

Supporting Information

Mechanical Properties and Degradation Studies of Poly(Mannitol- Sebacate)/Cellulose Nanocrystal Nanocomposites

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Table S1

Composition and molecular weight distribution of PMS pre-polymer 1:1 and PMS pre-polymer 1:2 after 13h and 5h of polycondensation reaction of sebacic acid and mannitol monomers respectively, under continuous stirring and nitrogen flow at 150 °C.

Table S1. Main PMS Pre-Polymer Properties	
Composition by ¹ H NMR	1.06:1
Composition by ¹ H NMR	0.83:2

CNC properties.

Charge concentration was determined by conductometric titration as described previously.^{1, 2} The concentration of sulphate groups on CNCs was calculated from the titration results according to a reported protocol.³ Dimensions and aspect ratio of CNCs were calculated as an average of randomly measures in TEM images at different magnifications (2950x, 3900x and 5200x). CNCs TEM micrographs were recorded in a Phillips CM10 microscope with an accelerating voltage of 80kV. Samples were prepared by drying a drop of dilute whiskers suspension in H₂O (0.1 mg/mL) onto a carbon-coated copper grid (Electron Microscopy Sciences) and subsequently dried under a lamp for 1h. ImageJ software (National Institute of Health in USA) was used to evaluate the length and width of the CNCs. The crystalline structure of the CNCs was investigated with an RXSiemens D5000 equipped with a Cu K α radiation source ($\lambda = 1540 \text{ \AA}$) operating at 40kV. A CNC sample was dispersed in water and dried in oven at 100°C for 0.5h. After drying the compact powder obtained was regrounded and transferred to scan. The scanning range was 2°-40°, step-size and count time per step were 0.02° and 8 seconds, respectively. Apparent crystallinity was calculated from X-ray diffraction pattern using www.magicplot.com software.⁴

Table S2. Main CNCs properties analysed through conductometric titration, TEM images and X-ray diffraction pattern.

Table S2. Main CNC Properties	
charge concentration (mM/kg _{cellulose}) ^a	104.3 ± 4
length (nm)	199 ± 14
width (nm)	18 ± 2
aspect ratio	11 ± 1
apparent crystallinity (%)	68

^a Determined by conductimetric titration

¹H-NMR studies

¹H-NMR spectra of PMS 1:1 and PMS 1:2 pre-polymers were obtained in deuterated dimethylsulfoxide (d₆DMSO), on a Varian Mercury VX-300 MHz NMR spectrometer. Samples were prepared dissolving the pre-polymers into 750 μL of d₆DMSO in a glass tube. The peaks from the mannitol appeared at 3.5-5.5 ppm due to central and terminal methylene units. The protons from methylene units of sebacic acid showed peaks at 1.3, 1.6 and 2.3 ppm. The peak at 3.3 was due to residual water.⁵

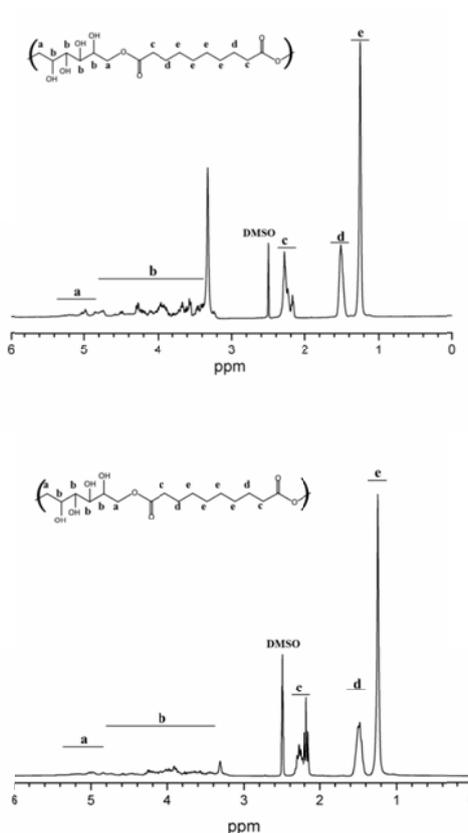


Figure S1. ¹H-NMR spectra of (a) 1:1 pre-poly(mannitol sebacate), and (b) 1:2 pre-poly(mannitol sebacate) were recorded in d₆DMSO. Signal intensities of the polyol were identified at 3.5-5.5 ppm, and for sebacic acid at 1.3, 1.6 and 2.4 ppm by hydrogens on the carbons “a” and “b” and “c”, “d” and “e” respectively. Simplified representations of the pre-polymers are shown.

Fourier Transform Infrared Spectroscopy (FTIR).

Transmission spectra were recorded using a Thermo Nicolet 5700 spectrometer, in the 500 to 4500 cm^{-1} region, with a 4 cm^{-1} resolution with an Attenuated Total Reflectance (ATR) cell. Backgrounds were acquired before every 3rd sample. All samples were vacuum-dried before measurement.

