Ph.D. theses

Synthesis and characterization of intelligent hydrogel/clay and hydrogel/gold nanoparticle hybrid materials

László Janovák

Supervisors:

Dr. Imre Dékány
Professor, member of Hungarian Academy of Sciences

Dr. Lajos Kemény
Professor, Chairman

Chemistry Doctoral School

University of Szeged
Department of Colloid Chemistry
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1. Introduction and objectives

Hydrogels are 3D lattice polymers that, due to the presence in them of hydrophilic functional groups, swell up to several times of their original volume in aqueous media. Many properties of hydrogels make them suitable for biomedical applications that require contact with living tissue. Hydrogels are capable of absorbing and retaining a large amount of water. The soft, rubbery consistency of swollen hydrogels minimizes frictional irritation of surrounding cells and tissue and may be fabricated in a variety of shapes and geometries. Hydrogel networks are useful for applications requiring a material that has good compatibility with aqueous fluids, without dissolution. Such applications include biomaterials, controlled release devices and electrophoresis gels.

A further important characteristic of these materials is their ability to respond to external physical/chemical/mechanical stimuli with a structural change (e.g. deformation, swelling, dissociation of functional groups). This ability is exploited in the preparation of “intelligent” materials possessing certain self-control mechanisms. If these gels also contain e.g. conductive metal particles, the reaction elicited by the change in the environmental parameter may also manifest itself in a change in the conductivity of the nanoparticle-containing composite, because, depending on the degree of swelling, the particles entrapped in the gel move closer together or farther apart. This properties can be advantageously applied in sensorics. In this case the conductivity of composite depends on the size, volume fraction and dispersity of the metal nanoparticles according to percolation theory.

Hydrogels are usually prepared from polar monomers. According to their starting materials, they can be divided into natural polymer hydrogels, synthetic polymer hydrogels and combinations of the two classes. Hydrogels can be classified as physically and chemically cross-linked gels. In the first case the networks are held together by physical forces, including ionic, H-bonding or hydrophobic forces, while in the second case the gel has covalently-crosslinked networks.

The properties of gels can be significantly enhanced by the incorporation of inorganic ordered systems, in particular clays, into the gels. The most frequently used fillers are the layer structured clay minerals, since they exist in a great amount in nature and can be also produced by synthetic routes. Many types of clay minerals have ion- exchange capacity. When the exchangeable metal ions of the clays are replaced by cationic surfactant (eg. alkylammonium ions of different carbon chain length), organophilized (hydrophobic) clays are obtained.

When the initially hydrophilic clay was hydrophobized, the prepared organophilized filler shows compatibility with the relatively hydrophobic polymer matrix due to the hydrophobic surface. In the case of composites, the properties of the hydrogel are basically determined by the inorganic filler: its addition may help to improve the swelling, the mechanical properties, as well as the thermal stability of the polymers.

My first aim was the development and characterization of copolymer and composite hydrogels that, when implanted under the skin, swell osmotically and thereby induce skin growth. We wanted to prepare a polymer- composite gel, that shows maximal swelling at 36.5 °C in physiological conditions. The utility of samples as potential skin expanders were examined in animal tests, in cooperation with the Department of Dermatology and Allergology, University of Szeged.

Gels of controllable degree of swelling can be prepared by the systematic combination of the three monomers (different acrylic compounds) and their molar ratios. I also studied the effect of the monomer/ crosslinker (M/C) ratio and the hydrophilicity and amount of fillers (Na-montmorillonite and hydrophobizid Na- montmorillonite) on the swelling of samples.

The next aim of my work was to prepare gel based films by photopolymerization. Gold nanoparticles were dispersed in the gel films in high concentration. Since the optical and electric conductivity properties of films change with the degree of swelling, they can be advantageously applied in sensorics.

