NR composites and the tensile tests showed that as the increment of SNC amount, the elongation at break decreased, while the tensile modulus and the tensile strength increased[12,13].

In this work, the structure and corresponding properties of SNC/CB/NR composites were systematically investigated. At first, SNC was prepared by the acidolysis of Cassava starch to achieve the size of nanoscale. And then the SNC/CB/NR composites were obtained by blending CB/NR master batch with SNC/NR master batch in the open mill. Furthermore, the mechanical properties, surface structures and thermal property of the composite were characterized.

EXPERIMENTAL

Natural rubber latex, 60 % (w/w) and natural rubber was kindly provided by the rubber processing factory of experimental farm which belongs to Chinese Tropical Agriculture Academy (Hainan, PR China). Cassava starch was purchased from starch factory of Qiongzhong, Hainan province (Hainan, P.R. China).

Preparation of the SNC/NR master batch: Cassava starch (300 g) were mixed with 3 L of 3.16 M H_2SO_4 for 5 days at 40 °C and were put on a thermostat water bath with a continuous stirring speed of 100 rpm. The suspension was washed by successive centrifugations with distilled water until neutrality, SNC was prepared[14]. SNC and NR latex were mixed and the contents of starch were 0, 5, 10, 15, 20 and 25 parts per hundred rubber (phr), respectively. The acetic acid was added to co-coagulate the rubber latex and SNC. After being washing for several times by water, the coagulum was dried in an oven at 75 °C to obtain SNC/NR master batch.

Preparation of SNC/CB/NR composites: CB, NR and aromatic oil were blended in an internal mixer until a homogeneous CB/NR master batch was obtained. After that, the CB/NR and SNC/NR master batch were mixed with the additional additives (stearic acid, zinc oxide, accelerator, antioxidant, sulfur and paraffin wax) by a two-roll mill, the formulations are shown in Table-1. The compound wasvulcanized for t_{90} at 145 °C and 15 MPa in a plate press machine and t_{90} was measured with a RPA.

Characterization: The scanning electron microscope (SEM) instrument was used to observe the morphologies of the abrasion fracture surface of the composites with an scanning electron microscope (FESEM, Hitachi S-4800, Japan). Dynamical mechanical analysis(DMA) measurement were performed using a Netzsch DMA 242 instrument operated in the tensile mode, at a frequency of 10 Hz and a heating rate of 5 °C/min, from -100 to 100 °C. The storage modulus E' and loss factor tan δ were evaluated. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were used to study the thermal behaviour of composites, DSC and TG measurements were carried out with Mettler DSC 822e and TGA-DSC1, respectively. DSC test was heated from -80 to 0 °C at a heating rate of 10 °C/min under a nitrogen atmosphere, in aluminum pans. For thermogravimetric analysis the composite test was heated from 25 °C up to 600 °C at 10 °C/min under nitrogen atmosphere. RPA was performed at the temperature of 145 °C, frequency of 1.67 Hz and strain amplitude of 0.5° arc. A strain sweep was carried at 60 °C at 6 cpm frequency and the strain was between 0.7 and 100 %.

The Shore A hardness was determined according to ISO 7619-1986. The stress at 300 %, tensile strength, elongation at break and permanent set were determined according to ISO 37-1994. The tear strength was determined according to ISO 34-1-1994.

RESULTS AND DISCUSSION

Mechanical properties: Table-2 shows mechanical properties of CB/NR composites with various SNC loadings. With the increasing of component SNC, the hardness, stress at 300 %, tear strength as well as abrasion resistance of the composites were significantly decreased. Correspondingly, the tensile strength slightly decreases and the elongation at break, permanent set were found to improve with increasing starch nanocrystal amount. This may have been due to the fact that starches include many hydroxy groups which have strong polarity, this leads to poor compatibility with nonpolar natural rubber, which makes it difficult to finely disperse starch in the rubber matrix. Another possible explanation is the decrease in the crosslinking density of thevulcanized rubber.

