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The effect of surface modification of layer silicates on the thermoanalytical properties of poly(NIPAAm-*co*-AAm) based composite hydrogels

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Abstract We studied the effect of variations in the composition of the 3D polymer matrix on the water adsorption properties of poly(*N*-isopropylacrylamide-*co*-acrylamide) [abbreviated as poly(NIPAAm-*co*-AAm)]-based gels containing fillers of diverse hydrophilicities (Na-montmorillonite and hydrophobized montmorillonite). The hydrophilicity of the polymer matrix was modified by varying the ratio of the initial monomers, since acrylamide (AAm) is hydrophilic, whereas *N*-isopropylacrylamide (NIPAAm) is relatively hydrophobic. Filler content was varied in the range of 1–25 wt%. The water content of polymers, fillers and composites, a parameter determined by their different hydrophilicities was characterized by gravimetry and/or thermoanalytical methods (TG, DSC). The water content of the samples was found to be controllable by varying the hydrophilicity of the polymer matrix and/or the amount and hydrophilicity of the fillers added. Swelling of the relatively hydrophobic poly(NIPAAm) can be increased by the addition of hydrophobic fillers, whereas that of the hydrophilic poly(AAm) can be enhanced by the addition of hydrophilic fillers. The effect of changes in composition on the desorption enthalpies of the samples was determined. The water content of the copolymer increases with increasing the ratio of the hydrophilic monomer, which is due to an increase in the so-called free water content. In the case of the hydrophobic poly(NIPAAm) it is primarily hydrophobic association interactions that dominate the interaction between the polymer matrix and the lamellae of the filler, whereas in the case of the hydrophilic poly(AAm) hydrophilic interactions are dominant.

Keywords Hydrogel · Composite · Hydrophobic surfaces · Swelling · Desorption enthalpy

Introduction

Hydrogels are 3D lattice polymers that, due to the presence in them of hydrophilic functional groups, swell to several times their original volume in aqueous media. Owing to its hydrophilic properties, the 3D polymer matrix is readily hydrated by water molecules, and this trait basically determines the properties of the hydrogel. Swelling of the copolymer gel being synthesized can be precisely tuned through variations in monomer composition, i.e. the ratio of hydrophilic and hydrophobic groups. The hydrophilicity dictated by the composition of the sample will determine its water content, which in turn also affects the thermoanalytical properties (TG, DSC) of the gel [1]. When, for example, the hydrophilic acrylamide (AAm) is copolymerized with the more hydrophobic *N*-isopropylacrylamide (NIPAAm), the swelling of the copolymer obtained will be intermediate between the swelling values of the two pure polymers. When the initial monomers are polymerized into an interpenetration polymer, gels possessing unusual swelling properties are often obtained [2, 3].

It is well-known that the properties of gels can be significantly enhanced by the incorporation of inorganic ordered systems, in particular clays, into the gels [4–13]. For example, with the application of adequately chosen fillers can be prepared magnetic- [14], or electric-field

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sensitive polymers [15]. As a model system, sodium montmorillonite layered silicates (Na-m) are widely used as additives to improve the physical properties of plastics [16–19]. The swelling stability of the gels are enhanced by the addition of fillers [Na-montmorillonite (Na-m) and Na-m hydrophobized with alkyl-ammonium ions [(C_n-m), $n = 4$, 12, 18]. Using this method we synthesized composite hydrogels. Incorporation of clay into polymers and copolymer gels was found to enhance the swelling of gels. Various clay minerals and other inorganic materials used as fillers can also be characterized by thermoanalytical methods [20–23].

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 [22, 24]. The hydrophilicity of the filler can then be modified by the addition of a surfactant adsorbable on the surface [21, 25]. In the case of composites, the properties of the hydrogel are basically determined by the inorganic filler: its addition may help improve the swelling [26], the mechanical properties [26, 27], as well as the thermal stability of the polymers [28–32].

