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ORIGINAL CONTRIBUTION

Investigation of the structure and swelling of poly(*N*-isopropyl-acrylamide-acrylamide) and poly(*N*-isopropyl-acrylamide-acrylic acid) based copolymer and composite hydrogels

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Abstract We synthesized, thermo- and pH-sensitive gels and tested them as skin extenders. Our aim is the development of copolymer and composite hydrogels that, when implanted under the human skin, swell osmotically and thereby induce skin growth. In the course of the polymerization reaction, we produced copolymers with variable compositions, starting from different acrylic compounds [*N*-isopropyl-acrylamide (NIPAAm), acrylamide (AAm), and acrylic acid (AAc)]. The mechanical strength and the swelling stability of the gels are enhanced by the addition of fillers [Na-montmorillonite and Na-montmorillonites organophilized with alkylammonium ions (C_n-m.), n=4, 12, 18]. With this method we synthesized composite hydrogels. We observed that in the case of composites synthesized with the addition of fillers, relatively low filler contents (1–5 wt.%) resulted in more extensive swelling and stronger gel structure. During the experiments, the monomer composition (0/100–100/0 mol% NIPAAm/AAm or AAc) and the cross-link density (50–1500 mol%) of the gels (M/C ratio) and, in the case of composites, the quality and quantity of fillers are varied. The filler content of composites varies between 1 and 25 wt.%. The extent of swelling and the viscoelastic properties can be manipulated through the ratios of these parameters. In the case of certain copolymer and composite gels, values of desorption enthalpy (ΔH_m) corresponding to the actual water contents were also determined by thermoanalytical measurements (differential scanning calorimetry, DSC). Swelling values determined by gravimetry and enthalpies calculated from DSC measurements were found to be in good correlation. Even in the case of the relatively hydrophobic poly(NIPAAm)-based gels, an enthalpy value of 98.41 kJ/mol was obtained, which is twice the value measured in pure water (41.74 kJ/mol). Evaluation and comparison of the rheological and DSC results also allowed conclusions to be drawn concerning the types of interaction operating among the three components of the system, i.e., the polymer skeleton and the filler and water molecules.

Keywords Swelling hydrogel · Copolymers · Clay-mineral composites · Skin expander · Mechanical properties · DSC

Introduction

Hydrogels are 3D lattices containing hydrophilic and hydrophobic parts in appropriate proportions. When placed in aqueous medium, they therefore swell to several times their initial volume without either dissolving or changing their shape to any considerable extent [1].

Owing to their advantageous properties, they are widely applied in medicine (controlled drug release, wound treatment, skin expansion, contact lenses, biosensors, and protein immobilization) [2–6] as well as in other areas (environmental protection and agriculture) [7, 8]. In the case of polymers synthesized of appropriately selected monomers, swelling can be elicited by variations in any of

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several environmental conditions (temperature, pH, electrolyte concentration, and solvent composition) [9–11].

The prediction and control of the mechanical properties of hydrogels are of great importance in assessing the applicability of hydrogels. Once the mechanical characteristics of a material have been determined, it is often necessary to improve them in some manner to make the material suitable for the desired application. The mechanical properties of gels can be enhanced by the incorporation of clays into the polymer matrix [12–18]. There are several methods available for controlling mechanical properties: altering the comonomer composition [19, 20], increasing or decreasing the cross-link density [21–24], and modifying the conditions of polymer formation [25, 26].

The effect of the monomer composition of various polymers [27] and hydrogel copolymers on the mechanical properties of gels has been studied and is described in the special literature. Jiang et al. determined the mechanical properties of chitosan/polyacrylate-based hydrogels. In the course of the experiment, they varied the molar ratio of the two polymers in the copolymer and the monomer/cross-linker ratio, i.e., they indirectly varied the water content of the samples obtained. They found that the mechanical properties of the gels deteriorated with increasing water content because the amount of polymer skeleton per unit sample volume decreased [19]. Jones et al. studied changes in the mechanical properties of *N*-isopropyl-acrylamide (NIPAAm)-hydroxyethylmethacrylate (HEMA) based copolymers. These authors found that the composition of the copolymer has a profound effect on its viscoelastic properties: poly(HEMA) is more elastic than poly (NIPAAm), and the sample with the best mechanical properties is the copolymer of the two monomers [20].

The water content, i.e., the swelling of the gels, may also be controlled through varying the monomer/cross-linker ratio [28, 29]. Cauich-Rodriguez et al. used various cross-linkers (glutaraldehyde and glyoxal) for the preparation of poly(acrylic acid)-poly(vinyl alcohol-vinyl acetate) copolymers and measured the mechanical properties of the resulting gels. They observed that the amount of cross-linker determines the water content of the samples, which has a fundamental effect on the resulting mechanical properties [21]. Masci et al. used methacrylated pullulan derivative for cross-linking the thermosensitive NIPAAm by varying the monomer/cross-linker molar ratio and studied, among others, the swelling and mechanical properties of the gels obtained. They found that the swellability of the samples decreases, but their mechanical properties improve with increasing the amount of NIPAAm [22]. Cabarcos et al. synthesized poly(AAm)-based gels containing glucose oxidase and examined the possibility of their utilization as biosensors. They also used *N*,*N*′ methylenebisacrylamide (BisAAm) as cross-linker and varied the monomer/cross-linker molar ratio. They established that increasing the number of cross-links enhances the elasticity of the gels and that mechanical properties can also be influenced by varying the amount of glucose oxidase added [23].

It must be remembered that these changes in the polymer will affect not only the mechanical properties but also other behavior of the material [30].

