

## Ultra Strong, Thermoresponsive Double-Network Hydrogels

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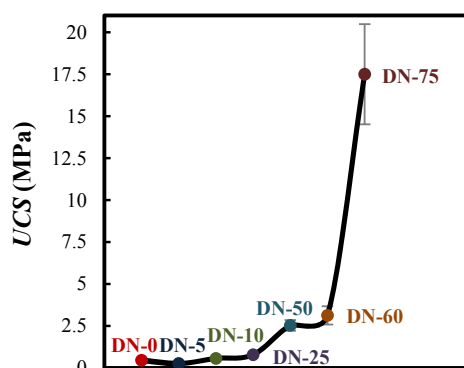
**Statement of Purpose:** Thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels reversibly switch from a water-swollen, hydrophilic state to a deswollen, hydrophobic state.<sup>1</sup> Due to their unique volume phase transition temperature (VPTT, ~33-35°C), PNIPAAm hydrogels have been widely studied for biomedical uses including microfluidic actuation, separation, controlled drug delivery and cell sheet tissue engineering. Thus, PNIPAAm-based hydrogels may be useful as “self-cleaning” membranes for implanted glucose biosensors.

PNIPAAm hydrogels are limited by their poor mechanical properties and slow responsiveness. One effective approach to overcome these issues is using a double-network (DN) hydrogel design.<sup>2</sup> DN PNIPAAm nanocomposite hydrogels containing polysiloxane nanoparticles have been previously reported.<sup>3</sup> In this study, PNIPAAm DN hydrogels were prepared with an ionizable comonomer, 2-acrylamido-2-methyl-propane-sulfonic acid (AMPS). Specifically, these DNs were comprised of tightly crosslinked, ionized 1<sup>st</sup> network [P(NIPAAm-co-AMPS)] and a loosely crosslinked, neutral interpenetrating 2<sup>nd</sup> network [PNIPAAm]. The weight % ratio of NIPAAm:AMPS (100:0 – 25:75) was systematically varied. The resulting changes to morphology, deswelling/re-swelling behavior and mechanical properties were evaluated and compared to single network (SN) and DN hydrogels containing no AMPS.

**Methods:** *Preparation of DN copoly(NIPAAm-AMPS) hydrogels.* **Step 1:** In a 50-mL round bottom (rb) flask equipped with a Teflon-covered stir bar, NIPAAm/AMPS (total weight equal to 1.0 g; wt% ratio of NIPAAm:AMPS = 100:0; 95:5; 90:10; 75:25; 50:50; 40:60 and 25:75), BIS (0.04 g), and Irgacure (0.08 g) were dissolved in DI water (7.0 g). Hydrogel sheets were prepared by pipetting the precursor solution into a rectangular mold formed by sandwiching polycarbonate spacers (1.5 mm thick) between two clamped glass microscope slides. The mold was submerged in an ice water bath (~7 °C) and subjected to UV light (UV-Transilluminator, 6 mw/cm<sup>2</sup>, 365 nm) for 30 min. After removal from the mold, the hydrogel sheet was rinsed with DI water and then soaked in DI water for 2 days with daily water changes to remove impurities. **Step 2:** The designated above hydrogel was soaked in a solution of NIPAAm (6.0 g), BIS (0.012 g), Irgacure-2959 (0.24 g), DI water (21.0 g) for 24 hr. The hydrogel sheet was then transferred to a rectangular mold (2.3 mm thick), photocured and purified as above. **Compression test.** Three discs (6 mm diameter) were punched from a single sheet with a die. Compressive tests were performed with an Instron 3340 at room temperature (RT). A swollen disc (6 mm diameter) was blotted with a Kim Wipe and clamped between the parallel plates with an initial pre-load force of ~0.5 N. Compressive strain

**Table 1.** Mechanical Properties

Notation	wt% ratio		%EL
	NIPAAm:	Modulus (kPa)	
DN-0	100:0	188 ± 7	52 ± 3
DN-5	95:5	192 ± 24	40 ± 2
DN-10	90:10	277 ± 60	52 ± 7
DN-25	75:25	341 ± 48	46 ± 1
DN-50	50:50	311 ± 35	73 ± 5
DN-60	40:60	303 ± 5	71 ± 5
DN-75	25:75	85 ± 18	95 ± 2



**Figure 1.** UCS of DN hydrogels

was applied at a rate of 1 mm/min until the disc fractured. The following parameters were determined: (1) compressive modulus; (2) ultimate compressive strength (UCS); and (3) % elongation at break (%EL).

**Results:** The compressive modulus of DN copoly(NIPAAm-AMPS) hydrogels increased to a maximum at **DN-25**. However, a further increase in AMPS caused a decrease in modulus (**Table 1**). The decrease is attributed to the high concentration of electrostatic forces which diminishes the effective crosslink density.<sup>4</sup> As AMPS content in 1<sup>st</sup> network increased from **DN-10** to **DN-60**, UCS and %EL steadily increased (**Table 1**, **Fig. 1**). The most notable was the UCS (~17.5 MPa) and %EL (~95) achieved by **DN-75**. The enhancement is attributed to the loosely crosslinked 2<sup>nd</sup> network, which effectively dissipates stress and prevents the potential crack propagation in the stiff and brittle 1<sup>st</sup> network.

**Conclusions:** Mechanical and thermosensitivity of PNIPAAm hydrogels was improved with a DN design and an electrostatic AMPS comonomer. For **DN-75**, UCS and %EL were dramatically enhanced. Future work will include adding hydrophilic NVP in the 2<sup>nd</sup> network to increase the VPTT to above human body temperature.

**Reference:** 1. Wu XS. *J Polym Sci.* 1992;30:2121-2129. 2. Gong JP. *Adv Mater.* 2003;15:1155-1158. 3. Fei R. *Soft Matter.* 2011;8:481-487. 4. Okay O. *Polymer.* 2002;43:1215-1221.