The 3D polymer lattice also contains a large amount of bulk-phase water; in other words, hydrogels can store large amounts of water without being dissolved. In general, interactions within the 3D lattice can be classified into four categories, namely ionic, hydrophobic, van der Waals and hydrogen bonds. The bonds established between the functional groups of the 3D lattice and water molecules, however, are nearly always hydrogen bonds. In the case of composites containing inorganic fillers, interactions between different polymer segments, between polymer and filler and between polymer matrix and liquid all have to be taken into consideration. For example, Haraguchi et al. [9] showed by thermoanalytical studies that in the pNIPAAm/hectorite system, at relatively high clay contents, micro-Brown movement characteristic of the polymer is stopped, which is indicated by the disappearance of glassification temperature. Thermoanalytical measurements are well suited for characterizing the interaction between the different segments of the polymer matrix, or between polymer and water molecules [33, 34], and for the exact determination of the water content of gels [35, 36]. When a hydrogel is dipped into an aqueous environment, the water molecules move inward and interact primarily with polar groups in the polymer network to form primary bound water. The free water (the additional water) that penetrates the hydrogel is induced by osmotic forces and leads to the polymer network expanding. These different types of water exhibit different freezing points because they are differently bound to the polymer network [37]. The most relevant DSC studies have argued that there are effectively three classes of water present in polymer-stabilized hydrogels. These are: (i) free water, i.e., unbound water with a transition temperature, enthalpy and peak shape comparable to those of bulk water, (ii) non-freezing water, which is tightly bound to the polymer and does not undergo a detectable phase transition and (iii) 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. Free water has good mobility since it has no interaction with polymer chains. However, bound water is involved in hydrogen bonding with polymers The bound water content depends on the chemical and higher-order structure of the polymer [8, 38, 39]. The bound water decreased with an increase in the molar ratio of hydrophilic groups of polymer [38].

In the case of thermosensitive gels such as poly(NIPAAm), heat effects associated with volume phase transition (VPT) events can also be detected by thermoanalytical methods [40–43]. Poly(NIPAAm) hydrogel exhibits a lower critical solution temperature (LCST) at around 32 °C in aqueous solutions. The thermosensitive behavior of poly(NIPAAm) gels has been extensively investigated and modelled in different laboratories [44–47]. The reversibility of swelling/shrinking is due to the fact that at relatively low temperatures (below ~32 °C) interactions between the polymer skeleton and water molecules are dominant, therefore the gel is swollen, whereas at relatively high temperatures the interaction between the hydrophobic segments of the polymer are enhanced, making the gel collapse. It was reported that the transition heat of the hydrophobic hydrogel collapse was endothermic [2]. The existence of an endotherm might be considered as the phase transition by disruption of hydrogen bonding in water or interpolymer.

In the study presented here we synthesized hydrogel-based composites with diverse hydrophilicities due to variations in composition. Our objective was to study the swelling characteristics of composites as a function of composition and to determine the effect of water content, set by the actual hydrophilicity, on the thermoanalytical properties of the samples by varying the molar ratio of the initial monomers and the hydrophilicities and concentrations of the fillers used.

Materials

NIPAAm, and AAm were used as monomers. Monomers and the cross-linking agent N,N′-methylenebisacrylamide (BisAAm) were obtained from Aldrich Chemical

Company, Inc., and were used without further purification. Other chemicals used were potassium persulphate (KPS) from Reanal Kft. as an initiator and N,N,N′,N′-tetramethylethylenediamine (TEMED) from Fluka Chemie AG as an accelerator.

NIPAAm- and AAm-based polymers and copolymers with 50/50 mol% compositions were prepared by radical polymerization. The appropriate amount(s) of monomer(s) were dissolved in 10 mL distilled water and BisAAm, the initiator (KPS) and the accelerator (TEMED) were added to the polymerization medium. The monomer/crosslinker molar ratio was 200 in each case and the amount of KPS (2×10^{-3} g/10 mL) and TEMED (7.75×10^{-3} g/10 mL) was also constant. KPS and TEMED formed a redox pair for the purpose of radical polymerization. Polymerization was carried out in test-tubes. The reaction was performed at 60 °C for 30 min under N_2 atmosphere. After polymerization the samples were removed from the thermostated water bath.