It is well-known that the properties of gels can be significantly enhanced by incorporation of inorganic ordered systems, in particular clays, into the gels [31–33]. Xia et al. proved for poly(NIPAAm)-based composites containing Na-montmorillonite (Na-m) that relatively low filler concentrations resulted in more extensive swelling and more favorable mechanical properties than those of the polymer without filler [34]. Churochkina et al. [35] did the same for poly(AAm)-based gels. Strachotová et al. synthesized a poly(NIPAAm)-based composite containing silica. They established that silica content affected the extent and rate of swelling and the mechanical properties of composites: The samples containing fillers swelled more extensively and faster than did the samples without filler, and the elastic properties of the former were also better by at least one order of magnitude [36].

Na-m-layered silicates are widely used as model additives to plastics to improve their physical properties [37, 38]. The mechanical strength and the swelling stability of the gels are enhanced by the addition of fillers [Na-m and with Na-m organophilized with alkylammonium ions (C_n-m.), n=4, 12, and 18]. We used this method to synthesize composite hydrogels.

When the initial hydrophilic layer silicate is hydrophobized, the filler obtained will be compatible even with relatively more hydrophobic matrices due to the hydrophobic surface formed. The hydrophilicity of the filler can then be modified by the addition of a surfactant adsorbable on the surface. In the case of composites, the properties of the hydrogel are basically determined by the inorganic filler: Its addition may help improve the swelling, the mechanical properties, and the thermal stability of the polymers.

Polymer gels are viscoelastic materials whose elasticity takes its origin in the 3D polymer network structure. The extent of the viscous component in the mechanical properties of polymer gels depends on the structure and the water content. The experimental method most suited for studies on the viscoelastic properties of 3D lattices of chemical compounds is oscillation rheometry [26, 39, 40], a method that allows examination of the mechanical properties of gels under appropriately chosen loads without breaking up the structure. There are two basic possibilities for studying viscoelastic properties, namely static and dynamic load tests. Oscillation rheometry only includes tests involving dynamic (oscillating) loads; the static test is an examination method in its own right besides rotation viscosimetry and oscillation rheometry.

In typical dynamic tests, the frequency dependence of the reaction of the material tested is obtained by keeping the amplitude of the external load (the shear stress or deformation) at a constant value and varying the dynamic loading frequency. The inverse of this test at a constant loading frequency yields the amplitude dependence of the response. The viscoelastic parameters of the material at the time of dynamic loading are the storage modulus (G'), the elastic component of rheological behavior, and the loss modulus (G''), the viscous component of rheological behavior). If the values of these moduli are independent of the frequency or the amplitude in a certain region of the measurement range, the values obtained are characteristic of the mechanical properties of the given material. This range is termed the range of linear viscoelasticity.

Differential scanning calorimetry (DSC) has been employed to study the states of water in a number of polymer-stabilized hydrogel systems [41–45]. The interaction of water with such polymers and its distribution within the gel are critical to the physicochemical behavior of the gel. The most relevant DSC studies have argued that there are effectively three classes of water present in polymer-stabilized hydrogels. These are (1) free water, i.e., unbound water with a transition temperature, enthalpy, and peak shape comparable to those of bulk water, (2) non-freezing water, which is tightly bound to the polymer and does not undergo a detectable phase transition, and (3) loosely bound water, which is characterized by a depressed freezing point attributable to weak interactions with the polymer chain, and/or increased ionic strength in the case of ionic polymers. The DSC peak associated with a phase transition of loosely bound water is generally observed as a shoulder on the endothermic peak of melting free water, rather than a discrete endotherm. The bound water content depends on the chemical and higher order structure of the polymer [44].

In our work, a series of temperature- and pH-sensitive copolymeric gels was prepared by redox polymerization of NIPAAm, AAm, and AAc. Copolymer gels were obtained by varying the initial molar ratios of NIPAAm, AAm, and AAc. In the course of the experiments, the monomer composition and the cross-link density of the gels and, in the case of composites, the quality and quantity of fillers were varied. The extent of swelling and the mechanical properties can be manipulated through the ratios of these parameters. The value of desorption enthalpy for each water content were determined by DSC measurements.

Experimental

Materials

The monomers used were NIPAAm, AAm, and AAc. The monomers and the cross-linking agent BisAAm were obtained from Aldrich Chemical and were used without further purification. Other chemicals used were potassium persulfate (KPS) from Reanal Kft. (initiator) and *N*,*N*,*N*′,*N*′-tetramethylethylene-diamine (TEMED) from Fluka Chemie AG (accelerator).

NIPAAm, AAm, and AAc polymers and random copolymers with different compositions concentrations were prepared by radical polymerization. A total of 0.01 mol of monomers was dissolved in 10 ml distilled water, followed by the addition of BisAAm, 2×10^{-3} g initiator solution (KPS) and 7.75×10^{-3} g accelerator solution (TEMED) to the polymerization medium. Copolymer gels were obtained by varying the initial molar ratios of NIPAAm, AAm, and AAc. The monomer/cross-linker ratio was varied in the range of 50–1,500 mol%; the amounts of KPS and TEMED were constant. KPS and TEMED formed a redox pair for the purpose of radical polymerization. Polymerization was carried out in test tubes at 60 °C for 30 min, under N_2 atmosphere.

For the synthesis of organophilized montmorillonite fillers, 0.01 mol alkylamine with the selected carbon chain length (C_nH_{2n+1}–NH_2, n=4, 12, 18) was dissolved in 250 ml ethanol–water mixture (1:1) (pH=4.0), the solution was added to Na-m swollen in distilled water at a ratio of 100 meq/100 g montmorillonite, and the system was stirred for 24 h. After the completion of ion exchange, the suspension was centrifuged, washed, and filtered. The hydrophobized filler obtained was dried and ground to 200-μm particle size.

Composites were synthesized in a similar way as described above, except that the fillers Na-m and organophilized Na-m were first suspended in distilled water thoroughly under ultrasonic irradiation for 1 h, followed by the addition of the monomers and other chemicals. In the course of the synthesis of composites, fillers of various qualities (Na-m and C_4-, C_{12}-, C_{18}-montmorillonite) and quantities (1, 5, 10, and 25 wt.%, referred to the amount of monomer(s) and crosslinker) were included in all samples.

