Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Strain-induced 3D-Oriented Crystallites in Natural Rubber/Chitin Nanofiber Composites

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Characterization of Cross-linking density. Cross-linking densities (v) of the samples were calculated using the Florye–Rehner equation (1) according the swelling data. A certain amount of the NR/ChNFsX was cut off from the vulcanized rubber test pieces and immersed in the solution of toluene for 3 days at room temperature to remove the organic additives, and then dried at 30 ºC in the blast drying oven for 1 days until the weight of specimen was stable.

$$v = -\frac{[\ln\left(1 - v_{rf}\right) + v_{rf} + \chi {v^2}_{rf}}{v_s\left(v_{rf}^{1/3} - v_{rf}/2\right)} \tag{1}$$

where v_{rf} is the volume fraction of the cross-linked polymer, the interaction parameter (χ) is the interaction parameter between NR and toluene, which value is 0.413,[1] v_s is the molar volume of the swelling solvent which value is 106.3 cm³ /mol. The v_{rf} was obtained by equation (2)

$$v_{rf} = \frac{\frac{m_3}{\rho}}{\frac{m_3}{\rho} + \frac{m_2 - m_1}{\rho_s}} \tag{2}$$

where m_1 and m_2 are the initial weight before equilibrium swelling and specimen weights at equilibrium swelling. m_3 is the specimen weight after drying. ρ and ρ_s are the densities of toluene and unswollen rubber vulcanizate, respectively. ρ is 0.866 g/cm³.

The soluble fraction was obtained by equation (3).[2]

$$S = \frac{m_1 - m_3}{m_3} \times 100\% \tag{3}$$

As shown in Table 1, the cross-linking density of NR/ChNFs composites increases with ChNFs contents increasing accordingly.

Table S1. The cross-linking densities of NR/ChNFs composites with different ChNFs contents.

Sample	Cross-linking density(10^{-4} mol/cm^3)	soluble fraction (%)
NR	0.9855±0.015	3.061
NR/ChNFs5	1.2262±0.011	3.484
NR/ChNFs10	1.8484±0.02	4.000
NR/ChNFs20	2.9507±0.017	4.362
NR/ChNFs30	3.5690±0.008	7.954

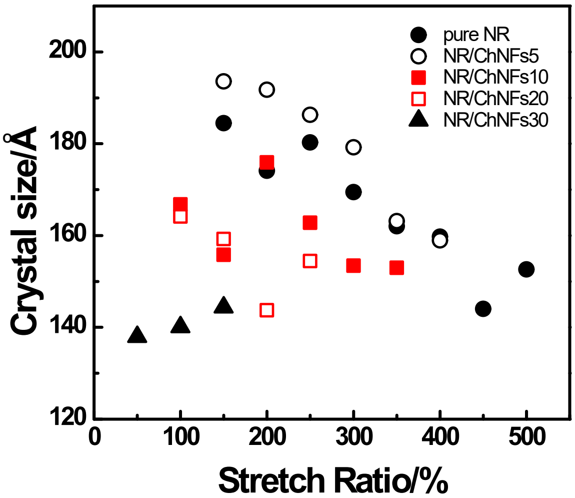

Figure S1. The crystallites size of NR/ChNFs composites under uniaxially-stretching process with different ChNFs contents.

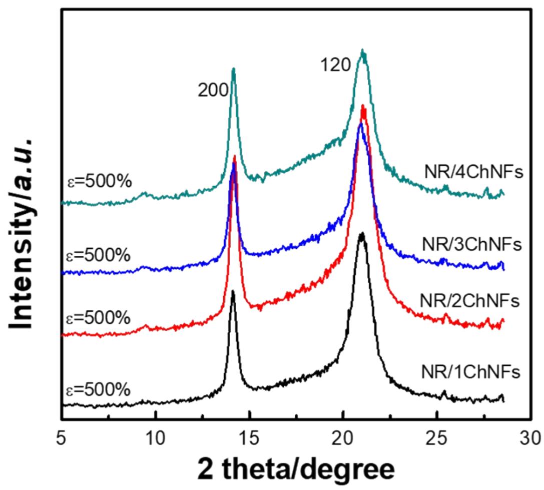

Figure S2. 1D-WAXD profiles along equatorial integration of NR/ChNFs composites after strain-induced crystallization at ε = 500 %.

