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Supporting Information

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Cross-Linkable Modified Nanocellulose/Polyester Resin-Based Composites: Effect of Unsaturated Fatty Acid Nanocellulose Modification on Material Performances

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Supporting Information

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2.1.1. Cellulose Nanocrystals (NC) Isolation

NC was obtained from cotton by acid hydrolysis with 64 % H_2SO_4 . In an Erlenmeyer flask of 1000 ml, 20 g of cotton and 200 ml of H_2SO_4 solution of different concentrations were added dropwise in an ice bath and stirred. The suspension was heated while stirred if necessary to reach the appropriate temperature (40 min, 40 °C). Afterwards, the cotton dispersion was washed with deionized water using repeated centrifugation ($n=6000$ rpm/min) and sonication cycles, *i.e.* the supernatant was removed from the precipitate and replaced by fresh deionized water, and cycle was repeated. The centrifugation step was repeated until pH value of 4 is achieved or the supernatant became turbid. The last wash was conducted using dialysis with deionized water until the wash water maintained at constant pH or washed with deionized water until the pH value reached 5.5.

2.2. Isolation of FAs and Preparation of Methyl Esters of FAs

In a four-necked glass reactor of 2 l, equipped with a reflux condenser, mechanical stirrer, thermometer and dropping funnel, 233 g (0.26 mol, 250 ml) of linseed oil (LO) dissolved in 700 ml of 96 % ethanol was added. The KOH solution in ethanol (30 %, 0.91 mol) was slowly added to oil with intensive mixing, and the obtained molar ratio of KOH/LO was 3.5/1. During the addition of KOH solution, the reaction mixture was maintained at constant temperature below 10 °C for an hour. Next two hours, the reaction mixture was heated to 50 °C, whereupon two-thirds of the solvent were removed by distillation. The resulting pasty residue was dissolved in the required amount of distilled water to get clear solution, and after addition of activated

carbon and filtration, the obtained solution was acidified by addition of appropriate volume of 10% HCl until pH of 3 was attained. Top layer of FALO was separated; the aqueous layer was extracted twice with 250 ml of diethyl ether and combined with organic layer. The resulting ethereal solution was dried with sodium sulfate. Evaporation of ether by atmospheric distillation was followed by assembling vacuum system which enabled drying and removal of low boiling component of reaction product. The isolation of sunflower oil (SO) fatty acid, named FASO, was performed in an analogous manner.

For isolation of methyl ester of LO, previously described in detail^[1], 929.0 g (3.3 mol) of LO were used, dissolved in 85 ml of methanol. The KOH solution in methanol (0.12 mol of KOH in 102 ml of methanol) was added dropwise. Afterward, the reaction mixture was heated at 58 – 62 °C for 3 hours, and then left to cool down. Bottom layer, *i.e.* mainly raw glycerin, was separated, and upper layer was treated with active charcoal and filtered through diatomaceous earth. After drying with sodium sulfate, the obtained linseed oil methyl ester was purified by vacuum distillation under nitrogen. The isolation of methyl ester of SO and soybean oil (SOYA) fatty acid fatty acid was performed in an analogous manner. Characteristics of fatty acids mixture (FA) and methyl ester of fatty acids (MEFA) are presented in our previously work.

2.3. Chemical Modification of NC with FAs and Methyl Esters of FAs

In order to change solvent for the modification, the obtained NC particles were washed with GAA, and 2 g of purified NC was charged into an Erlenmeyer flask of 250 ml. The 20 ml of GAA and 25 ml of toluene were added to purified nanocellulose and mixture was homogenized on ultrasonic bath (35 kHz) for 10 minutes. After homogenization, 0.1 ml of 60 wt.% perchloric