For the synthesis of hydrophobized 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 (10 g montmorillonite in 100 mL distilled water) and the system was stirred for 24 h at room temperature. 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.

The fillers with various hydrophobicity (Na-m, and montmorillonite hydrophobized with C_4-, C_{12}-, and C_{18}-alkyl-ammonium ions) were swelled in distilled water for the thermoanalytic measurements. From each clays 1 wt% suspension in distilled water were prepared and the systems were stirred for 48 h to reach the swelling equlibrium. Following this, suspensions were centrifugated (15 mins; 14500 rpm; Eppendorf miniSpin Instrument), then the resulting supernatant was isolated and the sediment was measured.

The synthesis of composites was carried out in a similar manner to synthesis of polymers In the case of Na-m and hydrophobized Na-m, however, before the addition of monomers and other chemicals, the appropriate amount of clay mineral was thoroughly suspended in distilled water under ultrasonic irradiation for 1 h. In the course of the synthesis of composites, fillers of various qualities (Na-m and C_4-, C_{12}-, and C_{18}-m) and quantities (1, 5, 10, and 25 wt%) were included in all samples mentioned above. In the case of each composite, the amount in grams of monomers and cross-linkers present in the given solution was first added up and the amount of filler to be added was calculated as a percentage of that amount.

Methods

Swelling was determined gravimetrically, using the following relationship: swelling (S) = (Gs − Gd)/Gd [g/g], where Gs and Gd are the mass of the gel in swollen and dried state, respectively. During the swelling of gels, dried samples were immersed in distilled water at regular intervals (48 h). Following this, swollen gels were removed from the distilled water, dried superficially with filter paper and weighed.

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.

To detecting of heat effects of swelling–deswelling of thermosensitive poly(NIPAAm) gels were carried out with a closed sample pan system. The heating rate was 2 °C/min, measurements were made in the temperature range of 15–50 °C. After the heating the samples were cooled with the same rate.

During TG-measurements the samples were heated from 25 to 500 °C at a heating rate of 5 °C/min (Mettler-Toledo TGA/SDTA 851^e Instrument). So we determine the amount of water of the samples and the heat stability of the gels.

Results and discussion

We first examined the swelling characteristics of the gels synthesized from the monomers with different hydrophilicities used in our experiments, and the effect of hydrophilicity, determined by monomer composition, on the desorption enthalpy values of the samples. Figure 1 displays the DSC curve of poly(NIPAAm-*co*-AAm) copolymer gels and the effect of changes in monomer composition on thermoanalytical (DSC) and swelling properties. In the case of the hydrophobic NIPAAm-based gel the measurement yields only one endothermic peak at 98–131 °C with a maximum at 120 °C. Following the method of Kim et al. [38] and Agrawal et al. [47], we also recorded the DSC curve of distilled water for reference. 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 heat of evaporation of distilled water was determined as 41.74 kJ/mol (The heat of evaporation of water varies between 45 and 40.6 kJ/mol at 0–100 °C). It is clear that the position of the endothermic peak characteristic of poly(NIPAAm) is identical with that of the peak characteristic of distilled water; however, the magnitude of the former is 98.41 kJ/mol. The difference between the two enthalpies is attributable to the interaction between the polymer skeleton and water molecules. When the molar ratio of the hydrophilic AAm is increased in the polymer lattice, on the one hand a novel peak appears at 75–80 °C; on the other hand, the value of desorption enthalpy increases [poly(NIPAAm-*co*-AAm), 99.39 kJ/mol; poly(AAm), 113.30 kJ/mol]. These results suggest that, with increasing the proportion of the hydrophilic monomer, the strength of the interaction between the hydrophilic parts of the gel and water molecules increases; on the other hand, the number of water molecules bound not directly to the hydrophilic groups of the polymer also increases, leading to the appearance of the novel peak at lower temperature. Yin et al. [3] observed a similar phenomenon, namely the appearance of two peaks in the course of DSC measurements on the hydrogel poly(acrylic acid-*co*-acrylamide)/*O*-carboxymethyl chitosan interpenetrating polymer network, indicating that the evaporating water was bound to the polymer matrix by forces of different strengths (free water and freezing bound water). 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 desorption enthalpies. 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.