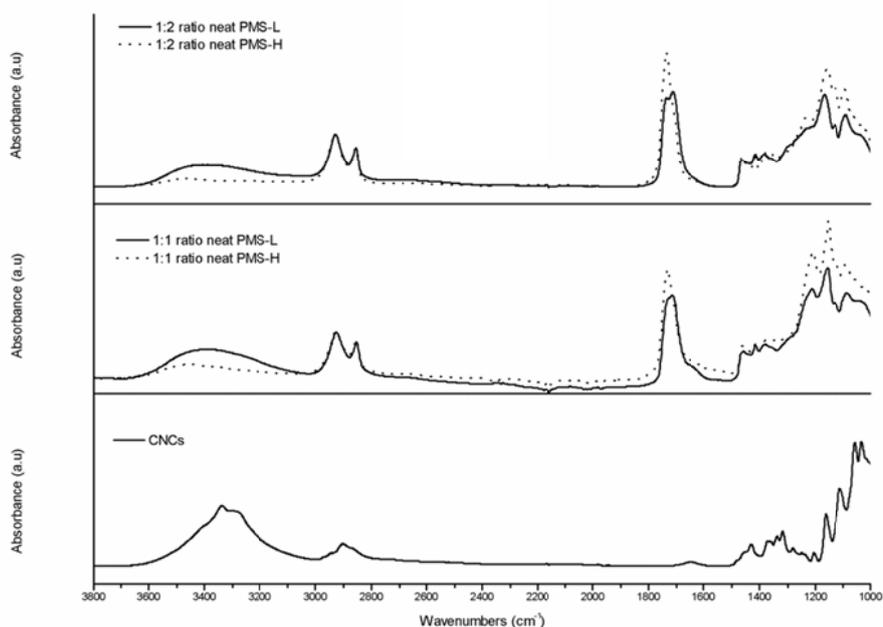


Figure S2. FTIR spectra from top to bottom, low crosslinked (**L**) and high crosslinked (**H**) PMS 1:2 stoichiometric ratio, low crosslinked (**L**) and high crosslinked (**H**) PMS 1:1 stoichiometric ratio, and CNCs.

Differential Scanning Calorimetry (DSC).

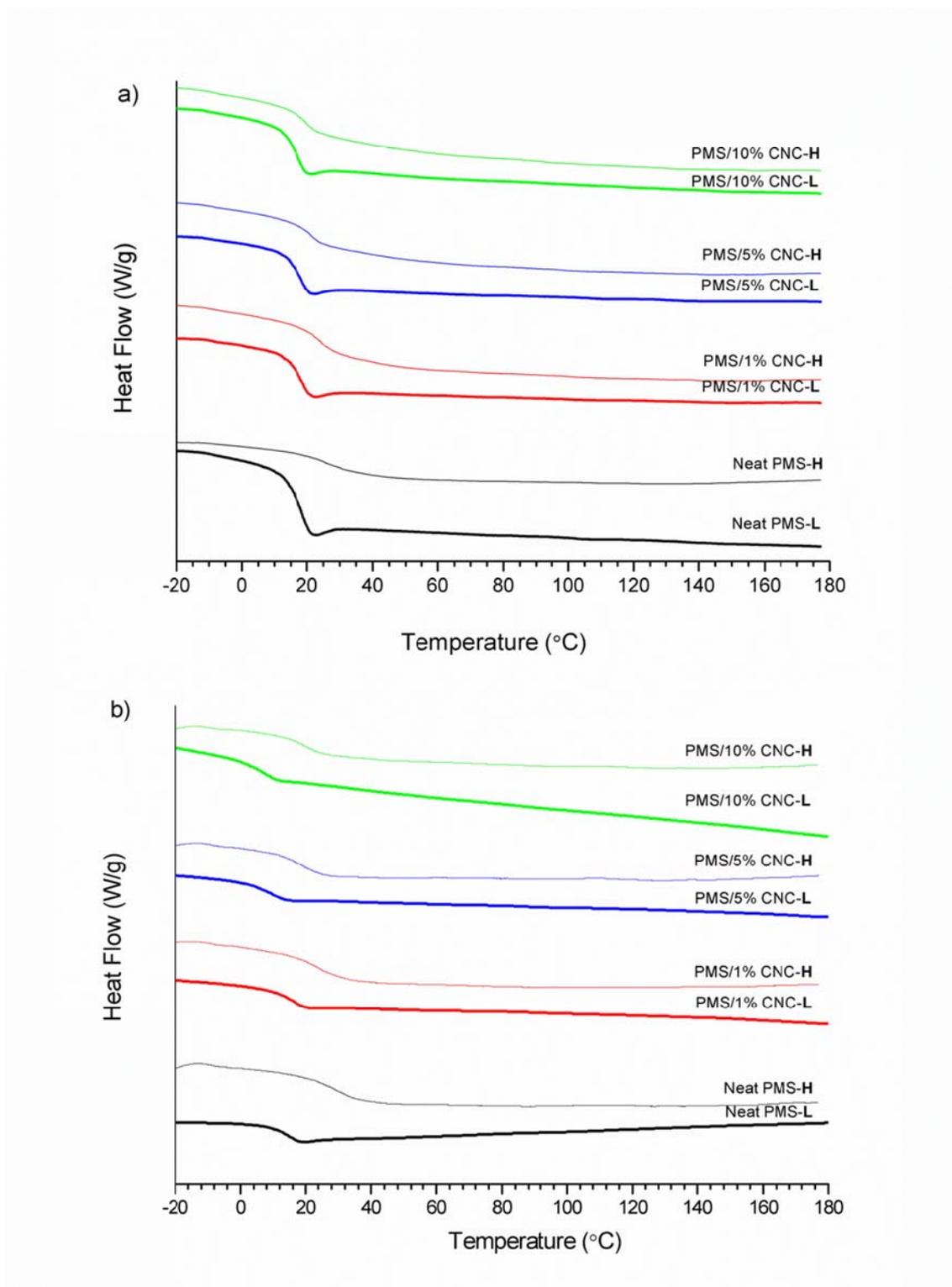


Figure S3. DSC second heating run thermograms (a) of 1:1 low (L), and high (H) crosslinked neat PMS and PMS/CNC nanocomposites, and (b) for 1:2 low (L) and high (H) crosslinked neat PMS and PMS/CNC nanocomposites.

References

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