Hybrid pNIPAAm hydrogels cross-linked by acid-activated Laponite®: Impact of nanoplatelets on swelling and thermodynamic properties

Samoylenko Olena[1], Samchenko Yurii[2], Solovieva Olena[2],· Kernosenko Liudmyla[2],· Poltoratskaya Tetiana[2] ,· Pasmurtseva Natalia[2],· Ganusevich Irina[1],· Vashchenko Olga[3],· Lisetski Longin[3], · Lebovka Nikolai[2]

[1]R.E. Kavetsky Institute of Experimental Pathology, Oncology and Radiobiology, NASU, Kyiv, Ukraine

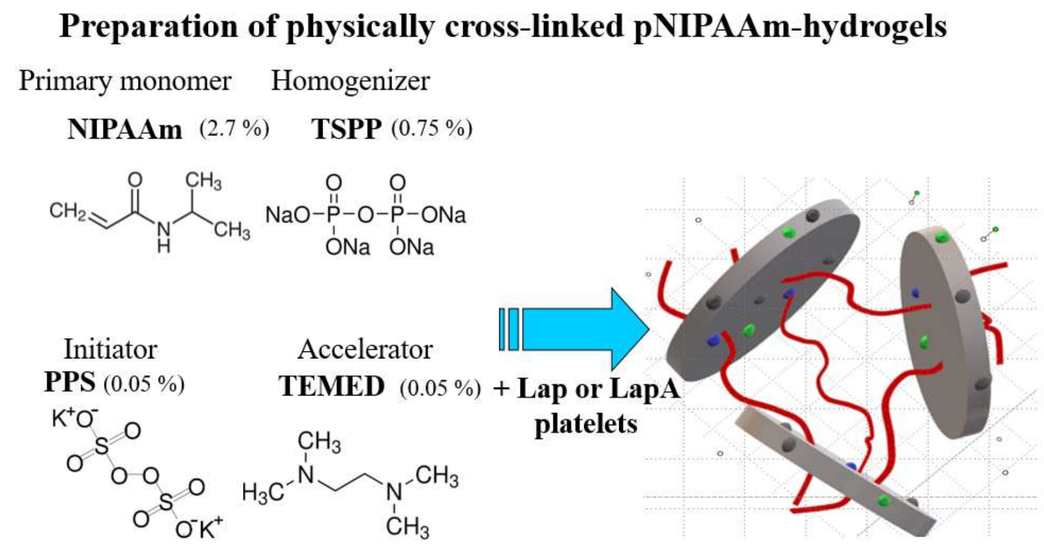
[2]F.D. Ovcharenko Biocolloidal Chemistry Institute, NASU Kyiv, Ukraine

[3]Institute for Scintillation Materials of STC "Institute for Single Crystals", NAS of Ukraine, Kharkov, Ukraine
e-mail: lcsciencefox@gmail.com

Aims: Study of the behavior of hybrid poly(N-isopropylacrylamide) (pNIPAAm) hydrogels cross-linked with Laponite® (Lap) and acid-activated Laponite® (LapA) platelets. The focus is on understanding how these fillers affect swelling and thermal responsiveness, key for applications in drug delivery, wound healing, and other biomedical uses.

Materials: Laponite RD® (Rockwood Additives Ltd., UK) (Lap), Poly(n-isopropylacrylamide) (Sigma–Aldrich, USA) (pNIPAAm)
The nanostructured clay fillers were incorporated into the hydrogel matrix to explore their role in modifying pore structures, swelling behavior, and thermal transitions. Nitrogen adsorption methods, employing BET and t-plot techniques, were applied to evaluate surface area contributions from nanopores, micropores, and external pores.

Characterization: The nitrogen adsorption based on application of BET and t-plot techniques were used for estimation of the contribution of small nanopores, micropores and external pores in surface area. Swelling studies showed that Lap and LapA increase water uptake compared to neat gels, while all samples collapsed near LCST (≈33–34 °C). DSC revealed broad endothermic peaks around 34.8 °C, with distinct enthalpy values reflecting different interactions between pNIPAAm chains and clay platelets.



