National Institute for Nano Engineering

SAND2011-5217C

Thermally Tunable Surface Wettability of Electrospun Fiber Mats: Polystyrene/Poly(N-isopropylacrylamide) Blended Vs. Crosslinked Poly(N-isopropylacrylamide-co-Methacrylic acid)

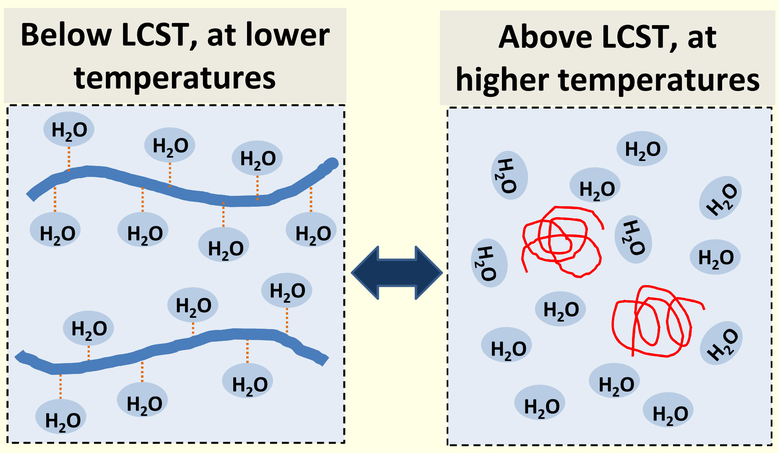
Palanikkumaran (PK) Muthiah[‡], Jeff Potts[§], Thu Doan[†], Sarah Hoppe[†], Timothy J. Boyle[†] and Wolfgang Sigmund[‡]

[‡]University of Florida, Gainesville FL 32611, [§]University of Texas, Austin 78712, and [†]Sandia National Laboratories, Albuquerque NM 87185

Abstract

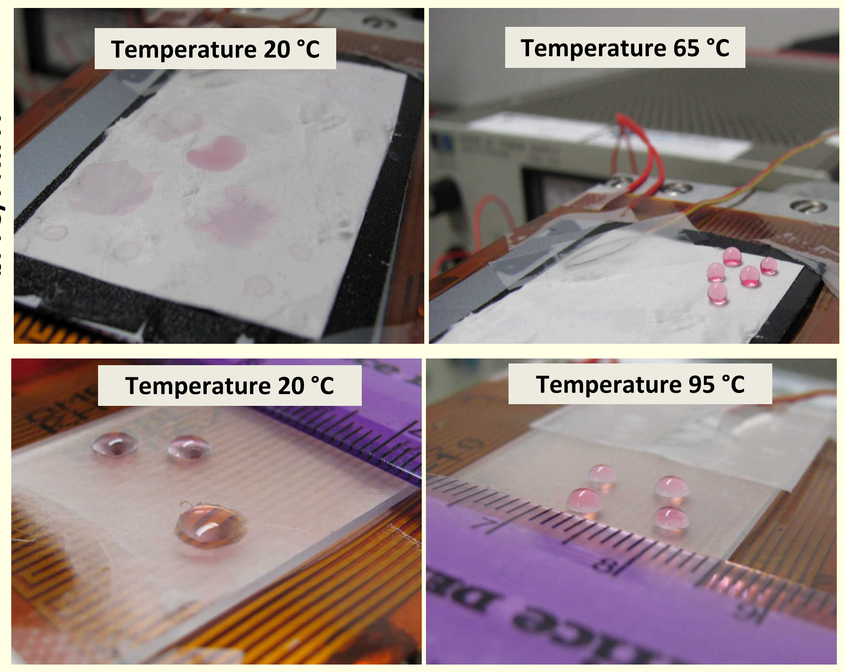
We report the temperature-tunable surface wettability of polystyrene (PS)-poly(N-isopropylacrylamide) (PNIPA) (bl-PS/PNIPA) and poly(N-isopropylacrylamide)-co-methacylic acid (PNIPAMAA) (xl-PNIPAMAA) fiber mats prepared by electrospinning. bl-PS/PNIPA fiber mat was obtained by blending and electrospinning the PS and PNIPA polymer solutions where as xl-PNIPAMAA fiber mat was obtained by preparing and electrospinning a formulation of PNIPAMAA solution with crosslinker. PNIPAMAA fiber mat was further heat treated at 160 C to produce a crosslinked network structure. These fiber mats were characterized for temperature dependent surface wettability by sessile drop method in Goniometer. Both the fiber mats showed temperature-tunable surface wettability and this property was reversible for the tested 5 cycles. Temperature responsive surface wettability of these fiber mats can be further explained from the polymer chemistry and Cassie-Baxter model.