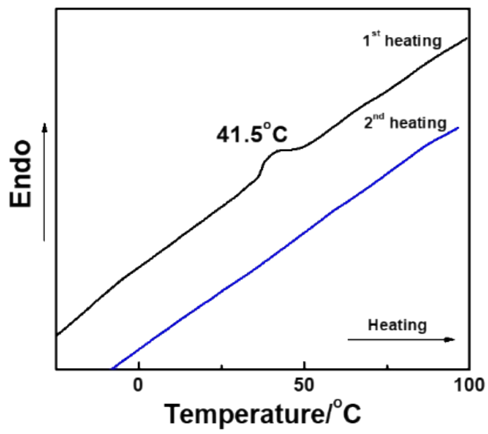

Figure S3. DSC curve of stretched NR/ChNFs30 composite film. Heating rate is 10 °C/min.

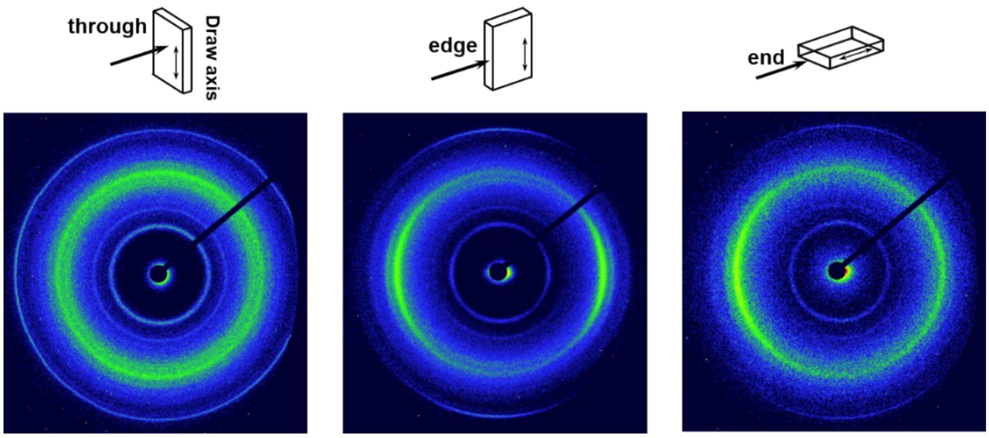

Figure S4. 2D-WAXD patterns of unstretched NR/ChNFs30 composite measured along the through, edge, and end directions.

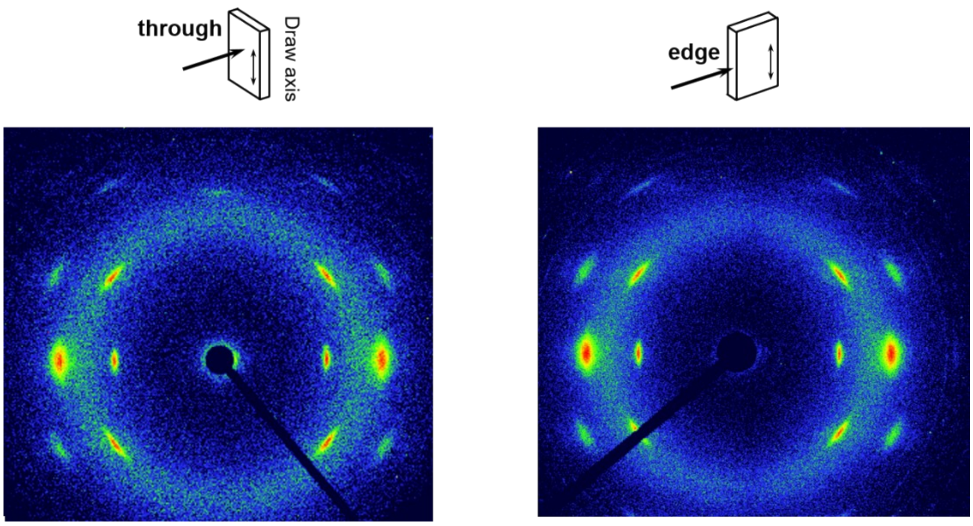

Figure S5. 2D-SAXS patterns of stretched NR composite measured along the through and edge directions.