2. Experimental (materials and methods)

The monomers used were N-isopropyl-acrylamide (NIPAAm; $H_2C{=}CHCONHCH(CH_3)_2$), acrylamide (AAm; $CH_2{=}CHCONH_2$) and acrylic acid (AAc; $CH_2{=}CHCOOH$) and the cross-linking agent was N,N'-methylenebisacrylamide (BisAAm; $(H_2C{=}CHCONH_2)_2CH_2$). Potassium persulfate (KPS; $K_2S_2O_8$) and Irgacure 651 ($C_6H_5COC(OCH_3)_2C_6H_5$) were the thermal and photo-induced initiators, respectively, while N,N,N',N'-tetramethylethylenediamine (TEMED, $CH_3)_2NCH_2CH_2N(CH_3)_2$) served as an accelerator.

Butylamine ($CH_3(CH_2)_3NH_2$), octylamine ($CH_3(CH_2)_7NH_2$), dodecylamine ($CH_3(CH_2)_{11}NH_2$), hexadecylamine ($CH_3(CH_2)_{15}NH_2$) and octadecylamine ($CH_3(CH_2)_{17}NH_2$) were used for the organophilization of EXM 838 Na-montmorillonite filler.

In the course of the synthesis of gold nanoparticles the metal precursor and the reducing agent were gold(III) chloride trihydrate ($HAuCl_4*3H_2O$) and trisodium citrate dihydrate ($HOC(COONa)(CH_2COONa)_2*2H_2O$).

The obtained polymer samples were subjected to IR and Raman measurements. The IR spectra of the samples were recorded by a Biorad FTS-60A FT-IR spectrometer equipped with a diffuse reflection accessory and the Raman spectra were recorded by a Biorad FT-Raman spectrometer at the Department of Physical Chemistry, Universitiy of Szeged.

The polymerization yield was determined gravimetrically. The amounts of accelerator, initiator and the polymerization time were changed during the experience.

XRD analyses of montmorillonite, organophilized montmorillonite and composites were performed by a Philips PW diffractometer (PW 1830 generator, PW 1820 goniometer, CuK_{α} radiation λ = 0,1542 nm, 40-50 kV, 30-40 mA).

The degree of swelling was determined gravimetrically. The swelling of hydrogel was investigated in distilled water and in physiological saline in the temperature range of 25–40 °C.

The thermoanalitical measurements were performed in a Mettler-Toledo 822^{e} differential scanning calorimeter and in a Mettler Toledo TGA/SDTA 851^{e} instrument. DSC measurements afforded the desorption enthalpies (ΔH_m) corresponding to the actual water contents and the corresponding temperatures, while during the TG measurements the amount of water of the samples and the thermal stability of the gels were determined.

A Rheotest RS 150 (HAAKE) and a Physica MCR 301 (Anton Paar) oscillatory rheometers equipped with 20 mm plates in parallel-plate geometry were used to measure the mechanical behaviors of the srunken gels at different temperatures. The values of storage modulus (G’) expressing the elasticity were used for the evaluation of mechanical properties of the samples.

Zeta potential and streaming potential mesurements were applied to characterize the surface charge properties of the polymers, co-polymers and fillers. The determination of zeta potential was carried out by Nano-Zetasizer (Malvern, UK) instrument, while the flow potential measurements were performed by Mütek PCD 02 particle charge detector.

The UV/VIS spectrophotometric evaulation of the prepared gold containing composite films were investigated by an Ocean Optics Chem 2000-UV-VIS spectrophotometer at wavelengths of 400-850 nm. The electric conductivity measurements were performed by a Keithley 2400 electronic multimeter. A Philips CM-10 transmission electron microscope was used to measure the morphology of the thin layer composite hydrogels applying 100 kV accelerating voltage.

3. New scientific results

T1. Synthesis of hydrogels and optimization of reaction conditions

1.1 Optimization of heat polymerization

The same gel samples were synthesized both by heat and photopolymerization. Yields determined by gravimetry evidenced that the optimal amounts of the initiator (KPS) and the accelerator (TEMED) were $7.5*10^{-4}$ and $6.65*10^{-3}$ mol% related to the amount of monomers. The times optimal for polymerization were found to be 30 min for NIPAAm and AAm containing samples and 120 min for the AAc based gels.

