Electrospinning and Fiber Stretching of Polymer Grafted Polystyrene Nanocomposites: Structures and Dymanic Mechanial Properties

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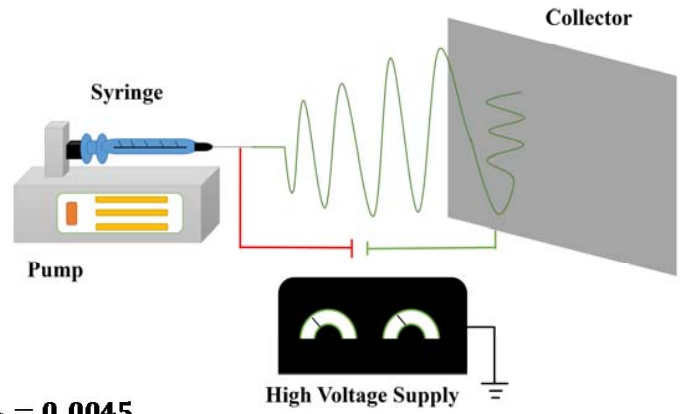
Electrospinning

- Simple set up
- Complex process
- Challenges in scaling up



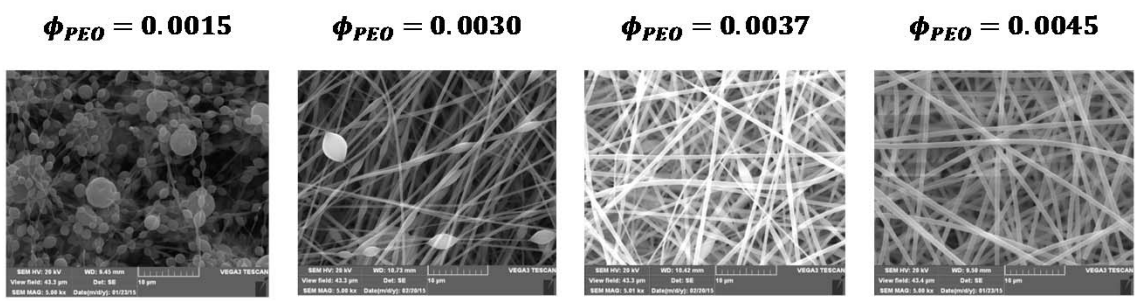
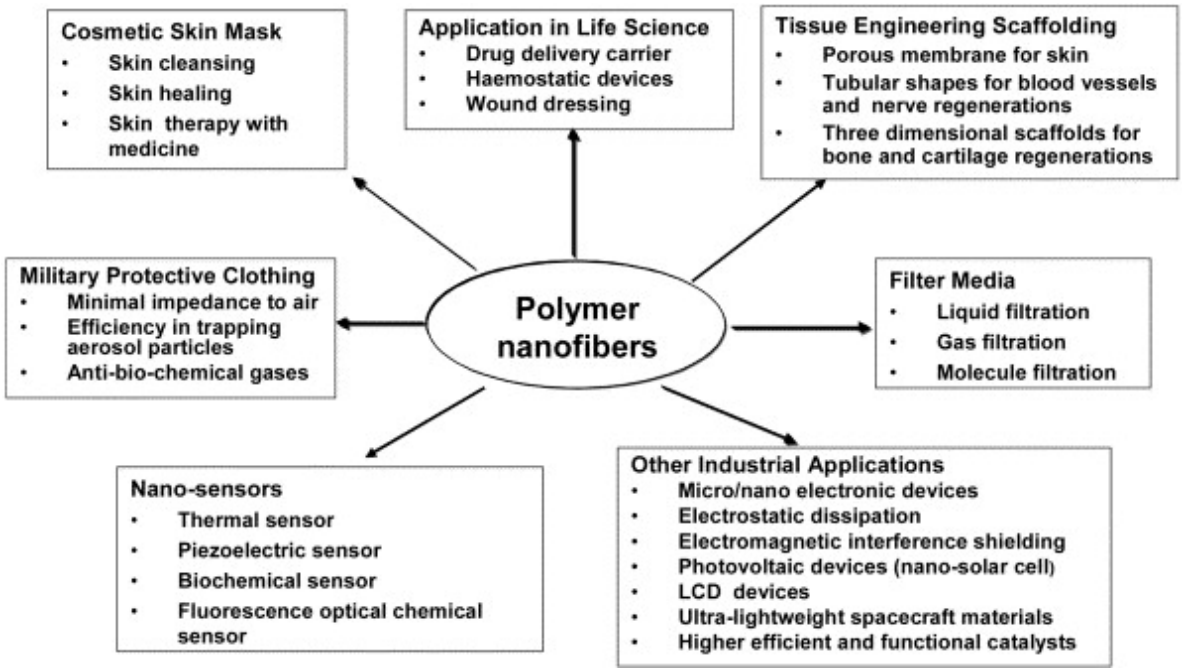


Fig. 1. Effect of **(a)** molecular weight and **(b)** volume fraction on bead schematic morphology and related SEM images.

Aslanzadeh, S.; Ahvazi, B.; Boluk, Y.; Ayranci, C. *Journal of Applied Polymer Science* **2016,** 133, (44).

Electrospun nanofibers: solving global issues



Ramakrishna, S., Fujihara, K., Teo, W.E., Yong, T., Ma, Z. and Ramaseshan, R., 2006. Electrospun nanofibers: solving global issues. *Materials today*, *9*(3), pp.40-50.

Huang, Z.M., Zhang, Y.Z., Kotaki, M. and Ramakrishna, S., 2003. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites science and technology*, *63*(15), pp.2223-2253.

Research on electrospinning

Polymer solutions

- Operation conditions
  - applied voltage
  - polymer solution flow rate at nozzle exit,
  - fiber collection distance,
  - nozzle diameter ,
  - relative humidity,
  - temperature;
- Properties of polymer solutions
  - viscoelasticity,
  - surface tension,
  - density, conductivity,
  - dielectric constant,
  - permittivity.