Morphology: Fig. 1 shows the SEM images of abrasion surfaces for the SNC/CB/NR composites. The size of raw starch particle was around 5-35 μm. However, after acidolysis, the size reduced to nano scale, between 50-80 nm[14]. As shown in Fig. 1, the SNC particle could not be observed. Although the size of starch particles had been greatly dropped, the size of SNC was still much larger than that of CB. Therefore, the interaction between SNC and NR was weaker than that between

TABLE-1 FORMULATION OF THE CB/NR COMPOSITES WITH SNC (phr/100 phr RUBBER)						
	Sample					
	S0	S5	S10	S15	S20	S25
Carbon black	60	55	50	45	40	35
Starch	0	5	10	15	20	25
Zinc oxide	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2
Accelerator CZ	1.36	1.36	1.36	1.36	1.36	1.36
Sulphur	1.7	1.7	1.7	1.7	1.7	1.7
Aromatic oil	6	6	6	6	6	6
Antioxidant 4010NA	1.0	1.0	1.0	1.0	1.0	1.0
Paraffin wax	1.0	1.0	1.0	1.0	1.0	1.0

| TABLE-2 MECHANICAL PROPERTIES OF CB/NR COMPOSITES WITH DIFFERENT SNC LOADINGS						
	Sample					
	S_0	S_5	S_{10}	S_{15}	S_{20}	S_{25}
Shore A hardness	71	69	68	66	65	64
Stress at 300 % (MPa)	17.9	16.69	15.21	14.42	12.71	11.30
Tensile strength (MPa)	24.11	23.74	22.87	22.37	22.11	21.43
Elongation at break (%)	600	620	630	650	660	670
Permanent set (%)	35	36	36	36	36	36
Tear strength (kN/m)	79.83	74.36	70.57	66.80	61.78	52.83
Akron abrasion (cm^3/1.61 km)	0.204	0.297	0.303	0.463	0.594	0.609
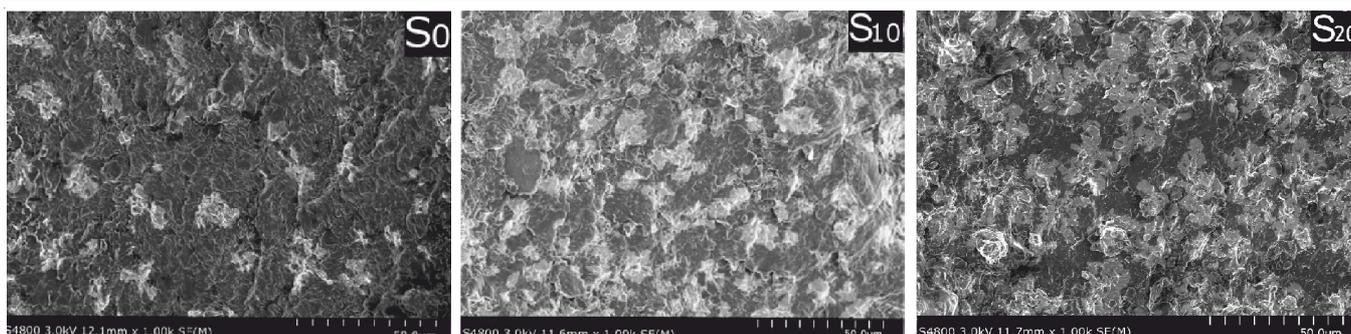
Fig. 1. SEM micrographs of abrasion surfaces of S0, S10 and S20

CB and NR. With the increment of SNC amount, the abrasion surfaces become rougher, which reaches the consensus on that the abrasion resistance is declined as the raise of SNC loading.

