Electronic Supplementary Material (ESI) for Nanoscale. This journal is © The Royal Society of Chemistry 2017

Supporting Information for

Biobased, Self-Healable, High Strength Rubber with Tunicate

Cellulose Nanocrystals

Liming Cao,[†] Daosheng Yuan,[†] Yukun Chen^{*,†} Chuanhui Xu,^{*,‡}

[†]The Key Laboratory of Polymer Processing Engineering, Ministry of Education, South China

University of Technology, Guangzhou 510640, China

[‡]School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

Corresponding Author: Yukun Chen (cyk@scut.edu.cn)

Chuanhui Xu (xuhuiyee@gxu.edu.cn)

Isolation and characterization of tunicate cellulose nanocrystals

Tunicates were collected from Weihai, Shandong province (China) and were used to isolate cellulose nanocrystals (t-CNs) via sulfuric acid hydrolysis as previously described.¹⁻² Small fragments of the tunicin were first deproteinized by several successive bleaching treatments. The bleached tunicin (purified cellulose from tunicate) was then disintegrated, and the resulting pulverized tunicin was mixed with 55wt% H2SO4 solution and hydrolysed at 60°C for 1h, with continuous stirring. An aqueous suspension of cellulose nanocrystals was obtained. Then the suspension was subjected to high speed centrifugation for about 10min, and the precipitate was washed 3 times with deionized water for re-dispersion and re-centrifugation. After sonication an aqueous suspension of well individualized cellulose nanocrystals of colloidal dimensions was resulted.

Stability of the t-CNs aqueous suspension

The zeta potential (ζ potential, ZP) of the pristine t-CNs (1.0 mg/mL) aqueous suspensions (pH value of 8.0) were measured using Zetasizer nano-ZS (Malvern, UK).



Figure S1. Digital images along with ZP of the obtained t-CNs aqueous suspension.

It has been reported that for a stable suspension solely stabilized by electrostatic repulsion, a ZP of \geq + 30 mV or \leq - 30 mV is necessary.³⁻⁴ As shown in Figure S1, the ZP of the pristine t-CNs aqueous suspension was -38.6 mV, which indicates the suspension property of the t-CNs. This may be attributed to the sulfate ester groups on t-CNs surfaces during isolation via sulfuric acid hydrolysis.⁵ After standing for a week at ambient condition, the suspension remained stable.

Curing curves

The curing experiments were performed on rubber compounds in a moving die rheometer (UR-2010, U-CAN Dynatex Inc.) at temperature of 140°C. The curing measurements were carried out at a frequency of 1.67Hz and an amplitude of 0.5°.

Figure S2 shows the vulcanization process of ENR based nanocomposites. The increased torque value is usually considered to represent the evolution of crosslink network in rubbers.⁶ As seen, the torque values increased sharply at the first 20min, and then increased slowly with curing time until 60 min. With 10 phr t-CNs incorporated, the final torque value increased from 1.08 to 1.15 dN.m, and further increased to 1.30 dN.m with 20 phr t-CNs, which was attributed to the filler-rubber interaction and the formation of filler-filler network.



Figure S2. Curing behavior of ENR nanocomposites with different t-CNs content.

Tensile stress-strain curves for self-healing performance



Figure S3. Typical stress-strain curves for all samples before and after healing. The samples were cut into completely separate pieces and the cut faces were gently brought together without waiting and allowed to heal at ambient temperature for 24h. Improved self-healing efficiency observed with the increase of t-CNs content (Figure 11), as more hydrogen bonds formed between rubber and filler. The dynamic hydrogen bonds supramolecular network facilitated the self-healing behavior of the

nanocomposites.

Tensile behavior of the healed samples

Figure S4. Snapshots during tensile test for ENR/t-CNs-20 nanocomposite healed for 24h at ambient condition without waiting. The healed sample can be stretched to a relatively high extension without fracture, indicating the excellent healing behavior.