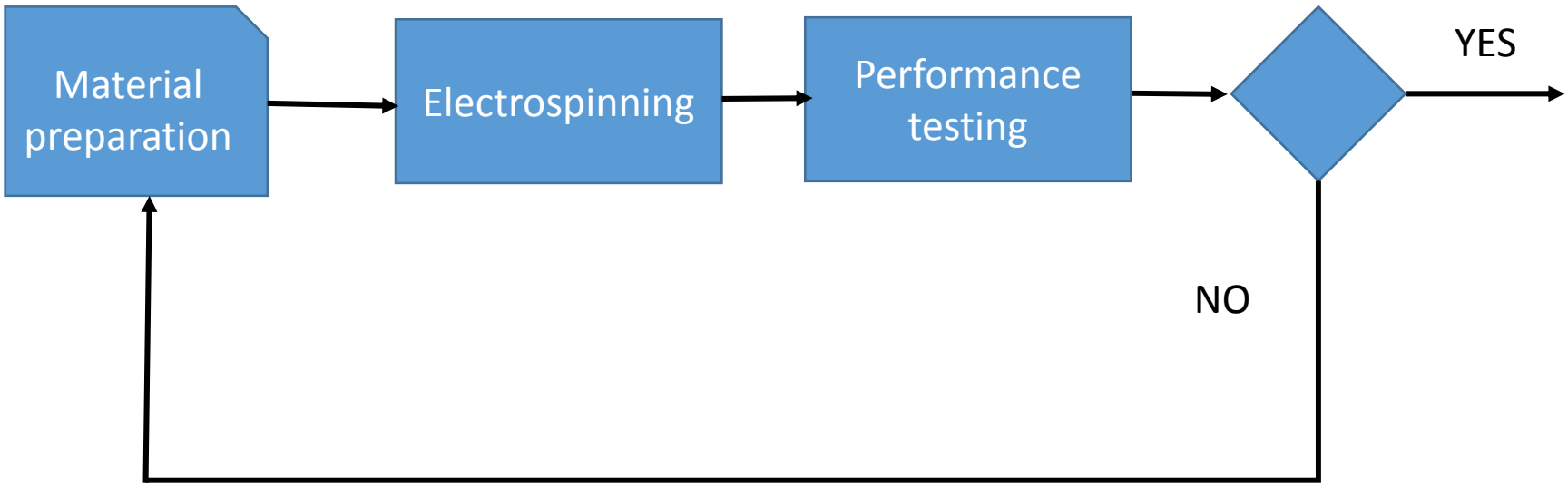
Nanoparticles in polymer solutions

- Particle morphology
- Particle-solvent interactions
- Particle-polymer interactions
- Dispersion
- Conductivity
- Dielectric constant
- Particle concentration

Reneker, D.H., Yarin, A.L., Zussman, E. and Xu, H., 2007. Electrospinning of nanofibers from polymer solutions and melts. *Advances in applied mechanics*, *41*, pp.43-346.

Current approach on electrospinning of colloidal systems in polymer solutions

Black box model



Electrospinning of nanoparticles in polymer solutions

Two objectives, two concentration regimes

1. Electrospinning of nanoparticles and use polymer as a processing aid

   Particle concentrations as high as possible

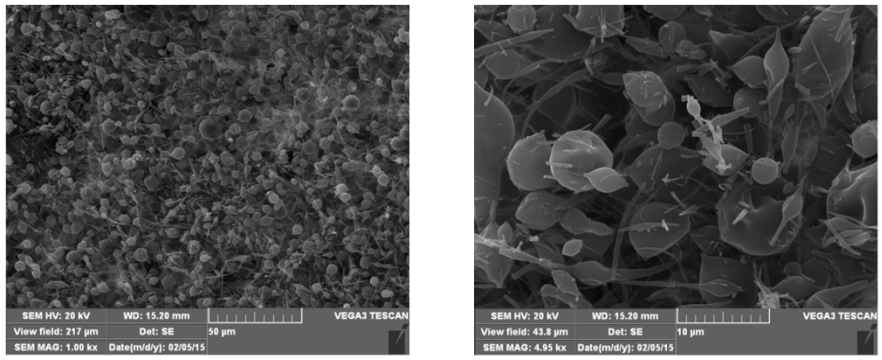
   Polymer concentration as low as possible