Methods

Swelling was determined gravimetrically. If G_s and G_d are the weights of the gel in equilibrium swollen and dried state, respectively, swelling was calculated from the following dependence: swelling (S)=(G_s−G_d)/G_d (g/g).

An oscillatory rheometer (RS 150, Haake, Germany) equipped with 20 mm plates in parallel-plate geometry was used to measure dynamic rheological properties, such as storage modulus (G') and loss modulus (G''). Measurements were done as a function of frequency from 0.1 to 1 Hz at a constant shear stress of 1 Pa at 25 °C. Sandpaper was stuck to both plates to avoid slippage of the gel. Temperature was controlled by a Haake DC 30/K20 thermostat.

The samples were pre-equilibrated at room temperature for at least 48 h before the measurements. Gels were also measured after swelling to equilibrium (gels swollen to equilibrium).

In order to measure linear viscoelastic properties, it is necessary to determine the linear viscoelastic region. This region was determined by measuring storage modulus (G') and loss modulus (G'') as a function of the strain amplitude, using poly(AAm) gel with various monomer/cross-linker ratios (50–1,500). The strain amplitude sweep was made between 0.1 and 100 Pa. It was observed that between strain amplitudes of 0.1 and 10 Pa, storage moduli (G') and loss moduli (G'') were both constant; therefore, a strain amplitude of 1 Pa was chosen for all the dynamic measurements.

The water content of the gels and the value of desorption enthalpy for each water content were determined in a Mettler-Toledo 822^e differential scanning calorimeter. In the course of the measurements, the sample holders were not covered; measurements were made in the temperature range of 10–200 °C at a heating rate of 5 °C/min. Following the method of Agrawal et al., we also recorded the DSC curve of distilled water for reference [44]. In the course of the evaluation of DSC curves, values of enthalpy of vaporization were calculated from the areas under the peaks and normalized to water contents determined from swelling values. The results are given in units of kJ/mol water. The results are reproducible within ±3% standard deviation.

Results and discussion

Varied parameters (monomer composition, M/C ratio, and filler content) and execution of measurements

The rheological properties of gels with various monomer compositions and cross-link densities were determined by rheological measurements. The rheological properties of composites containing fillers of various qualities and quantities were further studied in order to examine how the properties of the pure hydrogel are altered by the presence of nanostructured fillers. Both rheological and swelling measurements were carried out at 25±0.5 °C. The swelling values are shown in Table 1. The results are reproducible within ±7% standard deviation.

For varying the monomer composition, the relatively hydrophobic monomer NIPAAm was combined with the hydrophilic monomers AAm and AAc at ratios of 0/100–100/0 mol% to obtain poly(NIPAAm-co-AAm)- and poly(NIPAAm-co-AAc)-based gels. The questions addressed were as follows: (1) How is the mechanical state of the samples affected by the diverse compositions, i.e., by the

Table 1 Swelling values of polymers and composite gels

Type of hydrogel	Pure gel	Na-m				C_4-m				C_{12}-m				C_{18}-m			
		Amount of filler (wt.%)				Amount of filler (wt.%)				Amount of filler (wt.%)				Amount of filler (wt.%)			
		1	5	10	25	1	5	10	25	1	5	10	25	1	5	10	25
Poly(NIPAAm)	8.33	8.51	8.83	5.88	5.83	8.46	8.34	7.28	3.17	9.71	11.2	6.41	2.72	12.3	13.9	8.34	4.84
Poly(Aam)	28.57	48.33	38.27	35.8	30.45	35.2	27.6	20.2	20.3	32.1	35.89	32.1	30.4	32	42.7	30.49	23.45
Poly(Aac)	35.43	52.36	45.72	41.34	38.63	51.23	48.43	45.21	34.21	39.94	45.3	42.83	36.96	38.84	38.11	36.53	35.22

consistence of the polymers synthesized from monomers with different hydrophilicities, and (2) what is the relationship between swelling and mechanical properties? In the case of copolymers and composites, desorption enthalpies of the water content of the gels were also determined.

The effect of cross-link density on swelling and on rheological properties was studied on polymers synthesized from all three monomers. The M/C ratio was varied in the range of 50–1,500.

Storage moduli (G') expressing the elasticity and loss moduli expressing the viscosity of poly(NIPAAm-co-AAm)-based gels as a function of oscillation frequency are represented in Fig. 1. The monomer/cross-linker ratio was 200 in both cases. When the amount of NIPAAm is increased in the given copolymer, the value of storage moduli (G') is seen to decrease, i.e., elasticity is reduced in favor of viscosity. It is also observed that the value of storage moduli (G') changes continuously with composition, whereas the value of loss moduli (G'') is much less influenced by changes in monomer ratio. For this reason, we henceforth employ values of storage moduli (G') expressing the elasticity of the samples for the evaluation of mechanical properties by extrapolating the experimental data to the ordinate and plotting the values obtained in this way as a function of the varied parameters (monomer composition, monomer/cross-linker ratio, and the amount of fillers). From the repeated measurements, the standard deviation in the modulus values were less then 6%.

The effect of monomer composition on the mechanical and swelling properties of the gels

Figure 2 displays the elastic moduli (G') and the desorption enthalpy (ΔH_m) and swelling (S) values of the copolymers obtained by combining the three monomers as a function of monomer composition. The monomer composition is changed from 100/0 mol% NIPAAm/AAm or AAc to 0/100 mol% NIPAAm/AAm or AAc. Changes in monomer composition are explained below the abscissa.