1.2 Optimization of reaction conditions for photopolymerization

I have shown that the optimal amount of photoinitiator (Irgacure 651) is 0.01 mol% related to the amount of monomer, while the optimal time of irradiation is 30 min for all gels.

1.3 Comparison of the maximum yields of the two different polymerization processes

I have compared the maximum yields corresponding to the gels prepared by the two different polymerization techniques. No significant differences were found for these yields, which means that the optimization of these two methods results in roughly the same efficiency. For both methods, the highest efficiency (with ca. 96% yield) was observed in case of AAm.

1.4 Characterization of the swelling of heat and photopolymerized samples

Swelling properties of samples obtained by heat and photopolymerization were also compared. There were no significant differences in the measured values for most of the gels. However, NIPAAm based samples prepared by photopolymerization swelled ca. 40% better than those obtained by heat polymerization. This is because the heat polymerization was conducted above the lower critical solution temperature (LCST) of NIPAAm, which corresponds to the so-called collapse point in polymer or gel phase. Thus, gels possessing hydrophobic sites were obtained; in other words, the hydrophobicity of NIPAAm based gels can be increased by heat polymerization.

T2. Control of the hydrophylic/hydrophobic properties of the hydrogels

2.1 Swelling equilibria of polymer and copolymer gels in aqueous media

Upon the swelling studies using water, I have studied in detail and compared the equilibrium swelling values of the polymers [poly(NIPAAm), poly(AAm) and poly(AAc)] and the copolymers [poly(NIPAAm-co-AAm), poly(NIPAAm-co-AAc) and poly(AAm-co-AAc)] synthesized from the three starting monomers.

The measured values, depending on the composition, ranged between ca. 8 and 230 g/g. Application of this result enables for the preparation of gels, the swelling of which can be precisely controlled by the monomer composition.

2.2 Properties of the poly(NIPAAm-co-AAm) gels

For the poly(NIPAAm-co-AAm) copolymer gels, the values of swelling, desorption enthalpies (ΔH_m) and the storage moduli (G') characteristic for the elasticity of the gels increased by 60%, 15% and 250%, respectively, by the molar ratio of the hydrophylic monomer at room temperature. The degree of swelling and elasticity of the copolymer increase with the molar ratio of AAm, which is due to the strong hydrogen-bond network formed between the water molecules and the hydrophylic amide groups fixed to the polymer lattice.

2.3 Properties of poly(NIPAAm-co-AAc) gels

In the case of the NIPAAm-AAc based gels, the increase of the AAc ratio results in larger swelling values, but the storage modulus of the copolymer of 1:1 ratio is three times larger than those of the pure polymers. This is explained by the associative interaction between the O=C-NH groups of NIPAAm and the carboxylic group of AAc. This is also supported by DSC measurements: the desorption enthalpy of poly(NIPAAm-co-AAc) exceeds that of the poly(NIPAAm-co-AAm) gel of the same monomer ratio by more than 10 kJ/mol.

2.4 Properties of poly(AAm-co-AAc) gels

For the poly(AAm-co-AAc) gels, the copolymer of 1:1 monomer ratio afforded the highest swelling (111.3 g/g), desorption enthalpy (129.05 kJ/mol) and storage modulus (2500 Pa) values, that is, the 1:1 copolymer is highly swellable while it has adequate mechanical properties. This result is explained by the hydrogen bonding interactions between the carboxylic and amide groups of the gels and the water molecules.