2. Improve physical properties of fibers

   Particle concentration <5%

Electrospinning of lignin

(a) $\phi_{SFSL} = 0.58$



(b) $\phi_{SFSL} = 0.63$

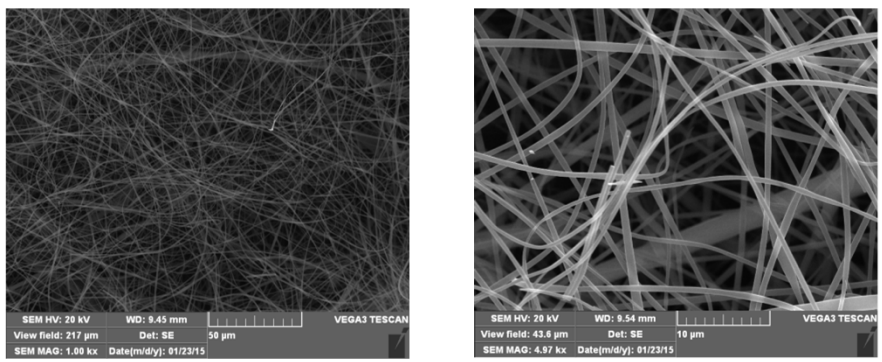
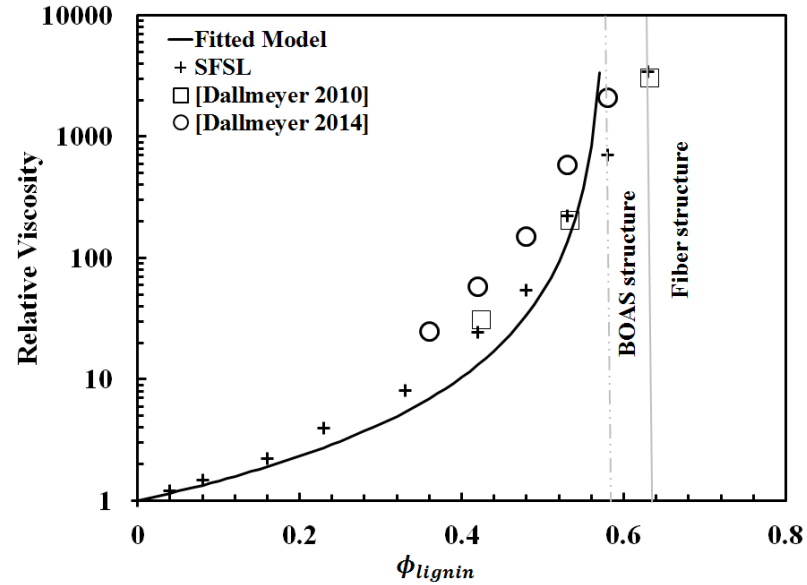


Fig. 1. (a) SEM images of the resulting materials at $\phi_{SFSL} = 0.58$ with Beads-On-A-String (BOAS) structure; **(b)** SEM image of the resulting material at $\phi_{SFSL} = 0.63$, fiber structure with the average diameter of 620 nm.

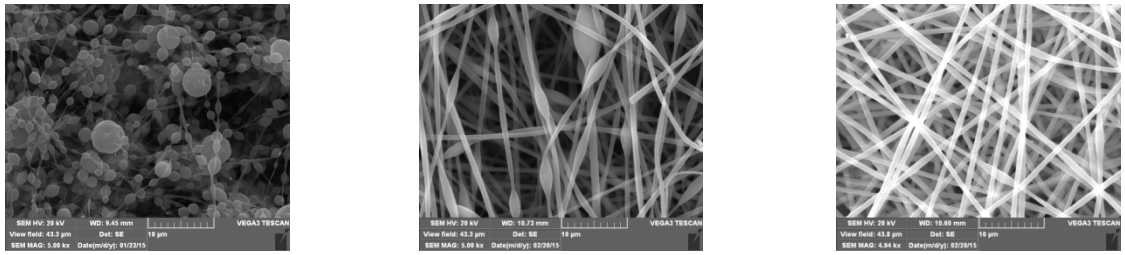


Aslanzadeh, S.; Zhu, Z.; Luo, Q.; Ahvazi, B.; Boluk, Y.; Ayranci, C. *Macromolecular Materials and Engineering* **2016,** 301, (4), 401-413.

PEO as a processing aid in lignin electrospinning

(a) Effect of different PEO Molecular weight, $\phi_T = 0.32$, $\phi_{PEO} = 0.0015$

Mv 1,000 kDa **Mv 2,000 kDa** **Mv 5,000 kDa**



(b) Effect of different PEO volume fraction, $\phi_T = 0.32$, PEO Mv = 1,000 kDa

$\phi_{PEO} = 0.0015$ $\phi_{PEO} = 0.0030$ $\phi_{PEO} = 0.0037$ $\phi_{PEO} = 0.0045$

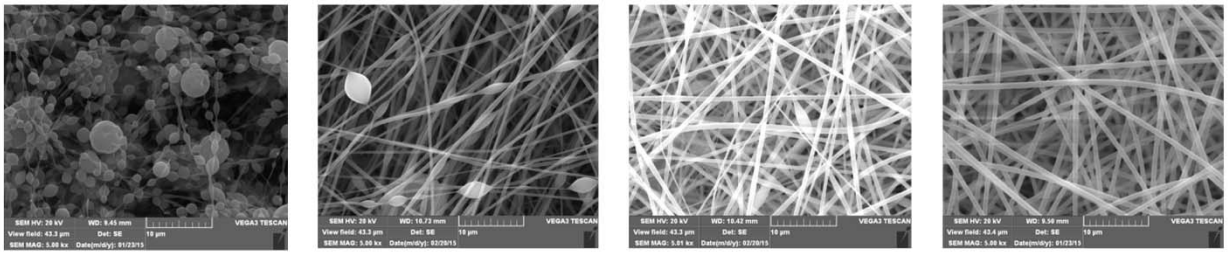


Fig. 1. Effect of **(a)** molecular weight and **(b)** volume fraction on bead schematic morphology and related SEM images.

Degradation of PEO due to elongational stretch

According to theoretical prediction, the onset of polymer stretching occurs when $\dot{\varepsilon}\tau_p \simeq 0.5$

$\dot{\varepsilon}\tau$ reached up to 50, which signified the extreme stretching of polymer chains during the electrospinning of 6% aqueous PEO (M_w= 400 kDa) solution (Reneker)

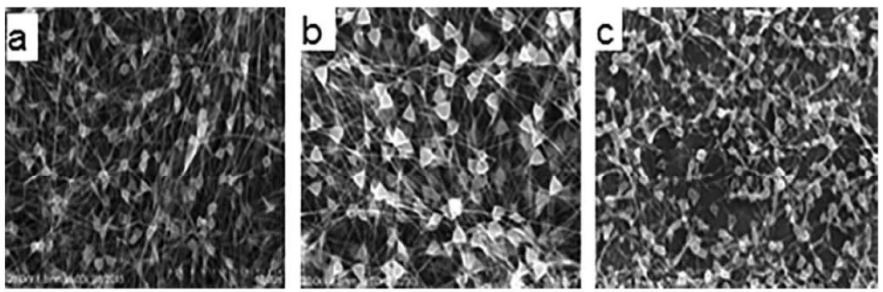


FIGURE 1 SEM images of PEO meshes. (a) PEO-5000 kDa mesh; (b) PEO-2000 kDa mesh; (c) PEO-1000 kDa mesh.