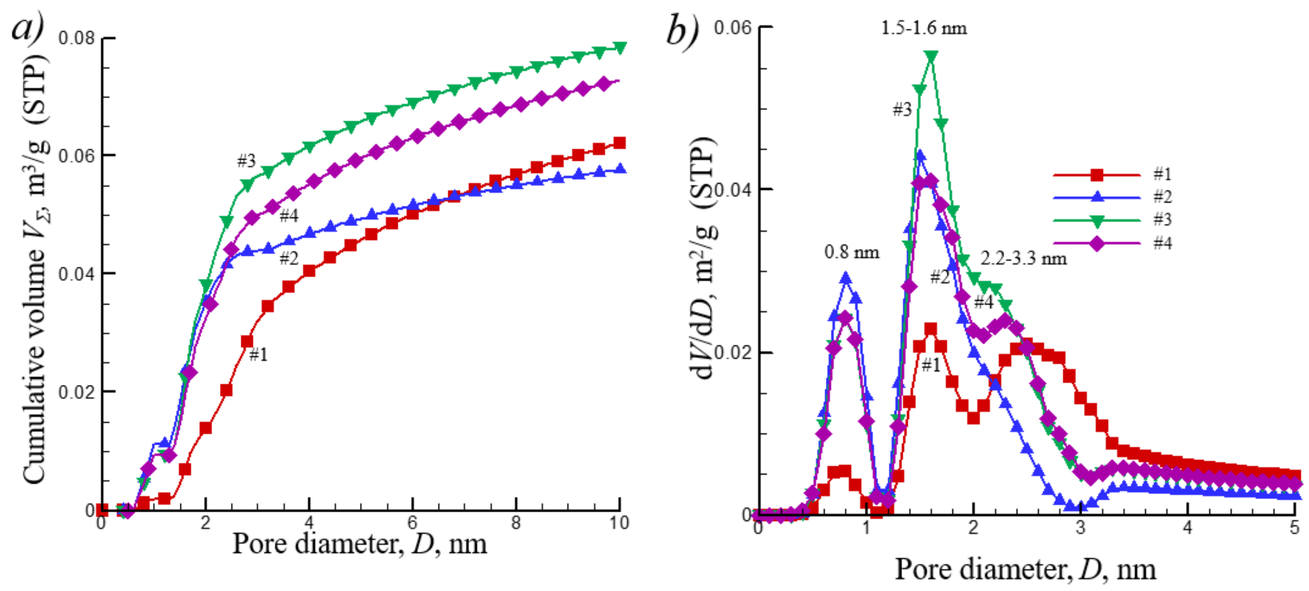


Fig. 1. Cumulative volumes V_Σ (a) and pore distribution functions dV/dD (b) for the samples #1(Lap), #2-4 (LapA)
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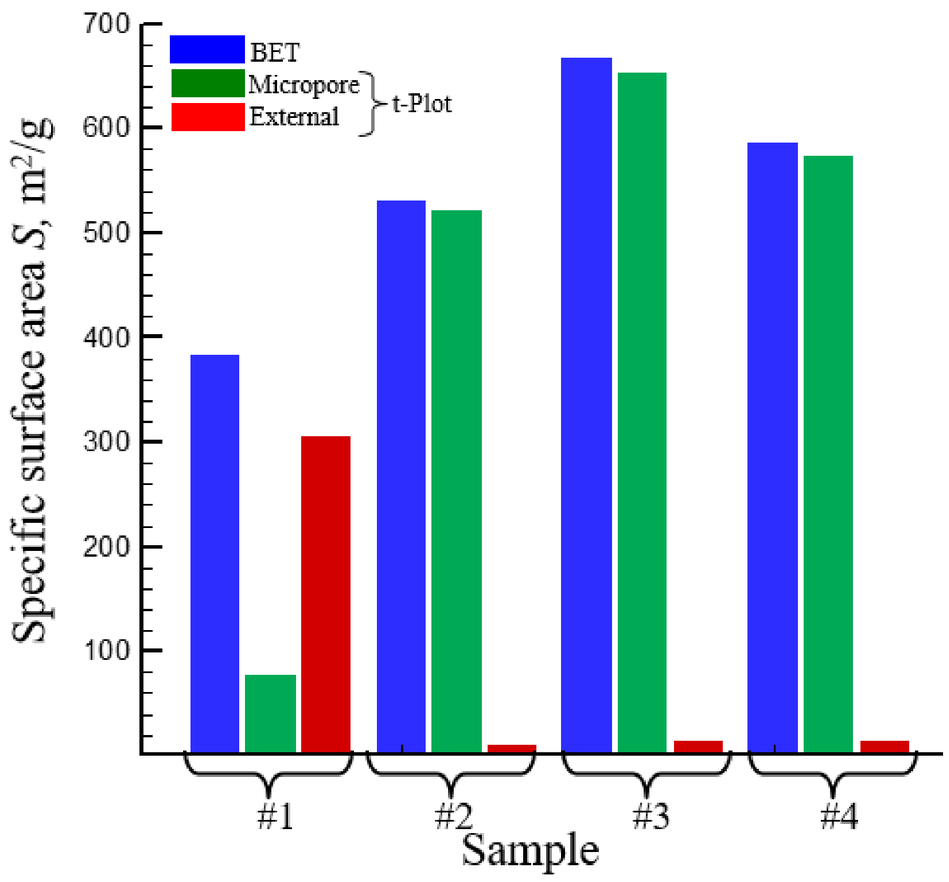