acid and 0.5 g of MA were added into the mixture and left in ultrasonic bath (35 kHz) for one hour. After completion of the reaction, the MA modified NC (NC-MA) was centrifuged and washed three times with toluene. Obtained NC-MA was modified with EDA. The NC-MA was placed in 250 ml four-necked flask and dispersed in 50 ml DCM for 10 min by using ultrasonic bath. After a condenser, thermometer, gas inlet tube and dropping funnel was assembled. In the NC-MA dispersion, mixed on a magnetic stirrer, was added 5.74 g of DCC and 0.73 g of DMAP in 30 ml DCM from dropping funnel providing inert atmosphere in a reaction system. Thereafter, dropwise addition of 1.2 g of EDA dissolved in 10 ml of DCM last for 30 min at room temperature, and continued with a mixing for 12 hours. After the reaction completion, modified product (NC-MA/EDA) was washed three times with DCM, and three times with toluene. The final NC-MA/EDA mass was 2g.

3.3. Curing Kinetics Analysis using Raman Spectroscopy

Table S1. Raman bands for the spectra from the UPe resin^[2]

Assignment component	Wavenumber, cm ⁻¹	Component
C=O	1725	UPe
C=C	1657/1644	UPe
C=C vinyl	1625	Styrene
C=C aromatic	1612/1596	UPe and styrene
C-H saturated	1450	UPe
C-H vinyl	1409	Styrene

3.4. Transmission Electron Microscopy (TEM) Analysis of Nanocomposite Materials

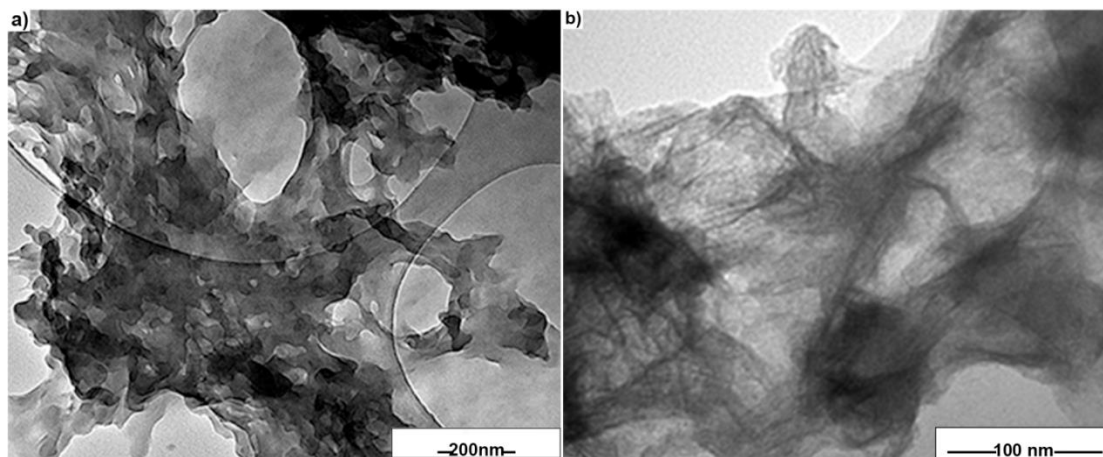
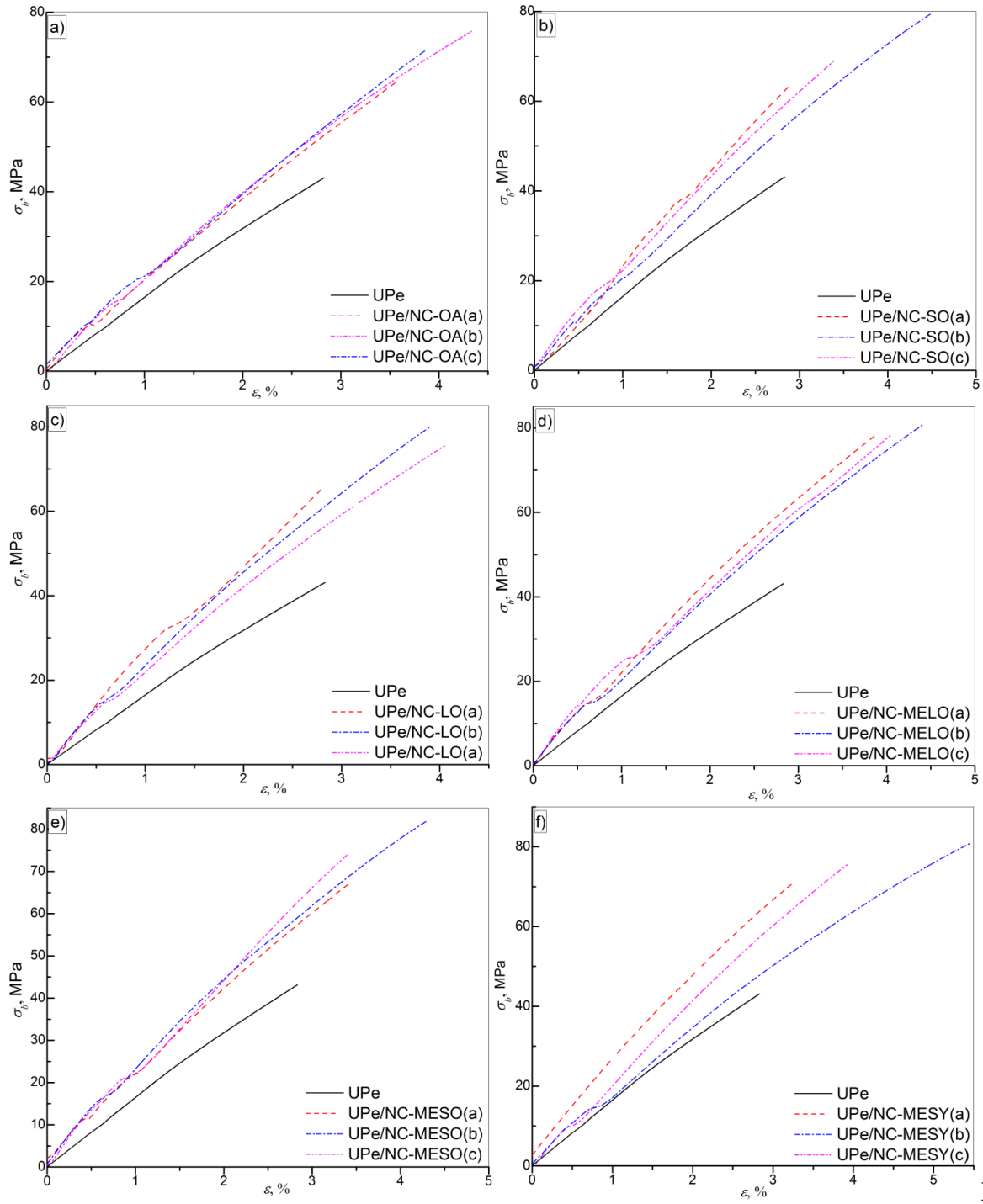