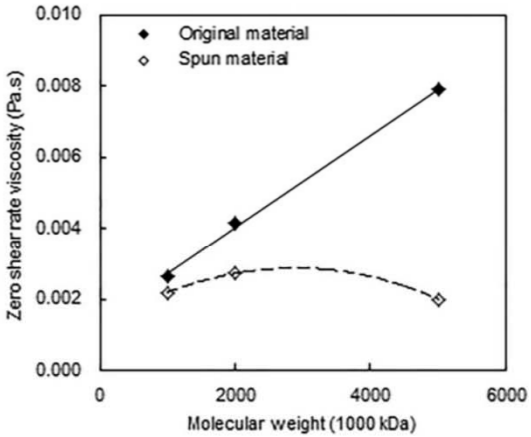
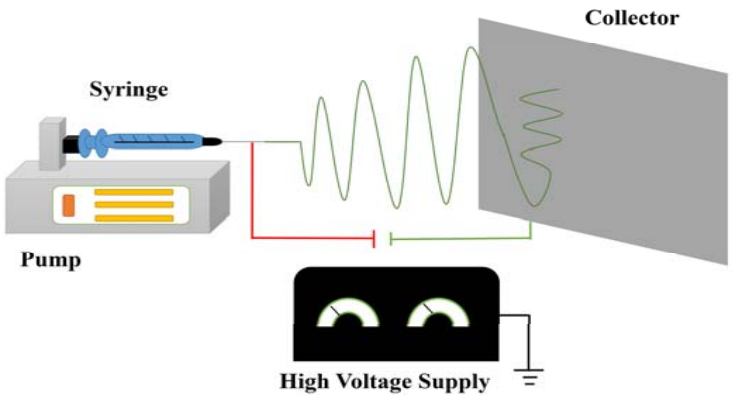


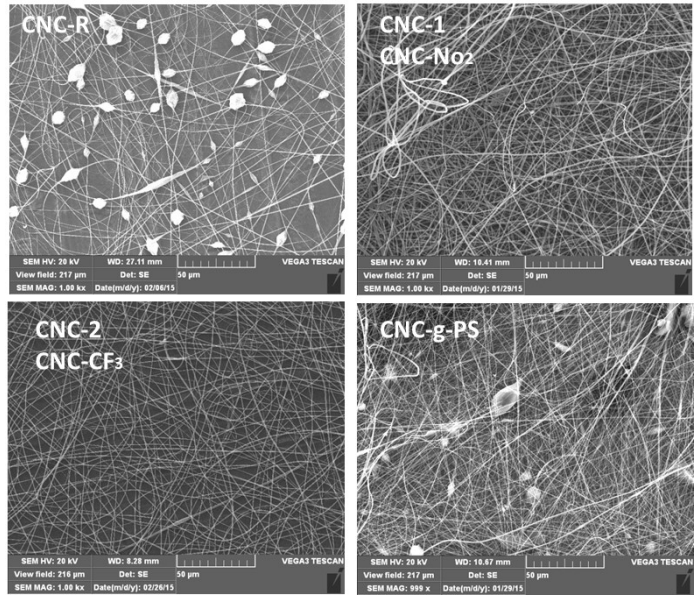
FIGURE 2 Rheological behaviors of 0.2 wt% aqueous solutions of PEO before and after electrospinning.

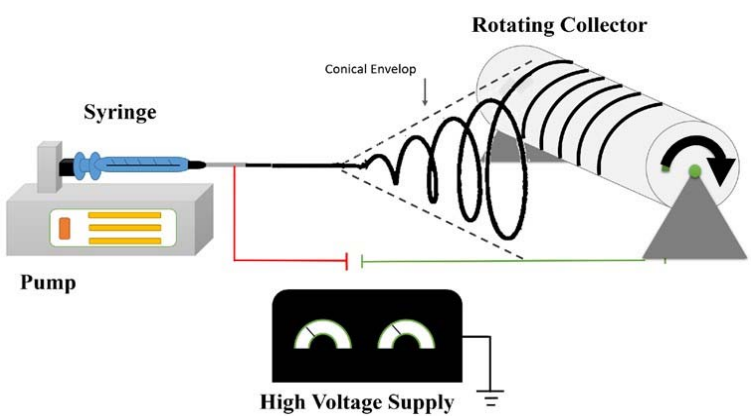
Sun, C., Ayranci, C., Chen, Y. and Boluk, Y., 2017. Can Extensional Flow Rupture Macromolecules in an Electrospinning Process?. *Journal of Polymer Science Part B: Polymer Physics*, *55*(14), pp.1051-1054.

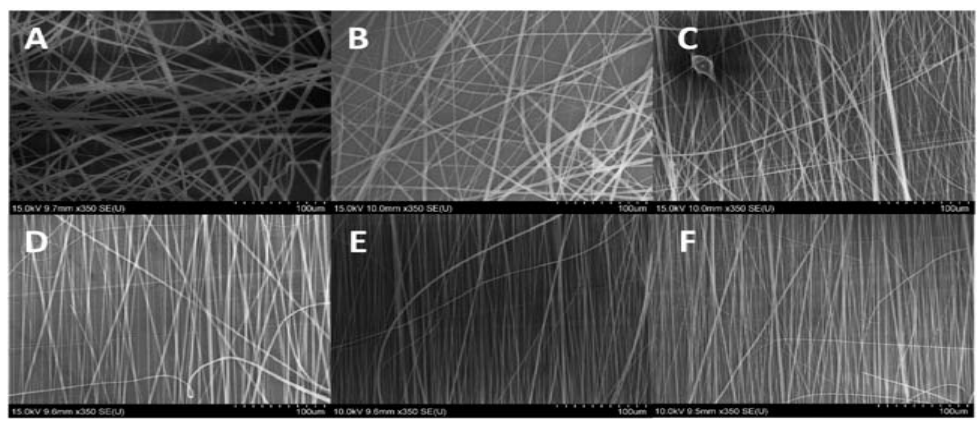
Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. Journal of Applied physics 2000, 87, 4531-4547.

