Dynamics and thermodynamics of polymer in nanoparticle packings under varying humidity conditions

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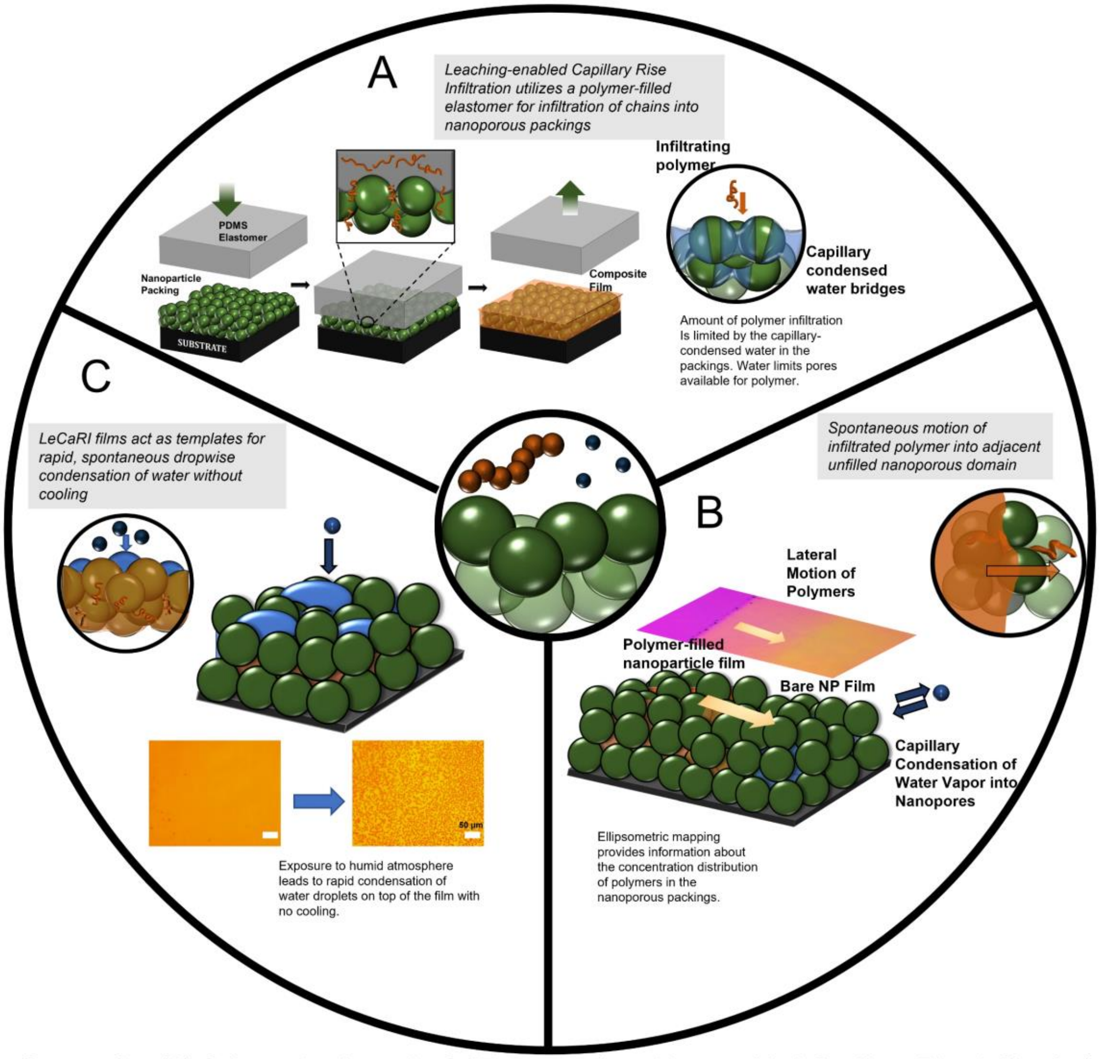
Infiltration of polymers into nanoparticle packings has emerged as a powerful strategy to prepare highly loaded composites with superb mechanical and transport properties. The high surface energy of the nanoparticles as well as the high curvature of the pores give rise to complex interaction of the nanoparticle packings with polymer and water. Leaching-enabled capillary rise infiltration (LeCaRI) is a novel technique of making polymer composites by inducing motion of mobile polymers from polymer-filled gels into nanoparticle packing. This presentation will **describe the dynamics and thermodynamics of polymer** infiltrated into **nanoparticle packings via LeCaRI under varying humidity conditions**. A hydrophobic low glass transition temperature polymer, polydimethylsiloxane (PDMS), is loaded into a PDMS elastomer. The PDMS-filled elastomer is contacted with a packing of SiO_2 nanoparticles to induce infiltration of PDMS into the pores of the SiO_2 nanoparticle packing by capillary forces**. Atmospheric humidity controls the amount of polymer infiltrated in the pores due to capillary condensation of water.** When polymer infiltration is localized by using patterned PDMS stamps, **polymer can then spread laterally to unfilled regions**. This room temperature, spontaneous lateral motion of polymer can be tracked to understand interfacial polymer diffusion under confinement. Results on polymer diffusivity inside silica particle packings shows that **higher humidity, unexpectedly, leads to faster spreading of the polymers within the packings** possibly due to reduced particle-polymer friction with water coverage on particle surface. Finally, we show that when the polymer-filled nanoparticle packings are exposed to humid atmosphere, heterogeneity in film surface composition along with unique nano structures at the surface leads to **spontaneous drop-wise condensation of water without any subcooling**. The interaction of composites with their environment can thus be harnessed for heat recovery, atmospheric water harvesting, and humidity sensing applications.



(clockwise from top) – (A) Schematic shows LeCaRI process(Leaching-enabled Capillary Rise Infiltration) – PDMS gels are made to contact nanoparticle(NP) packings – mobile chains move from gel into pores of packing making a composite film. Polymer fraction in composites is controlled by the amount of capillary condensed water in the packings. (B) When polymer is localized to one region of the packing(orange in schematic, pink in image), it spreads out into the adjoining region. The spreading of polymers occurs alongside capillary condensation of water into the nanopores. (C) LeCaRI films exposed to atmosphere are covered spontaneously and rapidly by condensed water droplets.