Elastomer	Pristine Tensile	Healed Tensile	Ref.
	Strength (MPa)	Strength (MPa)	
ENR ^a	0.85	0.84	7
NR ^b	0.56	0.30	8
NR	0.70	0.70	9
NR	1.89	1.87	10
Elastomer ^c	0.81	0.78	11
PDMS ^d	0.23	0.22	12
Elastomer ^e	3.70	2.12	13
PB^{f}	1.78	1.61	14
ENR	2.25	1.92	15
ENR	2.87	2.32	This work ^g
ENR	4.04	3.52	This work ^h

Table S1. Comparison of tensile strength before and after healing of ENR/t-CNs-10 and ENR/t-CNs-20 with previously reported self-healing elastomers.

^a ENR: epoxidized natural rubber; ^b NR: natural rubber; ^c systemic elastomer, poly(urea-urethane) elastomer; ^d PDMS: poly(dimethylsiloxane); ^e systemic elastomer based on a bifunctional diglycidyl ether of bisphenol A (DGEBA) and a tetrafunctional 4,4'-methylenebis(N,Ndiglycidylaniline) (TGMDA); ^f PB: polybutadiene; ^g ENR based nanocomposite with 10phr t-CNs in this work; ^h ENR based nanocomposite with 20phr t-CNs in this work.

Supporting Video Legend:

The Supplementary Video demonstrating the improved self-healing behavior of ENR based nanocomposite with 20phr t-CNs compared with neat ENR. The samples were cut into separate pieces with a razor blade and the cut faces were brought back in contact by hand pressure without waiting. Then the samples were left to heal at ambient condition for 30 min. The self-healed samples were stretched by hands until fracture. It can be seen that the healed nanocomposite with 20phr t-CNs can be stretched to a longer extension than neat ENR, indicating the higher self-healing efficiency ascribed to the formation of hydrogen bonds supramolecular network.

References

- Y. D. Zhao, Y. J. Zhang, M. E. Lindstrom and J. B. Li, *Carbohyd. Polym.*, 2015, 117, 286-296.
- 2 L. M. Cao, X. F. Fu, C. H. Xu, S. H. Yin and Y. K. Chen, *Cellulose*, 2017, 24, 2849-2860.
- 3 M. Cabuk, Y. Alan, M. Yavuz and H. I. Unal, Appl. Surf. Sci., 2014, 318, 168-175.
- 4 X. D. Wu, C. H. Lu, X. X. Zhang and Z. H. Zhou, J. Mater. Chem. A, 2015, 3, 13317-13323.
- 5 J. Cao, X. X. Zhang, X. D. Wu, S. M. Wang and C. H. Lu, *Carbohyd. Polym.*, 2016, 140, 88-95.
- 6 X. D. Cao, C. H. Xu, Y. H. Liu and Y. K. Chen, Carbohyd. Polym., 2013, 92, 69-76.
- 7 J. Cao, C. H. Lu, J. Zhuang, M. X. Liu, X. X. Zhang, Y. M. Yu and Q. C. Tao, *Angew. Chem. Int. Edit.*, 2017, **129**, 1-7.
- 8 M. Hernández, M. M. Bernal, A. M. Grande, N. Zhong, S. van der Zwaag and S. J. García, *Smart. Mater. Struct.*, 2017, 26, 085010.
- 9 C. H. Xu, L. M. Cao, B. F. Lin, X. Q. Liang and Y. K. Chen, ACS Appl. Mater. Interfaces, 2016, **8**, 17728-17737.

10 C. H. Xu, L. M. Cao, X. H. Huang, Y. K. Chen, B. F. Lin and L. H. Fu, ACS Appl. Mater. Interfaces, 2017, DOI: 10.1021/acsami.7b09997.

11 A. Rekondo, R. Martin, A. R. de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola. *Mater. Horiz.*, 2014, **1**, 237-240.

12 C. H. Li, C. Wang, C. Keplinger, J. L. Zuo, L. H. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X. Z. You and Z. N. Bao, *Nat. Chem.*, 2016, **8**, 618-624.

13 F. Sordo, S. J. Mougnier, N. Loureiro, F. Tournilhac and V. Michaud, *Macromolecules*, 2015, **48**, 4394-4402.

14 D. Wang, J. Guo, H. Zhang, B. Cheng, H. Shen, N. Zhao and J. Xu, *J. Mater. Chem. A*, 2015, **3**, 12864-12872.

15 Y. Y. Han, X. D. Wu, X. X. Zhang and C. H. Zhang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 20106-20114