Electrospinning of nonwoven webs vs. aligned fibers





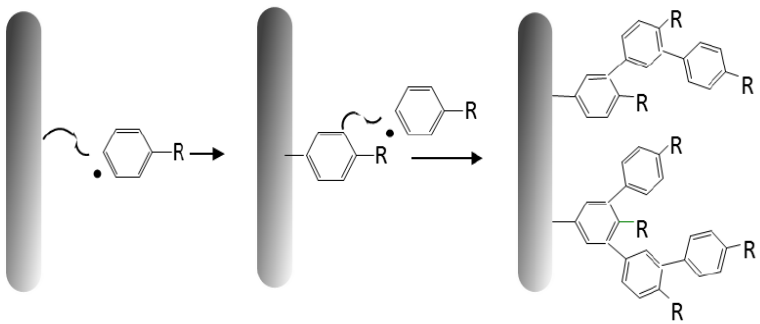




Surface functionalization of CNC

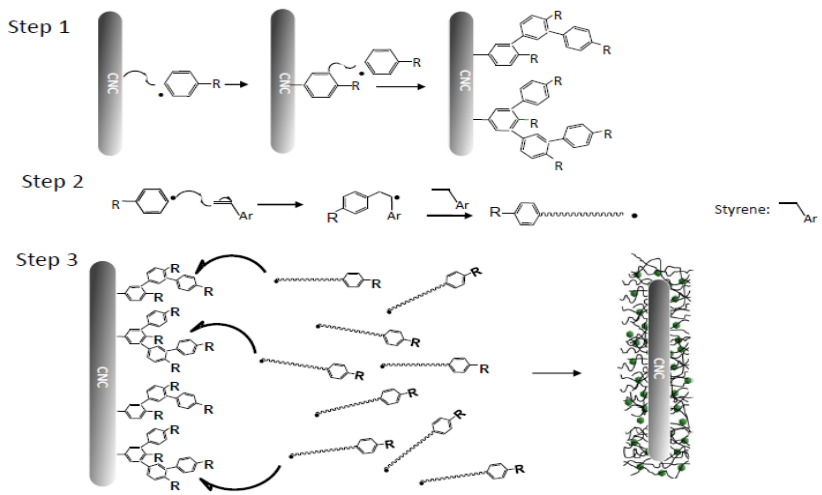
- Surface modification by
  - nitro benzene (CNC-1)
  - trifluoromethyl benzene (CNC-2)

- Grafting polystyrene by using "Graftfast Process"



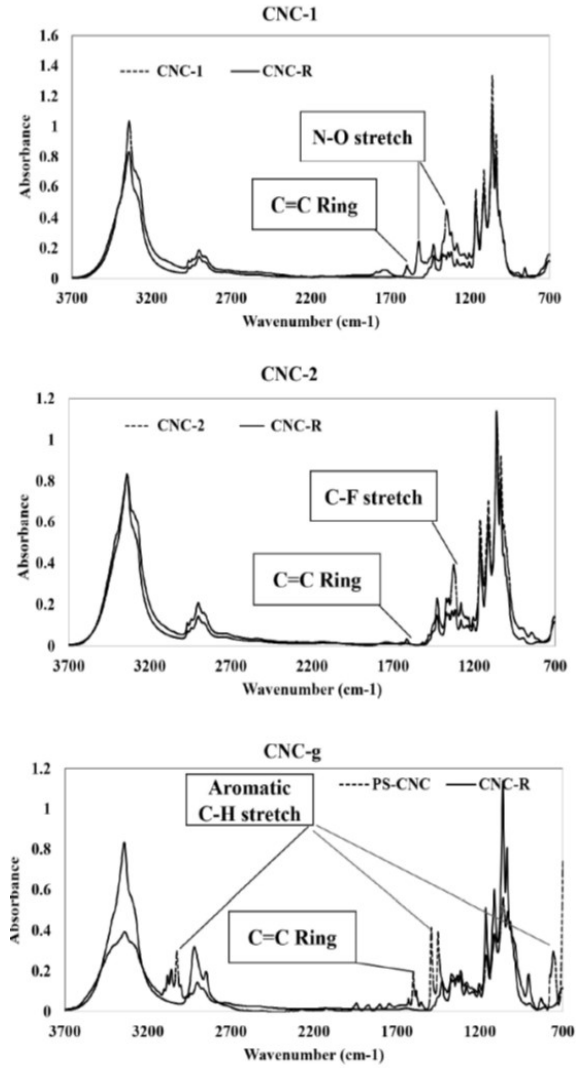
A. Mesnage, S. Esnouf, P. Jégou, G. Deniau, S. Palacin, Understanding the redox-induced polymer grafting process: A dual surface-solution analysis, Chemistry of Materials, 22 (2010) 6229-6239.

V. Mévellec, S. Roussel, L. Tessier, J. Chancolon, M. Mayne-L'Hermite, G. Deniau, P. Viel, S. Palacin, Grafting polymers on surfaces: A new powerful and versatile diazonium salt-based one-step process in aqueous media, Chemistry of Materials, 19 (2007) 6323-6330.