Temperature Responsive Surface Wettability



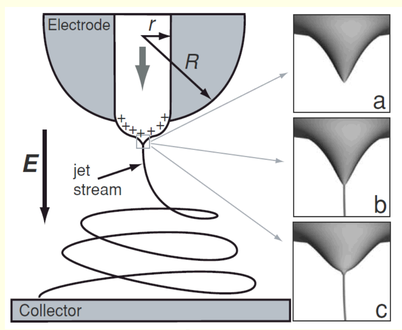
Schematic showing the hydrogen bonding of water and polymer molecules are temperature dependent

- LCST – Lower critical solution temperature
- LCST of Poly(N-isopropylacrylamide) (PNIPA) is at 32° C in water
- One state is in soluble form

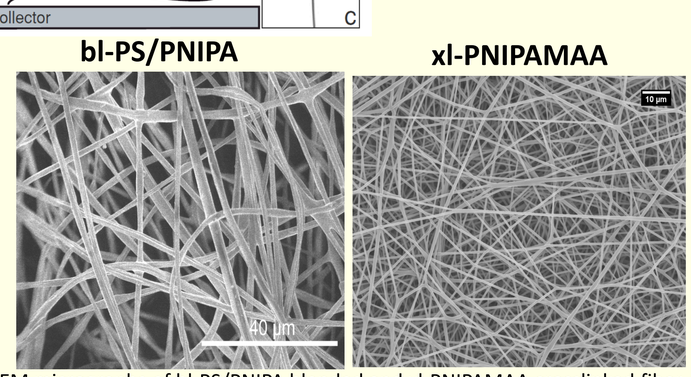


PS and PNIPA blended (bl-PS/PNIPA) and PNIPAMAA copolymer crosslinked (xl-PNIPAMAA) fiber mats showing the temperature responsive surface wettability

Electrospinning

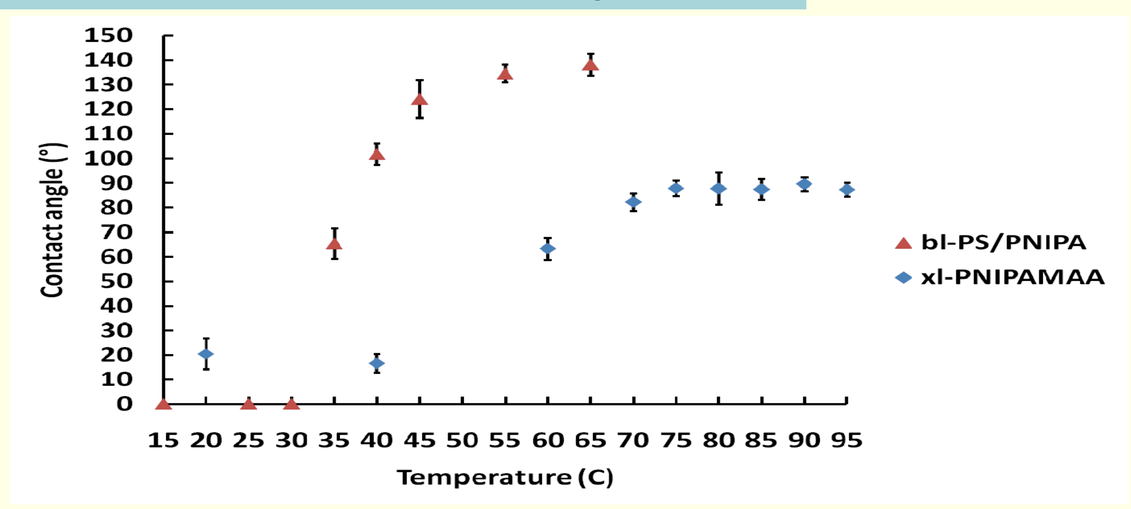


- Simple, versatile, continuous process
- Fiber diameter: from few microns to 100 nm
- High surface area to mass ratio
- Vast potential applications