Figure S1. TEM micrograph of UPe/NC at a) 30000 and b) 120000 magnification

3.5. Mechanical Testing of UPe/m-NC Nanocomposite Materials



Figur

e S2. The stress-strain curves of the cured UPe and a) UPe/NC-OA(n), b) UPe/NC-SO(n), c)

UPe/NC-LO(n), d) UPe/NC-MELO(n), e) UPe/NC-MESO(n) and b) UPe/NC-

MESY(n)nanocomposites

Calculation of tensile modulus using Cox-Krenchel model (E_{cox}) was performed according to Equation S1:

$$E_{cox} = \eta_0 \eta_L V_f E_f + (1 - V_f) E_M \quad (S1)$$

where E_f and E_M are the Young's modules for m-NC nanofillers and matrix, respectively, V_M and V_F are the volume fractions of matrix and nanofillers, respectively, η_0 and η_L are the NC orientation factor and NC length efficiency factor. For the randomly in-plane oriented NC the η_0 is 0.375^[3].

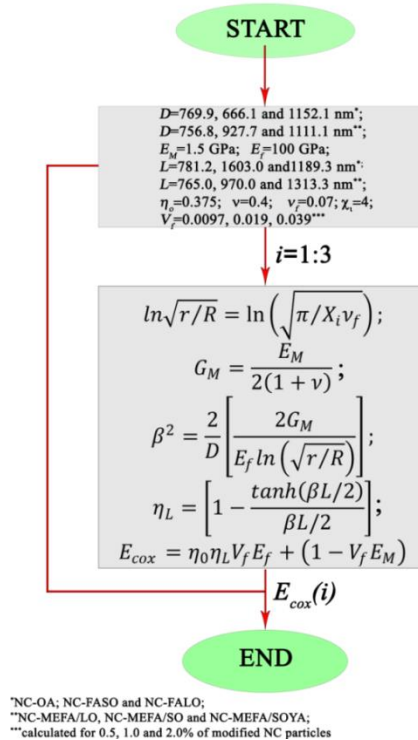


Figure S3.The proposed algorithm to Cox-Krenchel model the constitutive equation of polymers filled with m-NC nanoparticles

L, D, r, R, G_M , ν and ν_F are fiber length, fiber diameter, fiber radius, mean center-to-center distance between fibers, shear modulus and Poisson ratio of polymer matrix and modified NC.

Table S2. Stress at break (σ_b) and tensile modulus (E) of unmodified and modified unsaturated polyester resins reported in the literature

NC type	NC amount [%]	σ_b [MPa]	E [GPa]	References
Unmodified NC nanocrystal	0.5	55	-	[4]
	1.0	52	-	
	3.0	48	-	
ST modified ^{a)} NC nanocrystal	2.0	48	0.90	[5]
	4.0	46	0.91	
	6.0	42	0.86	
IsoraNanofiber	0.5	55.02	1.87	[6]
	1.0	51.6	2.03	
	3.0	45.97	1.89	
	5.0	38.02	1.27	

^{a)}*N*-(β -aminoethyl)- γ -aminopropyltrimethoxysilane modified NC nanocrystals

3.6. Dynamic-Mechanical Analysis of Nanocomposite Materials

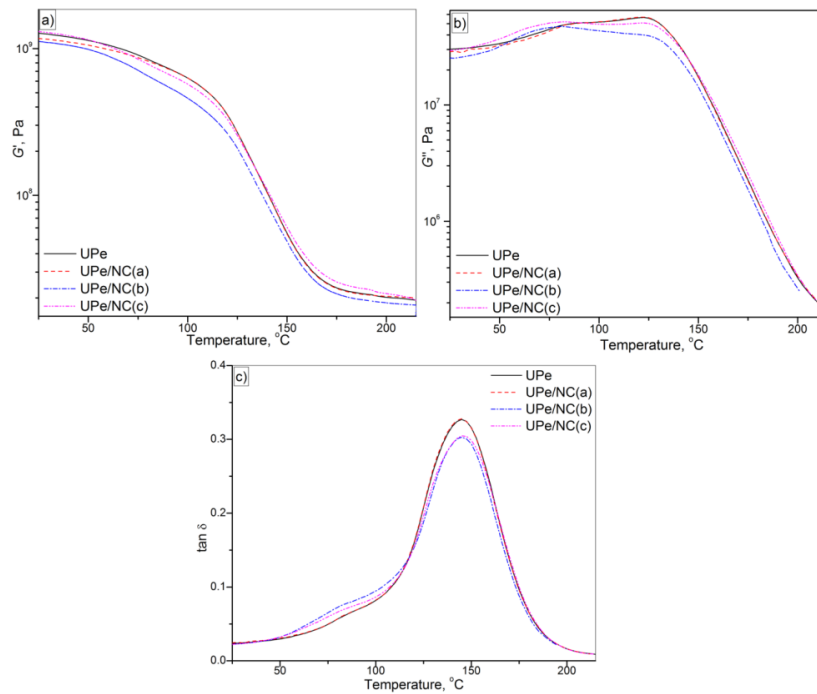


Figure S4. Temperature dependence of storage modulus (G'), loss modulus (G'') and $\tan \delta$ of pure UPe and UPe/NC(a-c) nanocomposites

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