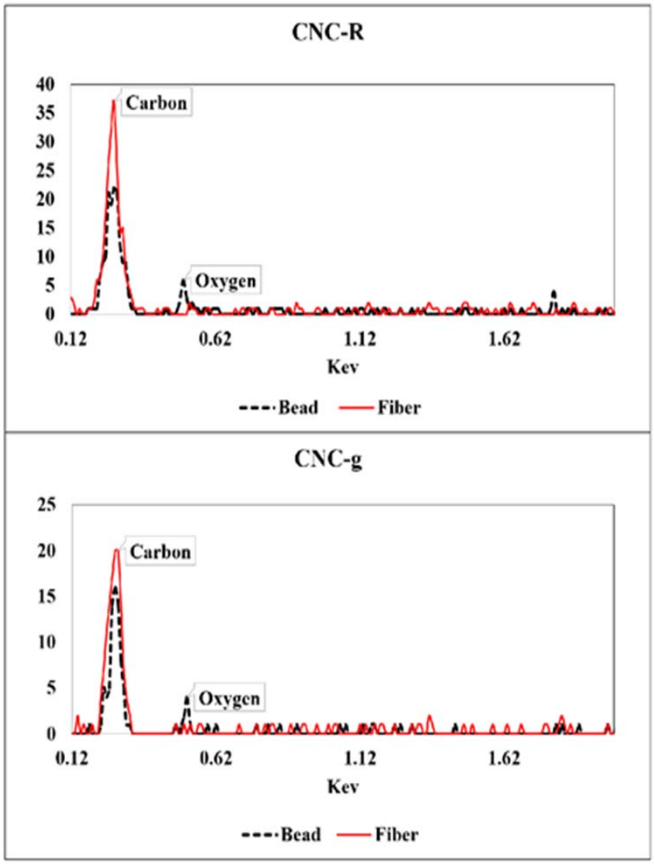


Surface functionalization of CNC

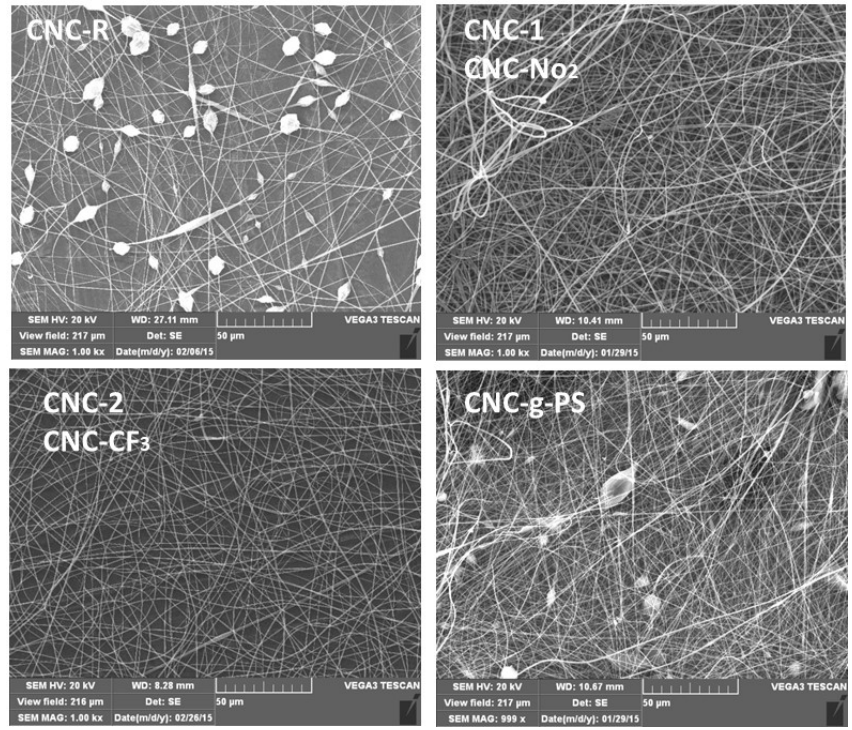
FTIR spectra of surface modified CNCs:
CNC-1 (a),
CNC-2 (b)
CNC-g (c)



Electrospinning on a stationary surface

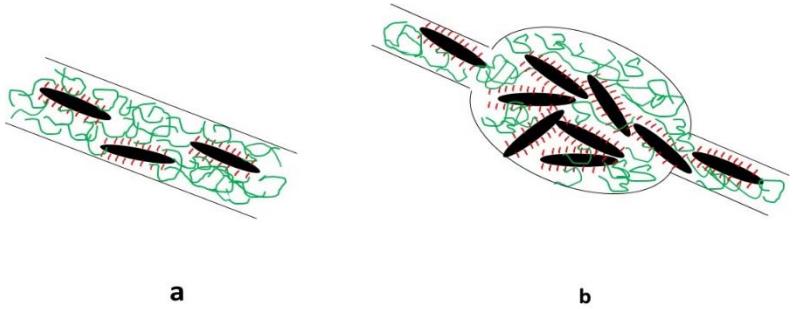


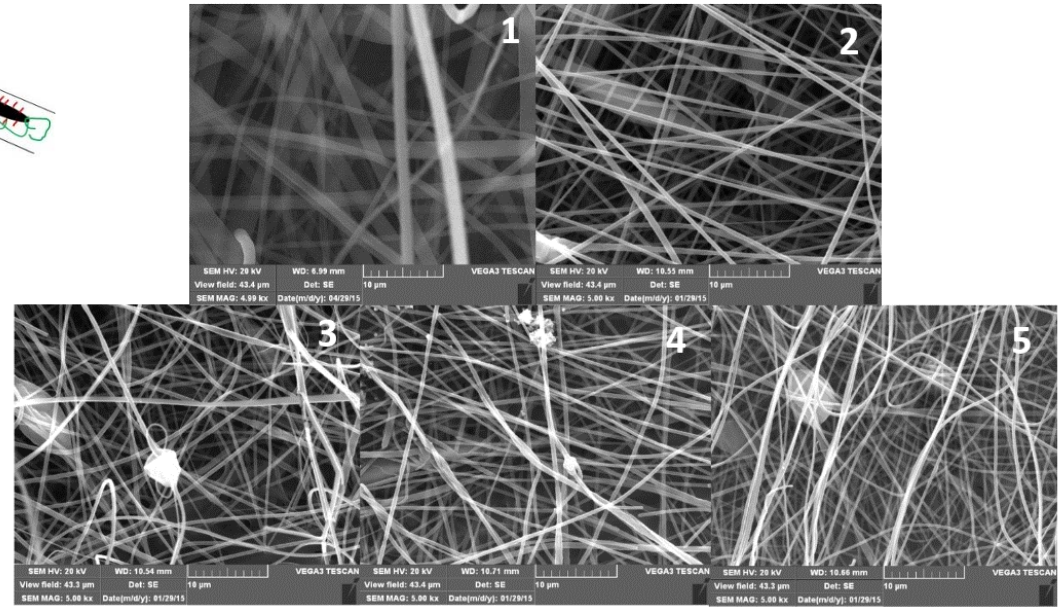
Energy-dispersive X-ray spectroscopy (EDX) of CNC-R and CNC-g