Our next aim was to quantify, by thermoanalytical methods, the different hydrophilicities of montmorillonite and hydrophobized montmorillonites used as fillers. Dehydration of fillers swollen under identical conditions and their DTG curves are shown in Fig. 2. The diverse hydrophilicities of the fillers swollen under identical conditions also manifest themselves in the course of TG measurements: the most water was lost by Na-m (86.92%), followed by C_4- (85.47%), C_{12}- (74.64%) and C_{18}- (67.54%) m. In other words, decreasing hydrophilicities unambiguously led to lower water contents. The maxima of DTG curves are shifted towards increasingly lower temperatures with increasing hydrophilicity: the maxima of Na-m, C_4-m, C_{12}-m and C_{18}-m are at 112, 100, 94 and 76 °C, respectively.

This observation is also confirmed by our DSC measurements presented in Fig. 3. The most hydrophilic Na-m produced the highest peak, followed by C_4, C_{12}, and C_{18}-m. Again the maxima of the peaks (as well as their starting and endpoints) are seen to shift towards lower temperatures with increasing hydrophilicities. Plotting the desorption

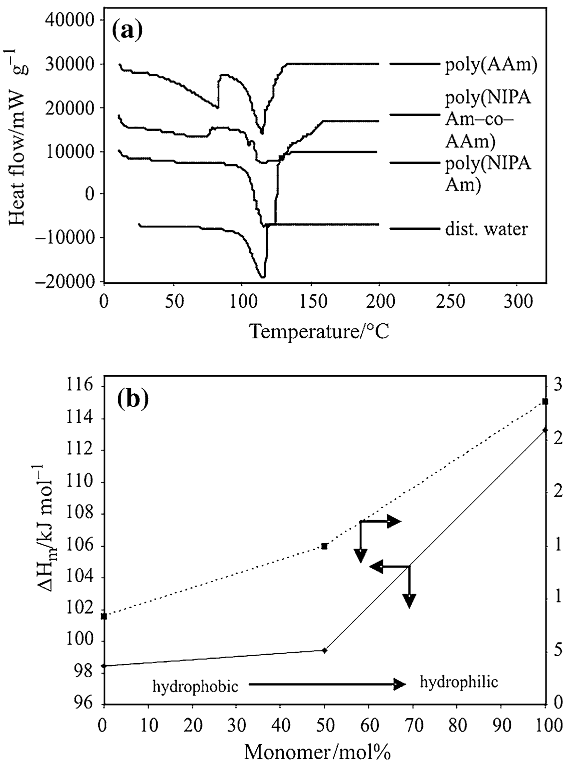

Fig. 1 The DSC curves of poly(NIPAAm-*co*-AAm) gels (*left upper panel*) and the effect of changes in monomer composition on thermoanalytical (DSC) and swelling (*dotted line*) properties