2.5 Temperature dependence of the swelling of copolymers

I have also shown by swelling experiments that the thermosensitive effect of NIPAAm in its copolymers [poly(NIPAAm-co-AAm) and poly(NIPAAm-co-AAc)] only manifested above 70 mol% NIPAAm content. At lower contents the swelling of copolymers steadily increases with the temperature, but the gels collapse at higher NIPAAm contents at its LCST (~ 32 °C). In contrast, the swelling values of poly(AAm) and poly(AAc) progressively increase with the temperature and the temperature-induced swelling was the most significant for poly(AAm-co-AAc). This implies that the more hydrophylic the gel is, the larger volume it swells to at higher temperatures. I have monitored the changes in temperature induced swelling by rheological measurements. I found that the elasticity of the hydrophylic poly(AAm) and poly(NIPAAm)-co-AAm) gels decreased with 50% and 30%, respectively, in the studied temperature range (25-40 °C). On the contrary, the storage modulus of the poly(NIPAAm) gel showed a 27-fold increase at the collapse point (~32 °C).

T3. Effect of the crosslink density on the swelling and structure of the gels

3.1 Influence of the crosslink density on the swelling and structure of poly(NIPAAm)

The degree of swelling and elasticity of gels with different crosslink densities were quantified by swelling and rheological measurements. Concerning the swelling values, I have shown that the decrease of the numbers of crosslinks caused the smallest change for the NIPAAm based gels, because the difference in the swelling values was only 40% at the two end points of the studied M/C range (= 50-1500). The reason is, given that the amount of hydrophobic regions is higher for this gel, that weaker interactions occurr between the water molecules and the polymer framework. This assumption was evidenced by DSC and rheological meaurements: for both cases, the changing crosslink densities caused the smallest changes in the studied M/C range when poly(NIPAAm) gels were investigated. The difference was as low as 5% in the first case, while in the second case, the measured storage moduli showed a tenfold decrease.

3.2 Effect of the crosslink density on the swelling and structure of poly(AAm)

It was proven by the results of swelling, thermoanalytical and rheological measurements that water molecules were strongly bound to the amide groups of poly(AAm) gels. Increasing the M/C ratio unequivocally resulted in higher degrees of swelling: at M/C = 50, 1 g of gel takes up 23.7 g water, while at M/C = 1500, 1 g of gel is capable for the uptake of 91.58 g water, which relates to an almost fourfold volume increase. At M/C values below this range, however, values of $G^{'}$ dropped from 767 Pa to 229.6 Pa (threefold decrease), while ΔH_m changed only by 16%.

3.3 Influence of the crosslink density on the swelling and structure of poly(AAc)

I have shown that, among the three polymers studied, poly(AAc) exhibits the most crucial changes upon the decrease of the crosslink density. In the studied range, the degree of swelling increased almost ten times (from 24.6 to 223.1 g water/ g dry gel) and, paralelly, the value of the desorption enthalpy decreased by 20% and G' showed a sixtyfold decrease. This is because the relative amount of „free" water (that is, which is not adjacent or close to the hydrophylic molecule segments) is the largest in poly(AAc).

3.4 Correlation between the water content and the hydrophylic/hydrophobic properties of the gels

Knowledge of the above issues enabled for concluding that, in proportion to the M/C ratio, the amount of free water increases as compared to the bound water adjacent to the hydrophylic regions. The more hydrophylic the gel is, the more the lowering of the number of crosslinks increases the degree of swelling (i.e. the less energy needs to be invested for the removal of water content). According to the DSC measurements, the enthalpy of desorption had the largest decrease (by 20%) for poly(AAc), and the measured storage moduli also had a sixty-fold decrease. With these alltogether, the structural order of the polymer framework decreases and the intruding water molecules will have higher and higher space in the loose gel network.

T4. Theses related to the hydrogel composites containing layer silicates

4.1 Effect of the fillers on the swelling and mechanical properties of the gels

It was shown that the fillers, at low concentrations (1-5 m/m%), increased the swelling of the hydrogels by 60-75% (Figure 1). The elasticity of the composites are also increased by 100-400 % as compared to the gels containing no fillers. It was established that the hydrophylic (Na- and C_4-montmorillonite) fillers favoured the swelling of the hydrophylic poly(AAm) and poly(AAc) gels (Figure 1.) because the fillers of hydrophylic surface provide further space in the polymer matrix for water molecules. On the other hand, the hydrophobic (C_{12}- and C_{18}-montmorillonite) fillers enhance the swelling of the hydrophobic poly(NIPAAm) owing to the looser structure formed as a result of hydrophobic interactions.