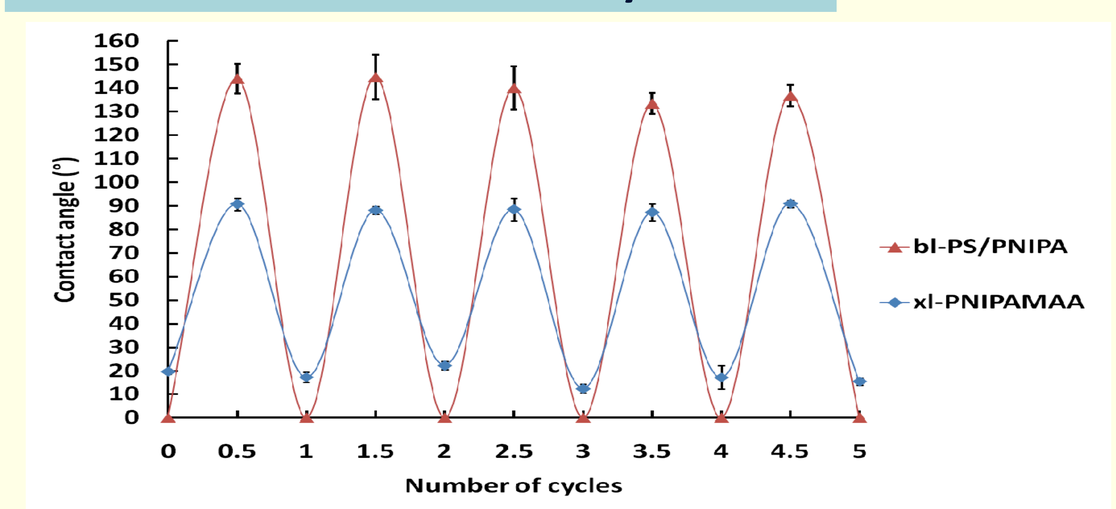
SEM micrographs of bl-PS/PNIPA blended and xl-PNIPAMAA crosslinked fiber mats. The average fiber diameter of bl-PS/PNIPA and xl-PNIPAMAA was 1947 and 870 nm, respectively.

Reversible Extreme Wettability



- Temperature responsive switchability of bl-PS/PNIPA and xl-PNIPAMAA fiber mats. bl-PS/PNIPA was studied between 15 °C and 65 °C where as xl-PNIPAMAA was studied between 20 °C and 95 °C

Reversible Extreme Wettability Cont.

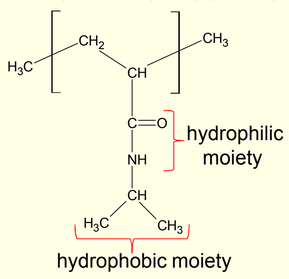


- Temperature responsive reversibility of bl-PS/PNIPA and xl-PNIPAMAA fiber mats. bl-PS/PNIPA was studied at 15 °C and 65 °C where as xl-PNIPAMAA was studied at 20 °C and 95 °C

Mechanism

PNIPA Chemistry

Ex. Poly(N-isopropylacrylamide) (PNIPA)



Hydrogen bonds break with water and forms intra molecularly (globular structure)

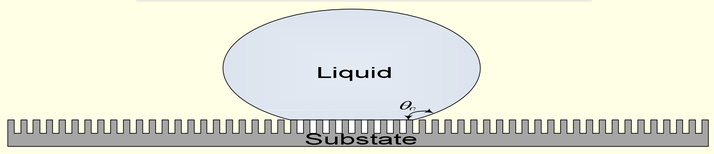
LCST = 32 °C

Hydrogen bonds form with water (Chain extends)

>LCST Van der Waals interactions

- **Competition between intra and inter molecular hydrogen bonding**

Cassie-Baxter model



- Cassie-Baxter model describes the wetting behavior of vapor pockets trapped between the grooves and the liquid droplet.

$$\cos(\theta_{CB}) = f_s \cdot (\cos(\theta_c) + 1) - 1$$

ϑ_{CB} = apparent contact angle on a rough surface
ϑ_c = intrinsic contact angle on the original smooth surface
f_s = fraction of the wet solid contact area

Summary

- bl-PS/PNIPA and xl-PNIPAMAA fiber mats have been prepared by electrospinning and their REW properties were characterized
- bl-PS/PNIPA fiber mat surface was more sensitive to REW properties and occured in a relatively narrower temperature range than xl-PNIPAMAA fiber mat surface
- Mechanism behind REW properties is reversible hydrogen bonding of PNIPA in combination with the Cassie-Baxter style micro/nano surface architecture
- **Potential application for these fiber mats is in car tires**
- **Ph.D. Thesis Title: High Speed Switching of Responsive Polymers**

Sandia is a multiprogram laboratory operated by Sandia Corporation a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000

Sandia National Laboratories