SEM images of polystyrene nanofibers containing: 1%wt. CNC in PS fiber: CNC-R (A); CNC-1 (B); CNC-2 (C); CNC-g (D).

Electrospinning of PS grafted CNC/PS fibers on a stationary surface





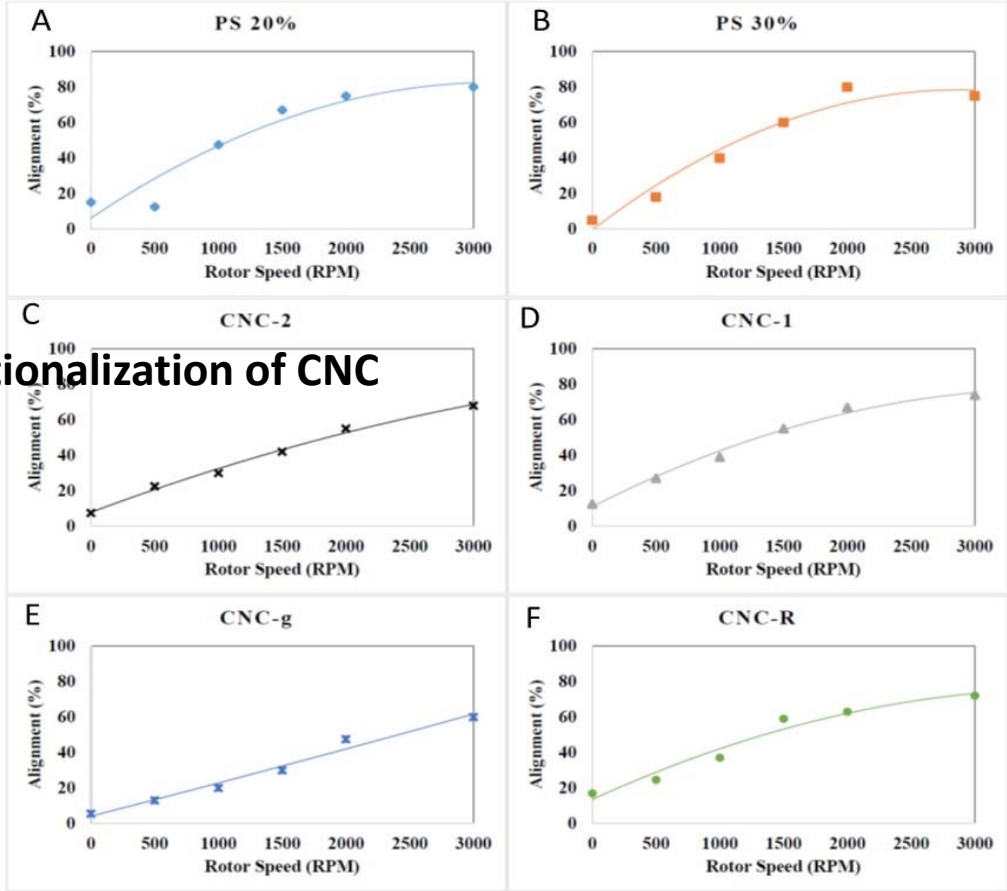
SEM images of the polystyrene nanofiber containing CNC-g at concentration levels of: 0.0 wt. % (1); 0.5 wt. % (2) 1wt. % (3) 1.5 wt. % (4) 2 wt. % (5).

Kalantari, M., Du, R., Ayranci, C. and Boluk, Y., 2018. Effects of interfacial interactions and interpenetrating brushes on the electrospinning of cellulose nanocrystals-polystyrene fibers. *Journal of colloid and interface science*, *528*, pp.419-430.

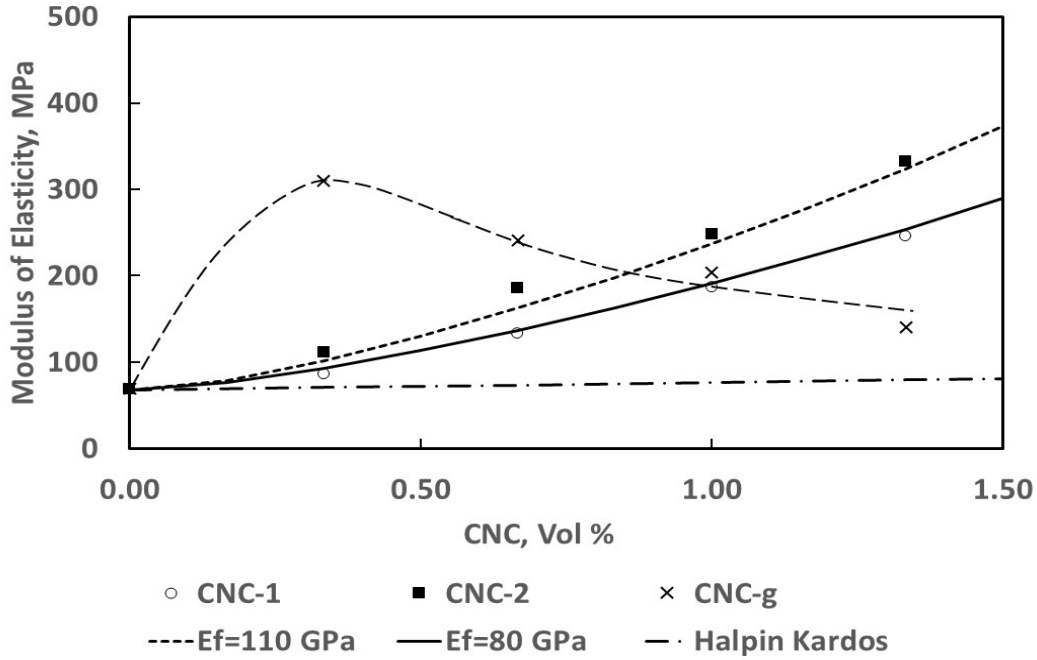
Orientations of electrospun fibers as a function of rotation speed of drum