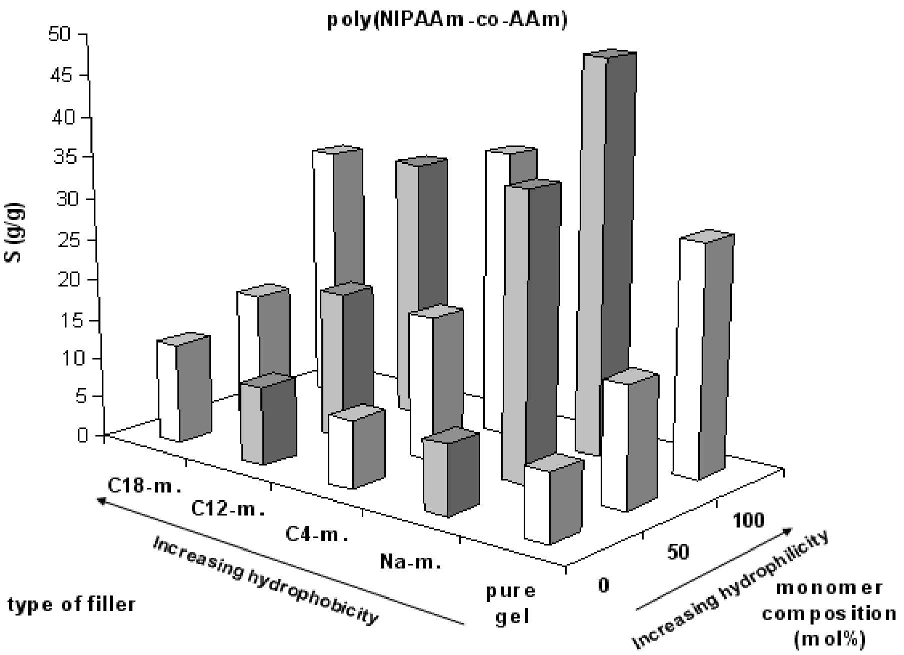

Figure 1. Swelling values of the composites containing 1 m/m% filler and of the pure poly(NIPAAm-co-AAm) gels as a function of the hydrophylicity of the fillers and the gels, respectively

4.2 Structure of the poly(NIPAAm) based hydrogel composites

The results of swelling, thermoanalytical and rheological measurements enabled me to deduce that, for the poly(NIPAAm) gels, the fillers of longer alkyl chain lengths (C_{12}, ill. C_{18}-montmorillonite) interact with the hydrophobic parts of the polymer matrix via the hydrophobic alkyl chains. Consequently, in the case of montmorillonite derivatives of longer carbon chains, the accessibility of water molecules to the hydrophylic groups is sterically more favourable. As a result, the hydrophobic fillers increase the swelling of poly(NIPAAm) gel by 34-67%, without any concomitant change in the storage moduli. In contrast, there are hydrophylic and hydrophobic interactions between the pure and „short-chain” (C_4) montmorillonite and the hydrophylic groups of the poly(NIPAAm) framework. Therefore, the swelling value of the composite gel exceeds that of the starting polymer only by 6-8%, while the measured storage moduli have a twenty-fold increase. This hypothesis is supported by thermogravimetric results, which conclude that the thermal stability of the poly(NIPAAm) based sample increases with the filler concentration.

4.3 Structure of the poly(AAm) based hydrogels

Incorporation of fillers into poly(AAm) gels affords extra hydrophylic spaces for water molecules. Thus, swelling of the composites containing C_4- and Na-montmorillonite increases by 23-70%. Moreover, these hydrophylic fillers also increase the elasticity of the starting gels due to the strong hydrogen bonds between the functional goups of the gel and the lamellae. For more hydrophobic fillers, both the degree of swelling and the elasticity decrease becasue the polymer segments and the lamellae lack functional goups that could constitute hydrogen bonds.