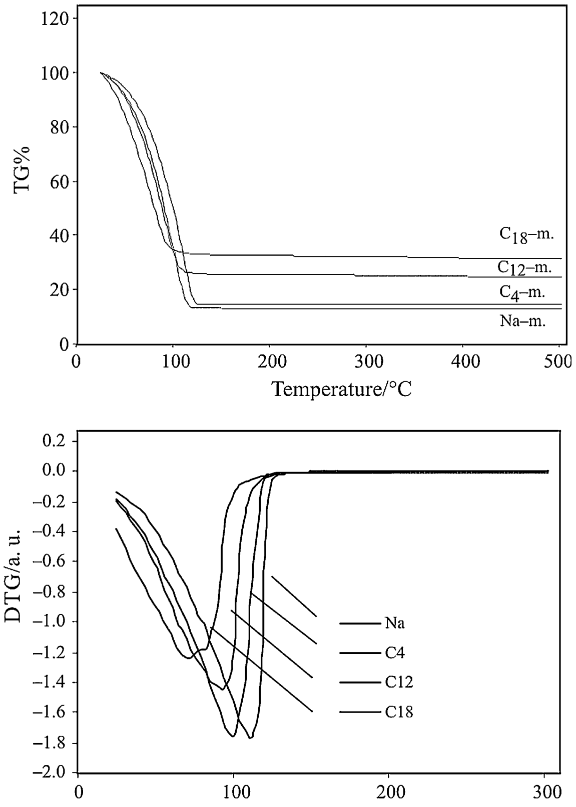

Fig. 2 The TG% and DTG curves of montmorillonite and organophilized montmorillonite

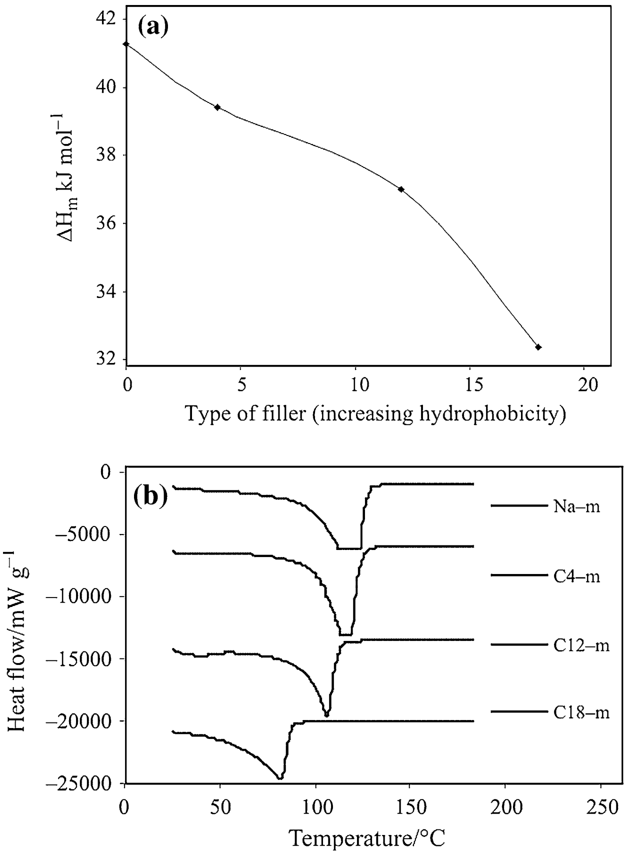

Fig. 3 The desorption enthalpy values and DSC curves (*left downer panels*) of fillers

enthalpy values obtained by integration of the DSC curves as a function of carbon chain length (i.e. increasing hydrophobicity) reveals that as hydrophobicity is enhanced, the removal of the water content of fillers requires increasingly less energy. The following values of desorption enthalpy were determined: 41.27 kJ/mol (Na-m), 39.41 kJ/mol (C_4-m), 37 kJ/mol (C_{12}-m), and 32.37 kJ/mol (C_{18}-m). Thus, in the case of the fillers used, increasing the hydrophilicity results in higher water contents and stronger interactions. It can therefore be established that the hydrophobicity of the initial montmorillonite can be controlled via surfactants with various carbon chain lengths. A similar result was obtained by Picard et al. [21] using a different set of surfactants.

We next set out to determine the effect of hydrophilicity, i.e. the final hydrophilicity resulting from the addition of fillers with various hydrophilicities to polymer matrices of various hydrophilicities, on the swelling values and the desorption enthalpies of the resulting composites. As shown in Table 1, fillers added at relatively low concentrations increase the swelling values of the composites, therefore desorption enthalpies were determined for this concentration range (Figs. 4, 5).