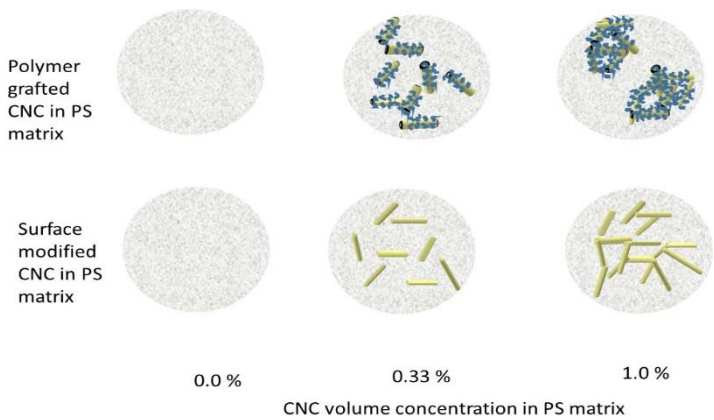
- Neat PS fibers electro-spun from 20% PS solution in DMF (A);
- Neat PS fibers electro-spun from 30% PS solution in DMF (B);
- CNC-2/PS fibers electrospun from 0.2 % CNC-2 and 20% PS in DMF mixtures (C);
- CNC-1/PS fibers electrospun from 0.2 % CNC-1 and 20% PS in DMF mixtures (D);
- CNC-g/PS fibers electrospun from 0.2 % CNC-g and 20% PS in DMF mixtures (E);
- CNC-R/PS fibers electrospun from 0.2 % CNC-R and 20% PS in DMF mixtures (F).

Surface functionalization of CNC



Comparison of experimental modulus of elasticity data with Ouali's percolation and Halpin-Kardos mean-field models





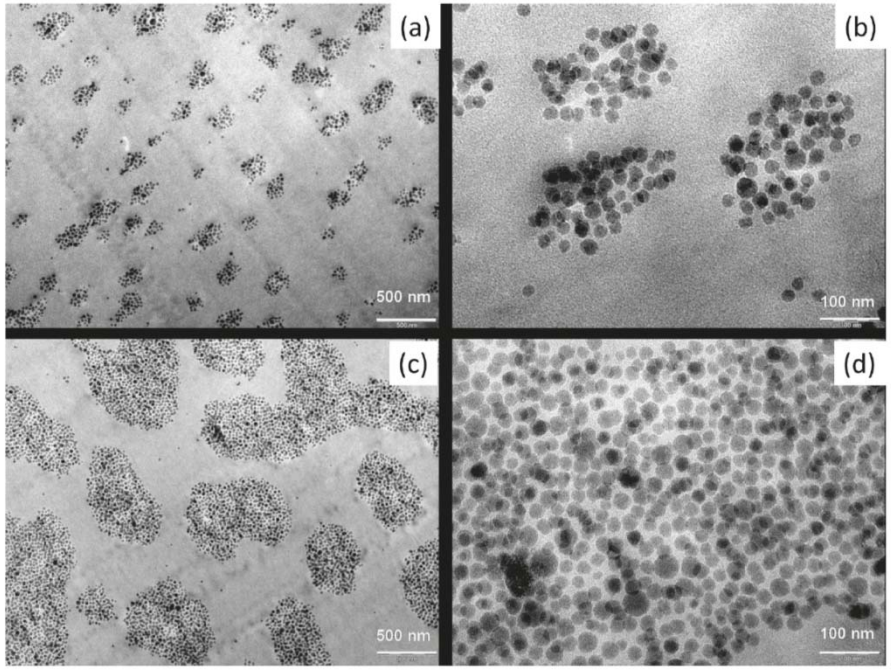


Figure 2. Transmission electronic microscopy on the nanocomposites ($M_{n\ matrix}$ = 140 000 g/mol) filled with 4% v/v of grafted silica particles ($M_{n\ grafted}$ = 24 000 g/mol) (the grafted-free chain length ratio R = 0.17) at low (a) and medium (b) magnification and filled with 11% v/v of grated particles at low (c) and medium (d) magnification.

Chevigny, C.; Dalmas, F.; Di Cola, E.; Gigmes, D.; Bertin, D.; Boué, F. o.; Jestin, J., Polymer-grafted-nanoparticles nanocomposites: dispersion, grafted chain conformation, and rheological behavior. Macromolecules 2010, 44 (1), 122-133

Concluding remarks

- Collecting on a rotating drum with a variable speed is good method to align CNC/PS fibers.
- Alignment at a constant speed is controlled by PS/CNC/DMF mixture characteristics.
- Aligned fibers are suitable to test the mechanical properties.
- In the case composites of polymer grafted CNC: Less is more

Thank you

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