Tuning the mechanical properties of cellulose nanofibrils reinforced polyvinyl alcohol composites via altering the cellulose polymorphs Xiaran Miao,^{b§} FengTian,^{a, b§} Jinyou Lin,^{*a, b} Hui Li,^c Xiuhong Li,^b Fenggang Bian,^b and Xiangzhi Zhang^{*b} ^a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials,

Donghua University, Shanghai 201620, China

^b Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics,

Chinese Academy of Sciences, Shanghai 201204, China

^c School of Materials Science and Engineering, East China University of Science and

Technology, Shanghai 200237, China

*Corresponding author. Tel: +86-21-33931904; Fax: +86-21-33931904.

E-mail address: jinyoulin82@gmail.com & linjinyou@sinap.ac.cn; Zhangxiangzhi@sinap.ac.cn

 $\ensuremath{\$}$ These authors have contributed equally to this work.



Fig. S1. FTIR spectra of CNF-I and CNF-II.



Fig. S2. Peak fit results of 1D SR-WAXS integral curves in the 2θ range of $10-22^{\circ}$: (a)

CNF-I and (b) CNF-II.





Fig. S3. Peak fit results of 1D SR-WAXS integral curves of PVA/CNF composite films.



Fig. S4. TGA curves of CNF-I and CNF-II at a heating rate of 10 °C/min.



Fig. S5. Typical stress-strain curves of (a) PVA/CNF-I and (b) PVA/CNF-II composite films.

| Table S | 1. The temperatures at | 10% weight loss (| T_{-10} °C) and | the maximum weig | ght loss rate (Tp) . |
|---------|-------------------------------|-------------------|-------------------|------------------|------------------------|
|---------|-------------------------------|-------------------|-------------------|------------------|------------------------|

| Samulas | Pure | PVA/ | PVA/ | PVA/ | PVA/ | PVA/ | PVA/ |
|------------------------------|-------|---------|---------|----------|----------|----------|-----------|
| Samples | PVA | CNF-I-1 | CNF-I-5 | CNF-I-10 | CNF-II-1 | CNF-II-5 | CNF-II-10 |
| <i>T</i> ₋₁₀ (°C) | 272.5 | 284.9 | 294.9 | 257.4 | 279.9 | 287.4 | 265.0 |
| <i>T</i> p (°C) | 317.5 | 319.9 | 324.9 | 307.4 | 319.4 | 320.0 | 312.5 |