DSC analysis: The DSC curves for all the SNC/CB/NR composites were presented in Fig. 2. With increasing SNC loading, both the glass transition temperature (T_g) and the endothermal peak decreased gradually. As discussed previously, the addition of SNC decreased the crosslinking density of vulcanized rubber, therefore, the motion of the rubber chains will earlier than the composite without filled SNC. As well as the endothermal peak, the rubber chains moved more easily and absorbed less heat at the time of glass transition occurred.
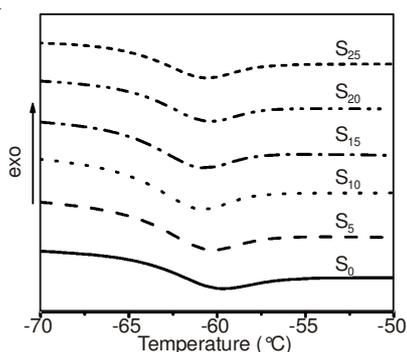
Fig. 2. DSC thermograms of SNC/CB/NR composites

TG analysis: Thermogravimetry and derivative thermogravimetry (DTG) curves of the SNC/CB/NR composites are shown in Fig. 3. The TG and DTG curves indicated that the thermal decomposition of all the samples gradually began at around 200 °C and the decomposition rate became faster at 360-400 °C. The TG curves of CB/NR composite (S0) showed that there was only one turn which corresponds to the single peak of the DTG curving. So the thermal degradation reaction of CB/NR composite was one-step reaction. With the increment of SNC, two peaks occurred in the DTG curve more and more obviously, which indicated that, the thermal degradation reaction of SNC/CB/NR composites was two-step reaction.

RPA test: The filler in rubber was able to form a network which will reinforce the rubber. With the increase of the stain amplitudes, the network was destroyed gradually and the elastic modulus (G') decreased rapidly. The phenomenon was called Payne effect[15].

The curves of G' *versus* strain of CB/NR compounds with different SNC load at 60 °C and a shear frequency of 60 cpm are presented in Fig. 4. It was seen that, with the increase of
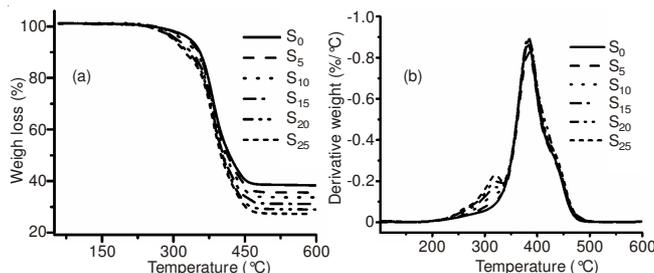

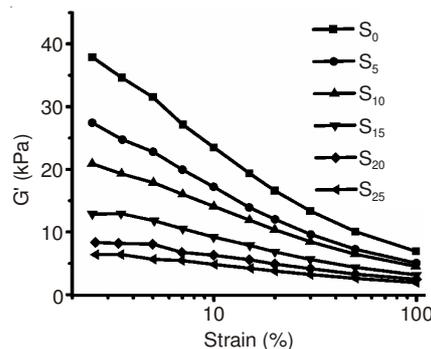Fig. 3. TG and DTG curves of SNC/CB/NR composites (a. TG curves and b. DTG curves)

Fig. 4. Dependence of G' on strain of SNC/CB/NR composites with the RPA 2000

SNC, the Payne effect of composites became weaker. This may be due to low interaction between polar SNC and nonpolar natural rubber and correspondingly, the filler network composed of SNC and CB became weaker with the increment of SNC. When the SNC content exceeded 15 phr (including 15 phr), the Payne effect was not obvious.

Fig. 5 presented the curves of tan δ *versus* the strain of SNC/CB/NR composites by RPA2000. With increasing strain amplitudes, tan δ increased. It was attributed to the destruction of the network formed by filler. Otherwise, tan δ increased with the increase SNC content, which was not expected.

Dynamic mechanical analysis: In tensile mode, the curves of tan δ *versus* the temperature for SNC/CB/NR composites were presented in Fig. 6. By adding SNC, the glass transition temperature of the composites decreased, which was in accord with DSC measurement. At 0 °C, when the content of SNC was less than 20 phr, tan δ increased with the loading of the SNC. This would benefit to improve wet-grip properties of tyre tread. As shown in Fig. 6, tan δ decreased gradually with the increase of SNC at 60 and 80 °C, which would be good for reduce rolling resistance and heat of tyre. At 60 °C,
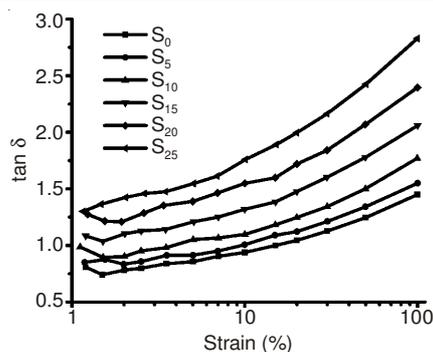
Fig. 5. tan δ *versus* strain curves of SNC/CB/NR composites with the RPA 2000