The data in the figure allow to establish that, in the case of NIPAAm-AAm gels, increasing the hydrophilic AAm content (from left to right) results in increased swelling and increased elasticity, since the dotted line of swelling values and the continuous line of storage moduli (G') values are nearly parallel, with identical slopes. Thus, in the case of poly(NIPAAm-co-AAm) gels, as AAm monomer concentration is increased at the expense of NIPAAm, gels with increasing swellability and improving mechanical properties are obtained. The reason for this is that AAm monomers containing hydrophilic amino groups bind water molecules via strong hydrogen bonds, resulting in a stronger gel structure. The same is indicated by the results of DSC measurements: As the molar ratio of AAm is increased, increasingly higher desorption enthalpies are required for the removal of the water content.

In the case of poly(NIPAAm-co-AAc) gels, it can also be observed that the swelling of the samples increases with increasing the concentration of the hydrophilic AAc; the

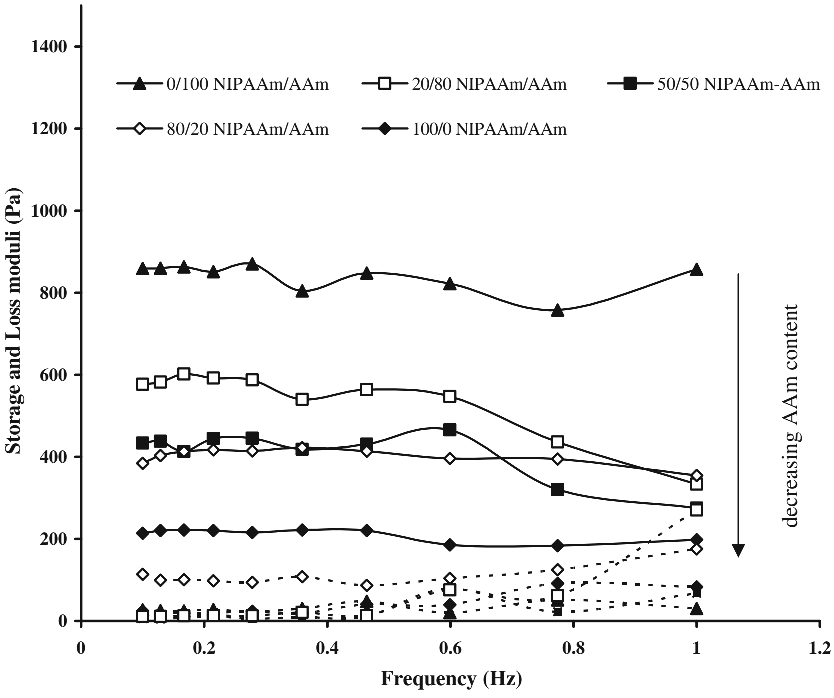

Fig. 1 The effect of monomer composition on the mechanical properties of poly(NIPAAm-co-AAm) gels. *Solid lines* and *dotted lines* represent storage moduli (G') and loss moduli (G''), respectively

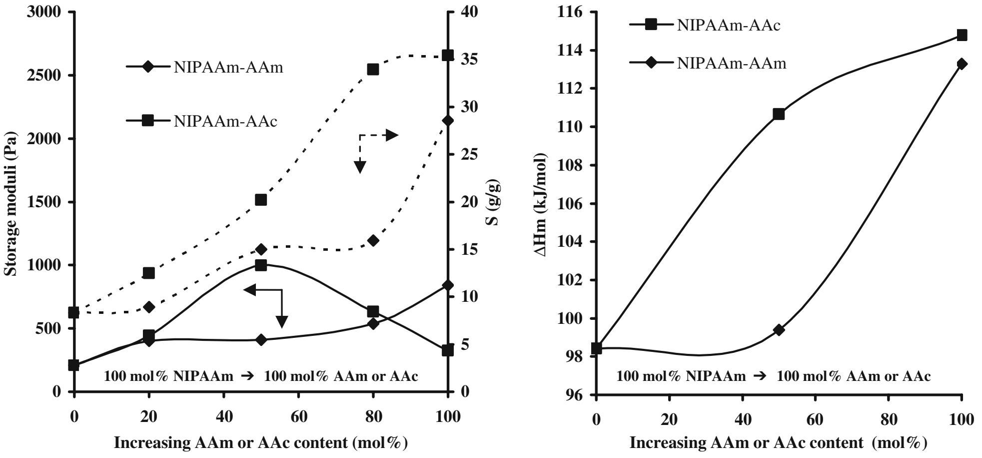

Fig. 2 The effect of changes in monomer composition on the swelling of the gels and on their elastic and thermoanalytical (DSC) properties (the symbols of various copolymers are shown in the *upper right corner*; *solid lines* and *dotted lines* represent *G*′ and swelling values, respectively) (from the repeated measurements, the standard deviation in the value were less then 6%)

value of storage moduli (*G*′), however, has a maximum at a composition of NIPAAm/AAc=50/50. This could be due to an associative interaction between the NH groups of NIPAAm and the carboxyl groups of AAc. This presumptive interaction is also supported by the results of DSC measurements: The desorption enthalpy of poly(NIPAAm-co-AAc) exceeds that of the poly(NIPAAm-co-AAm) gel of the same composition by nearly 75 kJ/mol. This means that, in the case of NIPAAm/AAc-based gels, the elasticity of the copolymer is better than that of the monomers, but its swellability is also lower than that of the polymer consisting of pure AAc. The more extensive swelling is due to the increasing AAc-content of the gel, i.e., to the higher number of carboxyl groups.

The effect of cross-link density on the mechanical and swelling properties of the gels

The water content of the samples, i.e., the swelling of the gels, can also be influenced through varying the monomer/cross-linker ratio. When the number of cross-links is decreased, more extensive swelling can be attained, but this also affects mechanical properties: A higher water content usually results in lower elasticity.

Figure 3 shows the storage moduli (*G*′) and swelling values (*S*) of the polymers with various cross-link densities, obtained by polymerization of the three different monomers as a function of the monomer/cross-linker ratio (M/C).

