MAGNETIC AND THERMOSENSITIVE PROPERTIES OF PHYSICALLY CROSSLINKED HYDROGELS BY MODIFIED LAPONITE® NANOPARTICLES

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Nowadays great attention attracts polymeric hydrogels with stimuli (pH, temperature, electric, magnetic fields etc.) [1] on the base of the acrylic monomers cross-linked using different chemical linker. For example, pH-sensitive hydrogels containing carboxylic or amine functional groups can be used for the controlled release of the selectively adsorbed drugs [2]. The main disadvantages of such hydrogels are related to their low optical transparency, mechanical strength, low response rate and swelling ability in water. These disadvantages can be avoided using the additive of layered clay mineral Laponite® (Lap) [3]. The temperature sensitive hydrogels on the base of N-isopropylacrylamide physicaly cross-linked by mLap were synthesized. The hydrogels cross-linked by Lap nanoparticles have exhibited extraordinary mechanical toughness, the tensile moduli and tensile strengths that were almost proportional to the clay content. The Lap nanoparticles can be magnetized and using of these modified particles is an efficient route to improve the functionality of hydrogels.

Magnetized Lap (mLap) nanoparticles were synthesized by a co-precipitation method with different weight ratios X= Fe_3O_4/Lap (=0–2). For characterization of the samples the particle size distributions and sedimentation behavior in an external magnetic field were studied. Fig. 1 shows examples of the separation of mLap aqueous suspensions by interaction with a permanent magnet.

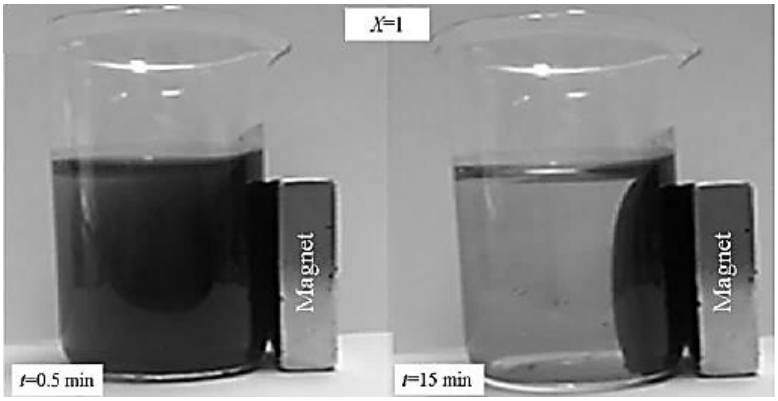

Fig. 1. Separation of mLap aqueous suspensions by interaction with a permanent magnet for weight ratio of Fe_3O_4 and Lap X=1 for t=0.5 and t=15 min.

The structure of magnetic laponite and composite hydrogels had been characterized by scanning electron microscopy and infrared spectroscopy..

An increased aggregation mLap particles in aqueous suspensions has been observed, but all the systems demonstrated high sedimentation stability. Significant effects of value of X on the rate of sedimentation mLap particles in magnetic fields and on the swelling ability of hydrogels have been demonstrared. For example at X=2 the increase in swelling by ≈2.7 was observed as compared with swelling for hydrogels based on pure Lap.

Using differential scanning calorimetry it was shown that all synthesized hydrogels exhibit a phase transition between the swollen and collapsed states around 32 °C and this temperature depends on the polymer cross-linking method. For hydrogels physically crosslinked by laponite, the phase transition temperature shifts toward higher temperatures compared to the chemically crosslinked hydrogels (using N,N'-methylene-bis-acrylamide). Diffusion of 5-FU from thermosensitive polyNIPAAm/LAM hydrogels (Fig. 2) is characterized by temperature-induced release of the incorporated anticancer drug. At temperatures above the phase transition of the hydrogel (e. g., 45 °C), the amount of released fluorouracil is 1.5–2 times greater than at room temperature (18 °C). This satisfies the prerequisites for the use of the specified thermosensitive hydrogel based on magnetically modified LAPONITEs for further development of systems for drug delivery and hyperthermia. The contactless heating of thermoresponsive HNCs to temperatures of about 40–45 °C, required for magnetic hyperthermia and triggered drug release can be achieved by applying an alternating magnetic field (due to oscillation of incorporated LAM nanoparticles) or by laser irradiation.

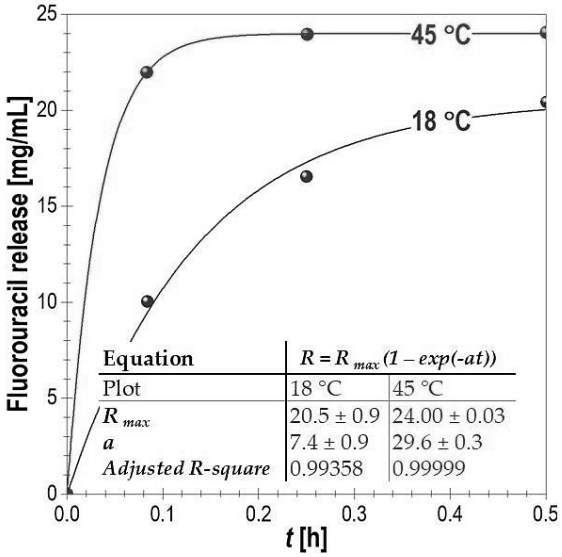

Fig. 2. Kinetics of fluorouracil release from polyNIPAAm/LAM1 nanocomposite at two temperatures: 18 and 45 °C. Experimental data (solid symbols) were fitted to an exponential equation. The fitting results are listed in the inserted table.

The combination of magnetic properties and ability to control the phase transition temperature by changing hydrogel structure suggests that the synthesized hydrogels can be potentially used (beside as a magnetic-driven platform for targeted delivery and drug release) also as actuators and elements of microfluidic devices.

References:

1. Gao S., Tang G., Hua D., Xiong R., Ha, J., Jian, S., Zhang Q., Huang C. "Stimuli-Responsive Bio Based Polymeric Systems and Their Applications" in J. Mater. Chem. B, 7(5), 2019, pp. 709–729.
2. Kouser R., Vashist A., Zafaryab M., Rizvi M. A., Ahmad S., "pH Responsive Biocompatible Nanocomposite Hydrogels for Therapeutic Drug Delivery" in ACS Appl. Bio Mater, 1(6), 2018, pp. 1810–1822.
3. Haraguchi K., Takehisa, T., Fan S. "Effects of Clay Content on the Properties of Nanocomposite Hydrogels Composed of Poly (N-Isopropylacrylamide) and Clay" in Macromolecules, 35(27), 2002, pp. 10162–10171.