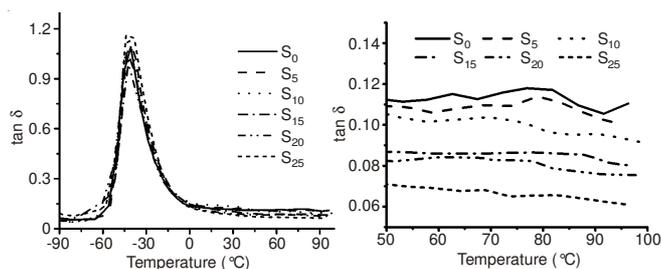Fig. 6. Curves of tan δ *versus* the temperature for composites tested by DMA

the decrease of tan δ with the increment of SNC was at variance with the RPA 2000 results. This phenomenon may be caused by the different test mode. DMA measurement was operated in tensile mode, the strain of tensile mode was weaker than the shearing mode.

Conclusion

By loading SNC, mechanical properties of SNC/CB/NR compositesdecrease,when the content of SNC was less than 15 phr. With the increment of SNC, the glass transition tempe-rature and the endothermal peak decreased gradually. The thermal degradation reaction of SNC/CB/NR composites was two-step reaction. The Payne effect weakened with the increase

of SNC. At 0 ºC, the loss factor of the composites increased and decreased at 60-80 ºC by adding SNC, so the wet-grip properties, rolling resistance and heat of tyre were improved.

REFERENCES

1. Z.F. Wang, S.D. Li and X.D. She, *Adv. Mater. Res.*, **160-162**, 1181 (2010).
2. Z.F. Wang, Z. Peng, S.D. Li, H. Lin, K.X. Zhang, X.D. She and X. Fu, *Compos. Sci. Technol.*, **69**, 1797 (2009).
3. Z.F. Wang, S.D. Li, X. Fu, H. Lin, X.D. She and J. Huang, *e-Polymers*, **10**, 1279 (2010).
4. S. Kanking, P. Niltui, E. Wimolmala and N. Sombatsompop, *Mater. Des.*, **41**, 74 (2012).
5. Y.D. Zhang, Q.L. Liu, Q. Zhang and Y.P. Lu, *Appl. Clay Sci.*, **50**, 255 (2010).
6. W. Kaewsakul, K. Sahakaro, W.K. Dierkes and J.W.M. Noordermeer, *Rubber Chem. Technol.*, **85**, 277 (2012).
7. Y.P. Wu, G.H. Liang and L.Q. Zhang, *J. Appl. Polym. Sci.*, **114**, 2254 (2009).
8. Y.P. Wu, M.Q. Ji, Q. Qi, Y.Q. Wang and L.Q. Zhang, *Macromol. Rapid Commun.*, **25**, 565 (2004).
9. P.H. Sandstrom, US Patent 6391945 (2002).
10. T.F.E. Materne, F.G. Corvasce, US Patent 6273163 (2001).
11. F.G. Corvasce, T.D. Linster, G. Thielen, US Patent 5672639 (1997).
12. H. Angellier, S. Molina-Boisseau and A. Dufresne, *J. Macromol.*, **38**, 9161 (2005).
13. H. Angellier, S. Molina-Boisseau and A. Dufresne, *J. Macromol. Symp.*, **233**, 132 (2006).
14. Y.J.S. Gao, S. Zhao, S.Q. Liao, L. Fang, Z.F. Wang and L.F. Li, *Appl. Mechanics Mater.*, **543-547**, 3886 (2014).
15. A.R. Payne, *J. Appl. Polym. Sci.*, **6**, 57 (1962).