It is clear that in the case of NIPAAm-based gels the increasing M/C ratio does not alter the swelling values significantly, but brings about a slight deterioration of mechanical properties: The extent of swelling is identical in the entire range, whereas the values of storage moduli (*G*′) form a straight line with negative slope. Thus, in the case of NIPAAm gels, a decrease in the number of cross-links does not result in a significant increase in swelling, but leads to a deterioration of mechanical properties. The reason for this may be the hydrophobic character of the polymer, which allows the polymer skeleton to bind little water to start with

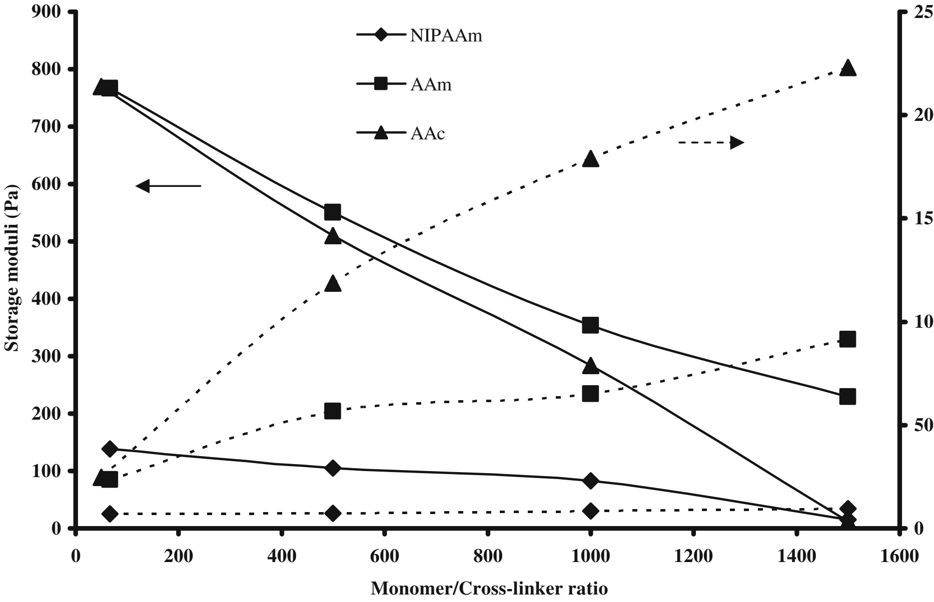

Fig. 3 The effect of crosslink density on the swelling and mechanical properties of the gels (the symbols of various polymers are shown in the *top middle*; *solid lines* and *dotted lines* represent *G*′ and swelling values, respectively)

and that through a weak interaction. The same is verified by the low values of swelling (S=6.9–9.4 g/g) and storage moduli (G') (138–15 Pa).

In the case of poly(AAm) gels, an increasing M/C ratio unequivocally leads to an enhanced swelling and a deterioration of mechanical properties: the two curves follow opposite courses. The values of storage moduli (G'), as a function of cross-link density, decrease considerably steeper than swelling values are seen to increase. Thus, it can be established that in the case of these gel types, a decrease in the number of cross-links has a more profound effect on mechanical properties than on the extent of swelling. This allows to conclude that the water molecules within the polymer skeleton are strongly bound to amino groups, and the 3D lattice is held together mostly by the cross-links; there are few water molecules locally bonded to more than one functional group.

In the case of poly(AAc)-based gels, it can again be observed that an increasing M/C ratio results in more extensive swelling and lower elastic moduli. This is the consequence of the fact that more extensive swelling means a higher water content, which enhances the viscous character of the samples and thereby decreases elasticity. At M/C=1,500, the sample swells to more than 220-fold, and the value of the storage modulus is nearly 0, since at this point, the polymer skeleton amounts to only 0.5% of the swollen gel and the rest is water. The high water content is due to the presence of the highly hydrophilic carboxyl groups.

The effect of fillers of different hydrophilicities on the mechanical properties of composites

The effect of various organic fillers on the individual properties of polymers is well-known from the literature [29–32].

The rheological properties of all three starting monomers (NIPAAm, AAm, and AAc) were determined in composites containing fillers of different hydrophilicities (Na-, C_4-, C_{12}-, C_{18}-montmorillonite). In this way, we determined the effect of the inclusion of clay minerals with different hydrophilicities on the rheological properties of polymer skeletons with different hydrophilicities. As the hydrophobicity of the filler was increased, the composites obtained were increasingly stronger due to the intensification of the apolar interactions between the polymer skeleton and the hydrophobic filler.

Figure 4 shows the mechanical characteristics and the desorption enthalpy values of the composites based on the most hydrophobic polymer, poly(NIPAAm). The quality and quantity of the filler component basically determine the swelling characteristics of the gels (Table 1): The values have a maximum at 5 wt.% filler content, and they decrease at higher filler concentrations. It can also be established that the more hydrophobic the filler, the more swelling is increased. The probable reason for this is that hydrophobized fillers get into contact with the hydrophobic parts of the polymer skeleton through the hydrophobic carbon chains. Thus, in the case of montmorillonites modified by relatively long surface-bound carbon chains, sterically more room remains available for water molecules to penetrate and approach the hydrophilic groups, whereas in the case of shorter carbon chains, the interaction between the clay mineral and the polymer skeleton acts as a steric barrier for the penetrating water.