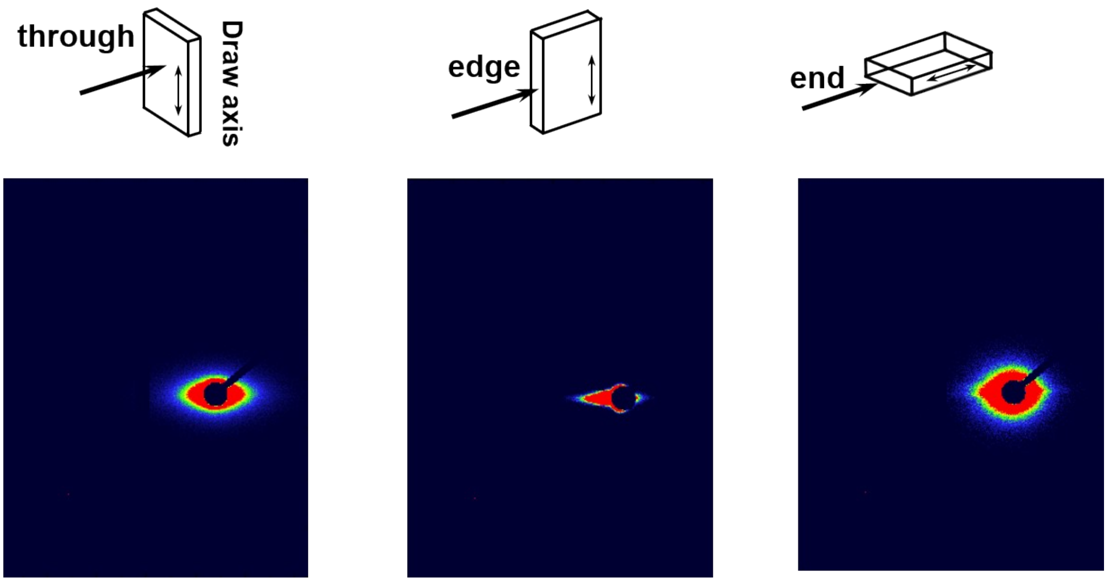

Figure S6. 2D-SAXS patterns of unstretched NR/ChNFs30 composite measured along the through, edge, and end directions. Comparing with 2D-WAXD measurement, the distance between the sample and the detector was moved to 2490 mm in 2D-SAXS measurement.

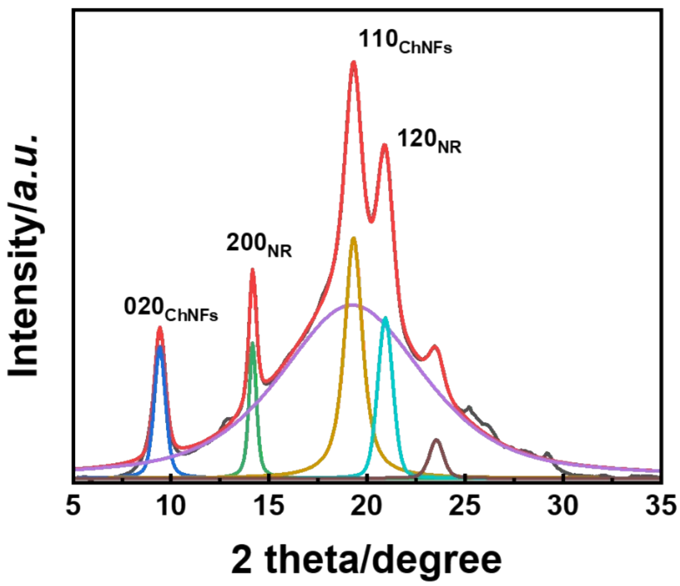

Figure S7. Multi-peak fitting of 1D-WAXD curves taken from 2D-WAXD end-pattern of NR/ChNFs30 composite.

Notes and references

1. C. Ryu, J. K. Yang, W. Park, S. J. Kim, D. I. Kim, G. Seo, *J. Appl. Polym. Sci.,* 2020, **137**, 49548.

2. S. Seghar, L. Asaro, N. Aït Hocine, *J Polym Environ*, 2019, **27**, 2318.