4.4 Structure of the poly(AAc) based hydrogel composites

I have demonstrated that the inclusion of negatively charged Na- and C_4-montmorillonites into negatively charged poly(AAc) results in gels of higher water contents but their elasticity decreases. This is explained by the formation of a more opened structure, which originates from the repulsion between functional groups carrying charges of the same sign. In contrast, swelling of the composites containing more hydrophobic fillers decreases, but the elasticity of the gels increases because there is no electrostatic repulsion between the gel and the surface of the lamellar filler, which is decorated by alkyl chains.

T5. Comparison of the swelling of hydrogels immersed into distilled water and in physiological saline solution

5.1 Swelling under physiological conditions

For a potential use in health care applications, the equilibrium swelling values of gels and composites under physiological conditions were determined. I showed that the swelling of poly(AAm) based gels fell the closest to that measured in distilled water; the difference here is only 35%. For poly(AAc), however, the samples swelled seven times better in distilled water, which is explained by the charge screening effect of the physiological saline solution.

5.2 Comparison of the swelling of composites immersed into distilled water and physiological solution

The swelling values of composites under physiological conditions were found to agree well with those measured in distilled water, i.e. 60-80% larger degree of swelling can be achieved with composites of low (1-5 m/m%) filler contents. At higher filler contents (10-25%), the swelling values decreased as the structure of the composites were more compact.

5.3 Kinetics of swelling for the composite hydrogels

Measurements regarding the swelling kinetics under physiological conditions revealed that the swelling equilibrium of the gels (at 36.5 ºC and in physiological solution) is established in ca. 50-75 hours, independently of the filler contents. This means that the fillers do not affect the rate of swelling because the degree and rate of swelling are mainly governed by the hydrophylicity of the polymer matrix.

T6. Gold/hydrogel nanohybrid systems as ultrathin films

6.1 Deposition of hydrogel based films loaded with gold nanoparticles

The final part of my work aimed at the fabrication of poly(AAm) and poly(NIPAAm) based films on interdigitated microelectrodes by photopolymerization, which may be feasible for application as sensors. Gold nanoparticles were used and their content in the films were constant; only the volume of the interparticle polymer matrix was varied. TEM micrographs showed that the successive increase in the Au content increased the space filling of gold particles, which was also indicated by the increasing absorbance at 532 nm of the thin layers.

6.2 Effect of swelling on the optical properties of gold/hydrogel nanohybrid films

Swelling of the films synthesized from the two kinds of monomers were also monitored by spectrophotometry. For both composites, the plasmon resonance band, which is characteristic for the gold particles, shifted towards lower wavelengths. This indicates the divergence of nanocrystals in the polymer matrix. At one minute of swelling time, the maximum of the absorbance spectrum showed a larger shift (from 547.6 nm to 533.9 nm) in the case of poly(AAm) than for the poly(NIPAAm) based film (from 540.8 nm to 535.3 nm).

6.3 Effect of the temperature on the UV-VIS spectra

I showed that the temperature induced shrinkage of poly(NIPAAm) and the swelling of poly(AAm) could be monitored by spectrophotometry. A red shift of 18.1 nm and a blue shift of 16.6 nm were measured for poly(NIPAAm) and poly(AAm), respectively, in the studied temperature range (25-40 °C). The red shift is due to an aggregation effect, i.e. the convergence of the particles in poly(NIPAAm), while those in poly(AAm) have separated from each other.