Among the values determined by DSC, the gel containing 1 wt.% C_{12}-m had the highest enthalpy of vaporization (138.86 kJ/mol), followed by C_4- (134.8 kJ/mol), C_{18}- (120.04 kJ/mol), and Na-m (102.11 kJ/mol). In other words, the removal of the water content of the gels containing C_{12}-m was associated with the largest energy change. The measured value is thrice the value measured in pure water

This assumption is supported by the results of rheological measurements: The smallest storage moduli (G') value was measured for the composite containing the C_{18}-filler,

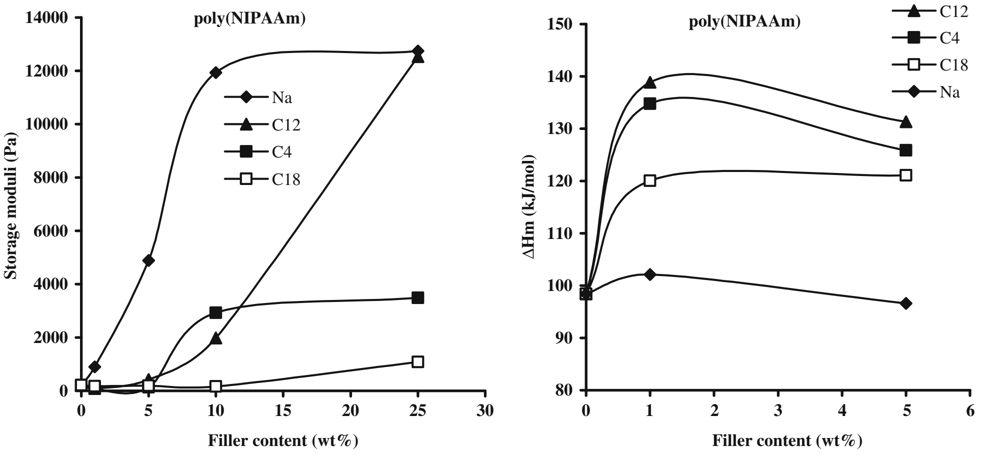

Fig. 4 Storage moduli and desorption enthalpy values of poly (NIPAAm)-based gels with different fillers as a function of filler content (standard deviation values have been omitted to enhance clarity; however, in all cases, the coefficient of variation was less than 7%)

only because of the higher water content; the value of storage moduli (G') increases with the decrease in carbon chain length.

In Fig. 5, the storage moduli (G') and ΔH_m values, respectively, of hydrophilic AAm-based composites are presented. Low concentrations of filler enhance the extent of swelling (Table 1) as compared to gels without filler, but the effect is non-uniform: Maximum swelling of the composites containing the hydrophilic Na-m or the next most hydrophilic composite, C_4-m is at 1 wt.%, whereas that of the composites containing fillers modified by longer carbon chains is at 5 wt.%, i.e., the maxima shift towards higher filler concentrations with increasing carbon chain lengths. The reason for this may be that in the case of Na- and C_4-m, the fillers are positioned in the vicinity of the hydrophilic amino groups of the polymer skeleton; therefore, when present at higher concentrations, they block accessible sites for the incoming water molecules. Fillers with longer carbon chains are preferentially localized in the vicinity of the hydrophobic regions of the polymer, leaving enough room for the incoming water molecules to interact with the hydrophilic regions even at high filler concentrations.

The same assumption is also supported by the values of enthalpy of vaporization: In the case of Na- and C_4-m, the largest enthalpy was consumed by the removal of the water content of the composite containing 1 wt.% filler (122.74 kJ/mol and 118.52 kJ/mol, respectively), whereas in the case of the minerals modified by longer carbon chains (C_{18}- and C_{12}-montmorillonite), it was gels containing 5 wt.% filler that showed a maximum (124.22 and 131.17 kJ/mol, respectively). It is also clear that in each case, the values presented in this paper are several times higher than the value of the enthalpy of vaporization of water (41.74 kJ/mol), which means that these composites bind water via strong interactions.

As regards rheological properties, the highest values of storage moduli (G') were recorded for the samples containing Na-m, i.e., these are the most elastic of the samples studied. The reason for this is the strong interaction between the hydrophilic parts of the polymer skeleton and those of the filler. The resilience of the gels decrease with increasing the hydrophobicity of the filler, but no unequivocal correlation can be established between the carbon chain length (i.e., hydrophobicity) and the values of storage moduli (G').

Values of storage moduli (G') and ΔH_m of the most hydrophilic poly(AAc)-based composites are shown in Fig. 6, respectively. As regards swelling values (Table 1), again, swelling maxima are seen at relatively low filler concentrations and the extent of swelling decreases with increasing the carbon chain length, i.e., hydrophobicity. Swelling values measured at relatively low filler concentrations exceed those of the polymer without filler in all cases. Similarly to swelling, values of storage moduli (G') measured at relatively low filler concentrations are higher than the values characteristic of the polymer. Thus, the composites with filler contents of 1–5 wt.% possess higher swellabilities and more favorable mechanical properties than do the polymers.

This phenomenon also manifests itself in the course of DSC measurements: The enthalpy of vaporization of the sample without filler is 114.74 kJ/mol, whereas the values for the samples containing 1% filler vary between 128.02 and 130.26 kJ/mol. The hydrophilicities of the fillers and the storage moduli (G') values of the composites, however, do not exhibit an unambiguous correlation in this case either: The gels containing C_{12}-m are the most resilient, followed by the samples supplemented with C_4-, Na-, and C_{18}-montmorillonite in this order.

The mechanical properties and the swelling values of composites with various hydrophilicities as a function of carbon chain length—i.e., hydrophilicity—are presented in