Fig. 2. Specific surface areas S for the samples #1(Lap), #2-4 (LapA). The data are obtained using BET and t-plot analysis

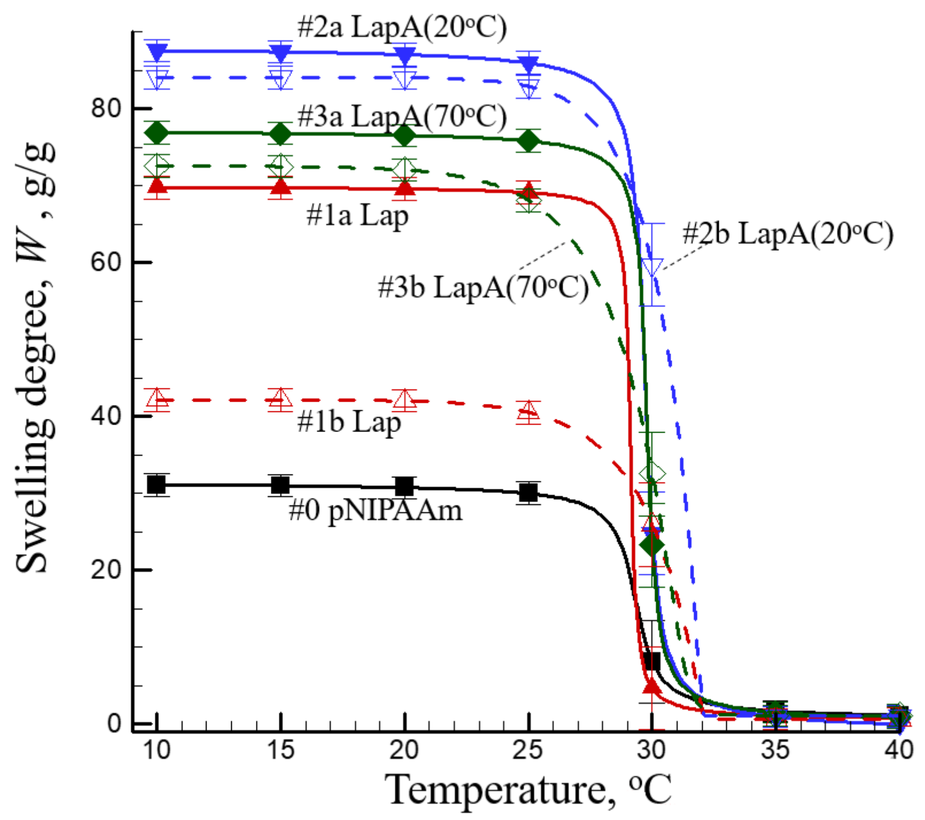

Fig. 3. Temperature dependencies of the swelling degree W(T) (g/g) for the samples #0 pNIPAAm, #1a Lap, #1b Lap, #2a LapA (20°C), #2b LapA (20°C), #3a LapA (70°C), and #3b Lap (70°C)

Conclusions

- The incorporation of Laponite® and acid-activated Laponite® platelets into pNIPAAm hydrogels significantly enhances their swelling capacity and modulates network interactions compared to neat systems.
- Thermal analysis confirmed distinct enthalpic responses and broadened transitions near the LCST, reflecting the influence of clay-induced physical cross-links on polymer chain dynamics.
- These findings underline the potential of hybrid hydrogels as tunable, stimuli-responsive materials for advanced biomedical applications.