Figure 4 shows the desorption enthalpy values of composites based on the 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 higher the increase in swelling. 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, more room remains sterically 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. Our assumption is supported by the earlier results of Haraguchi et al., who showed that in the initial phase of the polymerization reaction the starting materials (NIPAAm, KPS and TEMED) are adsorbed on the surface of the clay mineral, creating a so-called clay-brush structure [8].

Among the values determined by DSC, the gel containing C_{12}-m had the highest enthalpy of vaporization, followed by C_4-, C_{18}- and Na-m. In other words, removal of the water content of the gels containing C_{12}-m was associated with the largest energy change.

Figure 5 presented the desorption enthalpy values of hydrophilic AAm-based composites. Low concentrations of filler enhance the extent of swelling as compared to gels without filler (Table 1.), but the effect is non-uniform: maximum swelling of the composites containing the hydrophilic Na-m or the next most hydrophilic composite, C_4-montmorillonite is at 1 wt%, whereas that of the

Table 1 Swelling values of polymer 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	32.2	27.6	20.2	20.3	32.1	35.89	32.1	30.4	38.01	42.7	30.49	23.45

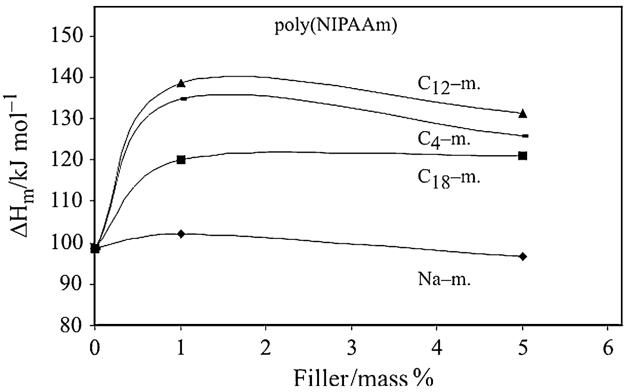

Fig. 4 Desorption enthalpy values of poly(NIPAAm)-based gels with different fillers as a function of filler content

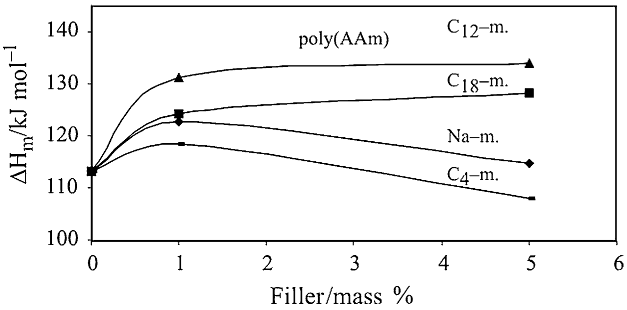

Fig. 5 Desorption enthalpy values of poly(AAm)-based gels with different fillers as a function of filler content

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 removal of the water content of the composite containing 1 wt% filler (122.74 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 here 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.

It is revealed by the two previous figures that the increasing filler content initially increases both the swelling of the composites and the magnitude of the desorption enthalpies determined (1–5 wt%), whereas at higher filler contents (10–25 wt%) the values decrease. We next examined whether the same phenomenon is also detected by TG measurements. Poly(NIPAAm)-based composites containing Na-m were used for this purpose. The TG%, DTG and DTA curves of the composites are presented in Fig. 6. Starting from the initial temperature of 25 °C, the gels loose their mass continuously; the first step is produced by loss of water. In the course of this step, the poly(NIPAAm) gel containing 1 wt% of filler looses 96.5% of its mass (i.e. the water content of the swollen NIPAAm composite amounts to 96.5 wt%). The gels containing 5 and 10 wt% of Na-m loose 90.2 and 85.9 wt% of their mass, respectively, in the course of the first step. The endothermic nature of the DTA curve also demonstrates the phenomenon of water elimination. It can therefore be established that the composite containing 1 wt% of Na-m has the highest water content, and water content decreases with increasing filler content. Another observation is that