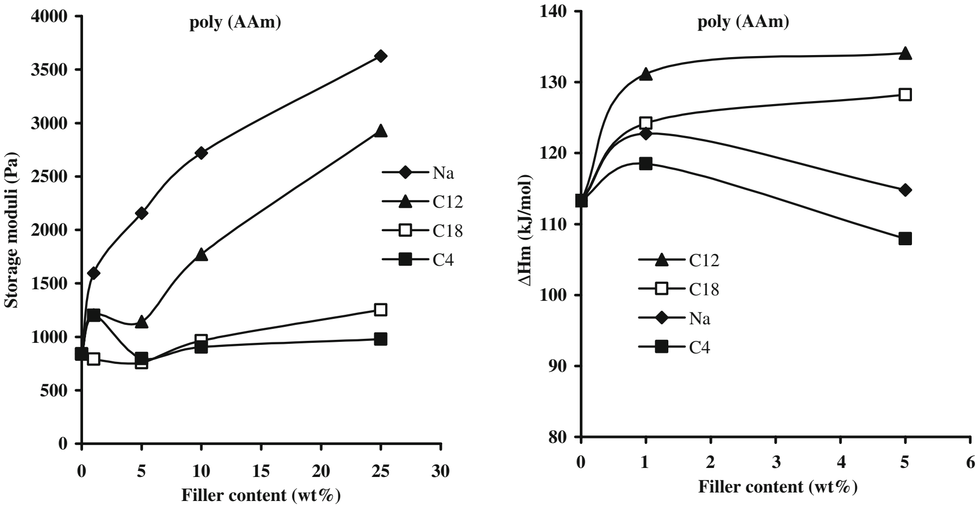

Fig. 5 Storage moduli and desorption enthalpy values of poly (AAm)-based gels with different fillers as a function of filler content (the results are reproducible within ±7% standard deviation)

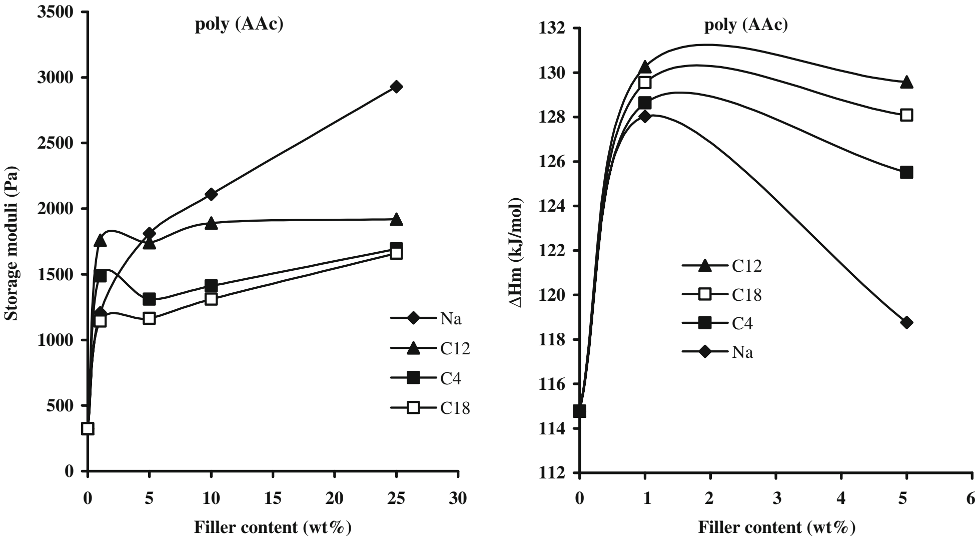

Fig. 6 Storage moduli and desorption enthalpy values of poly (AAc)-based gels with different fillers as a function of filler content (the results are reproducible within ±9% standard deviation)

Fig. 7. The samples studied contained 1 wt.% filler in all cases. The samples containing Na-m are plotted on the leftmost side of the abscissa, followed by those containing C_4, C_{12}, and C_{18} amines, i.e., the hydrophobicity of the samples increases from left to right. Figure 7 reveals that the swelling values of NIPAAm gels are nearly constant over the entire range, only the filler modified with C_{18} exhibits a small increase. The reason for this may be that apolar interactions between the carbon chain of the alkylamine and the isopropyl groups of NIPAAm dominate in the gel matrix, and in the case of a longer carbon chain, more room remains for the incoming water molecules. Evaluation of the mechanical properties of the same composites reveals that the composite containing Na-m has a much higher storage moduli (*G*′) value than do those containing hydrophobized fillers. This is due to the electrostatic interaction between the partially positively charged NH groups of the NIPAAm monomer and the negatively charged lamellae. Evaluation of the storage moduli (*G*′) and swelling values of poly(AAm)-based composites shows that in the case of Na-montmorillonite as filler, both parameters have maxima, and the values measured decrease with increasing carbon chain length of the modifying alkylamine, clearly indicating the formation of electrostatic interactions between the lamellae of the filler and the amino groups, leading to an increase in both swellability and mechanical properties. In the case of hydrophobic fillers, however, alkylamines increase the extent of hydrophobicity and shield the negative charges of the lamellae. Thus, electrostatic interactions dominate in these gels. Our studies on the mechanical properties of AAc-based gels reveal that the storage moduli (*G*′) values obtained have a maximum at a carbon chain length of C_{12}, whereas the swelling values reach their maximum in the case of Na-m. In the case of Na-m as filler, an electrostatic repulsion develops between the negatively charged lamellae and the carboxyl groups, which at the same time means accessible hydrophilic groups for the incoming water

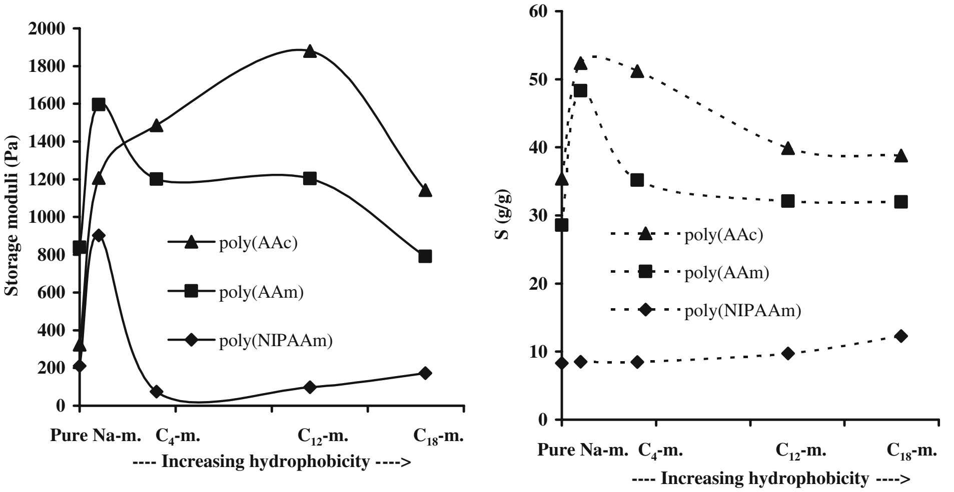

Fig. 7 Elastic properties and swelling values of composites with different fillers as a function of the hydrophobicity of the filler (*solid lines* and *dotted lines* represent *G*′ and swelling values, respectively; the *lines* represent a guide to the eye)