6.4 Electric conductivities of the gold/hydrogel nanohybrid films

It was proven that the electric conductivity of the films measured in distilled water could be increased by the incorporation of larger amounts of gold particles. I showed that the electric conductivity of the films in distilled water could be increased by the Au loading. It can be concluded from the conductivities of the samples at different temperatures that the composites needed to contain high (99 m/m%) amounts of Au for any observable change in the conductivity upon the swelling or shrinkage of the gel matrix. For the poly(NIPAAm) based samples it was shown that, due to the collapse, the conductivity of the composite changed at least by tenfold in 2 °C near the collapse point of NIPAAm (~32 °C) applying 0.5 V voltage. The measure conductivity value is 1.8 μA at 32.5 °C, while at 35 °C it rises to 23,4 μA. On the other hand, the conductivity of the poly(AAm) composite progressively decreased with the temperature (~ 0,1 μA/ °C) because of the swelling crosslink-network.

7. Health care application of the gels as skin expanders

7.1 Results of the animal tests

Animal tests demonstrated that the polymers and the nanocomposites retained their chemical stability embedded under the skin, and kept their aspect ratio upon expansion owing to their mechanical and shape stability. The following histological examinations showed no changes as compared to the healthy skin.

7.2 Practical utility of the hydrogel nanocomposites

Comparing the swelling of the as-synthesized polymer and composite gels with those of other, commercially available skin expanders, it can be concluded that the volume expansions of my samples are significantly larger. Under physiological conditions, they swell up to 35-40 times of their original volume. The reason for this is the incorporation of filler that are delaminated and their surface energy can be controlled, due to which the swelling is doubled and the elasticity is increased as compared to other skin expanders. Accordigly, we have two submitted patents for the sample synthesis and their application as skin expanders.

Publications

Papers related to the dissertation:

1. **L. Janovák**, J. Varga, L. Kemény, I. Dékány
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2. **L. Janovák**, J. Varga, L. Kemény, I. Dékány
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   Colloid and Polymer Science 286 (2008)1575–1585 **IF$_{2007}$: 1,62**

3. **L. Janovák**, J. Varga, L. Kemény, I. Dékány
   The effect of surface modification of layer silicates on the thermoanalitical properties of poly(NIPAAm-co-AAm) based composite hydrogels
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4. **Janovák L**, Király Z, Dékány I
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5. **L. Janovák**, J. Varga, L. Kemény, I. Dékány
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6. J. Varga, **L. Janovák**, E. Varga, G. Erős, I. Dékány, L. Kemény,
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ΣIF: 4,964

Patents

1. Kemény Lajos, Dékány Imre, Varga János, **Janovák László**
   N-izopropil-akrilamid, akrilamid és akrilsav polimerizációjával szintetizált hidrogélek rétegszilikátokkal készült nanokompozitjai, eljárás ezek előállítására és alkalmazásuk ozmotikusan aktív hidrogél szövettágító expanderekben bőr nyerésére
   Magyar Szabadalom, bejelentés ideje: 2007. május, Ügyiratszám: P0700384

2. L. Kemény, I. Dékány, J. Varga, **L. Janovák**
Layer silicate nanocomposites of polymer hydrogels and their use in tissue expanders
International Publication Number: WO 2008/146065 A1

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1. **L. Janovák**, J. Varga, L. Kemény, I. Dékány
Dermatological application of thermo- and pH-sensitive hydrogels
20th Conference of the European Colloid and Interface Society and 18th European Chemistry at Interfaces Conference, Budapest, 2006. szeptember 17-22., p. 300 (poster)

2. **Janovák László**, Varga János, Dékány Imre, Kemény Lajos
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3. Varga J., Erős G., Varga E., **Janovák L.**, Dékány I., Kemény L.
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5. D. Sebők, **L. Janovák,** E. Pál, I. Dékány
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6. Varga J., Erős G., Varga E., **Janovák L.**, Dékány I., Kemény L.
New possibilitis of skin expansion
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7. **Janovák László**
Intelligens hidrogél/ rétegszilikát és hidrogél/ arany nanohibrid rendszerek szintézise és tulajdonságai
MTA- SZAB Anyagtudományi Munkabizottsági előadás, Szeged 2009. február 20. (lecture)