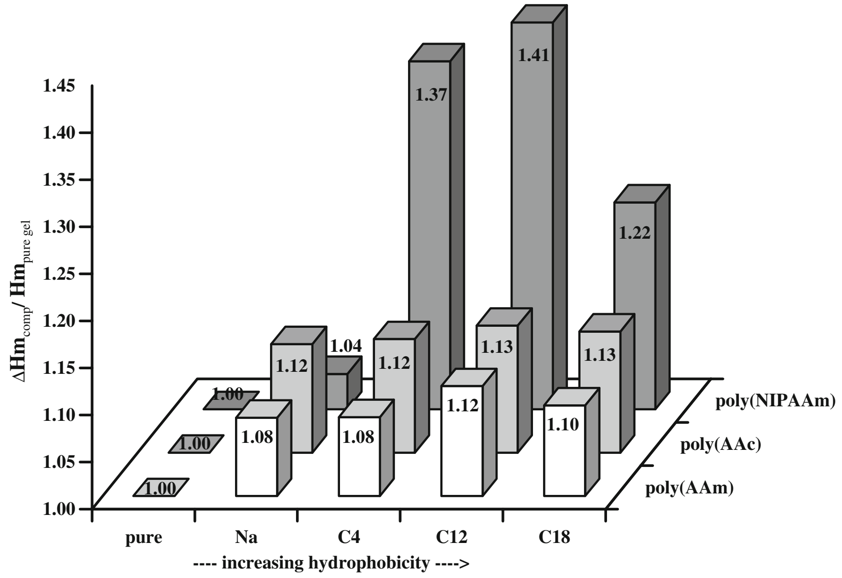

Fig. 8 Desorption enthalpy excess values of composites with different fillers as a function of the hydrophobicity of the filler; the samples contained 1 wt.% filler in all cases

molecules, resulting in the large swelling and small storage moduli (G') values. When the length of the carbon chain modifying the lamellae is increased, they increasingly shield the surface charges and make the samples increasingly hydrophobic. This double effect leads to a decreased swelling and more favorable mechanical properties.

The extent of swelling is enhanced at low concentrations of filler as shown in Table 1. In Fig. 8, the desorption enthalpy excess values of composites with various hydrophilicities as a function of carbon chain length—i.e., hydrophilicity—are presented. The values are referred to the values of pure gels ($\Delta H_{\mathrm{m\ composite}}/\Delta H_{\mathrm{m\ pure\ gel}}$). The data in the figure establish that the enthalpy values of composites are higher compared to gels without filler in all cases. It is also clear that, that the fillers enhance mostly the enthalpy values characteristic of poly(NIPAAm) gels; the composites containing C_4- and C_{12}-m are obtained 40% higher value than the pure gel. The value decreases with a higher hydrophobicity (C_{18}-m) that means weaker interaction between the composite and the water molecules. In the case of hydrophilic polymers, the effect of fillers is not so significant: The poly(AAc)-based gels show 12% excess referred to the pure gel, whereas in the case of poly(AAm)-based gels, the values show a maximum at C_{12}-m (12%). Thus, it can be established that in the case of hydrophobic poly(NIPAAm), the higher water content due to the fillers results stronger interaction among the composite and the water molecules. In the case of hydrophilic gels, however, the higher water content does not mean stronger interaction. The reason for this is that in the case of these composites, electrostatic interaction forms among the hydrophilic parts of fillers and polymer matrix. Therefore, the interpenetrating water molecules increase the amount of free water in the gel, not interact directly with the hydrophilic parts.

Conclusion

We synthesized polymers and copolymers of various monomer compositions and varying cross-link densities starting from NIPAAm, AAm, and AAc monomers. Composites were also prepared using fillers with different hydrophilicities. The effect of the varied parameters on the swellability and the rheological properties of the gels obtained was studied. Based on the experimental results, it can be established that swelling and mechanical properties can be manipulated through monomer composition, cross-link density, and concentration and hydrophilicity of the fillers.

Copolymerization of the hydrophobic NIPAAm monomer with the hydrophilic AAm or AAc monomer yields poly(NIPAAm-co-AAm) and poly(NIPAAm-co-AAc), respectively, gels with increasing swellability and concomitant improvement in mechanical properties.

Reducing the number of cross-links increases the extent of swelling but decreases the resilience of the gels. Changes in cross-link density have the largest effect on the swellability and mechanical properties of hydrophilic poly (AAm) and poly(AAc) gels.

In all cases when fillers are used, a range can be designated in which composites are more swellable and have more favorable mechanical properties than do polymers or copolymers without fillers. We determined the effect of the inclusion of clay minerals with different hydrophilicities on the swelling and rheological properties of polymer skeletons with different hydrophilicities. The addition of various clay mineral fillers improved swelling and rheological properties of the gels but only when applied at low concentration (1–5 wt.%). It was also established that swelling of hydrophilic polymers and copolymers is improved by hydrophilic Na- and C_4-m fillers, whereas that of hydrophobic polymers is increased by hydrophobic C_{12}- and C_{18}-m fillers. In the case of composites, swelling and rheological properties are determined by the hydrophilicity of the polymer skeleton, the hydrophilicity and amount of the filler, and most probably also by the way the lamellae of the filler are arranged within the polymer matrix.

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