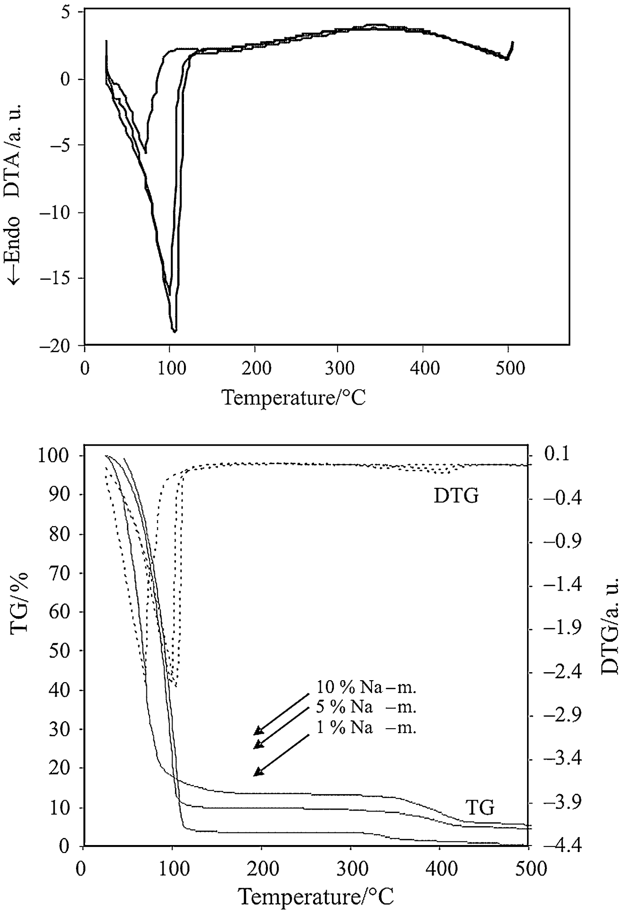

Fig. 6 The TG- and DTA-curves of poly(NIPAAm)-based polymer and composites. The samples have Na-m as filler

the maxima of the DTG curves (indicated by broken lines) are shifted to increasingly lower temperatures with increasing filler content: 99.75 °C (1 wt%), 97.83 °C (5 wt%) and 71.2 °C (10 wt%). Thus, the higher the filler content, the more readily composites part with their water content. In the next temperature range of 123–306 °C neither sample exhibits any phenomenon associated with changes in mass or quantity of heat. The second step appears at 320 °C and is shifted to increasingly higher temperatures with increasing filler content (the positions of the maxima of the DTG peaks increase as a function of filler content to 343.2, 402.58 and 408.25 °C, respectively). This is a result of the decomposition/burning of the polymer skeleton, as also confirmed by the exothermic character of the DTA curve. Thus, it can be established that fillers also enhance the thermal stability of the samples, since decomposition temperatures are shifted to higher values with increasing filler concentrations. Similar results were obtained by Wang et al. [29] in the course of their studies on organoclay-containing, polyamide-based composites treated with various surfactants.

In the case of poly(NIPAAm)-based samples, the endothermic/exothermic peaks characteristic of swelling/shrinking, respectively, can also be determined (Fig. 7). In the course of heating the polymer (continuous line), the endothermic peak associated with shrinking appears at 33.3 °C, in good agreement with the data in the literature [37–40]. The magnitude of the peak is 5.83 J/g. In the course of re-cooling, the exothermic peak associated with swelling also appears, although at a lower temperature (30.5 °C); its magnitude is 5.24 J/g, indicating that the process is reversible. The phenomenon of the shift of the exothermic peak associated with swelling has already been described by Lin et al. [40]. We also examined the collapse of composites containing Na-m. According to the data in Fig. 7, the increasing filler content has no effect of any significance on the position of the peaks or on the enthalpies measured. Although Li et al. [41] consider the properties of poly(NIPAAm)-based gels to be sensitive to the conditions of synthesis, they also found that the VPT of the gel is not affected by, e.g., the monomer/crosslinker ratio.

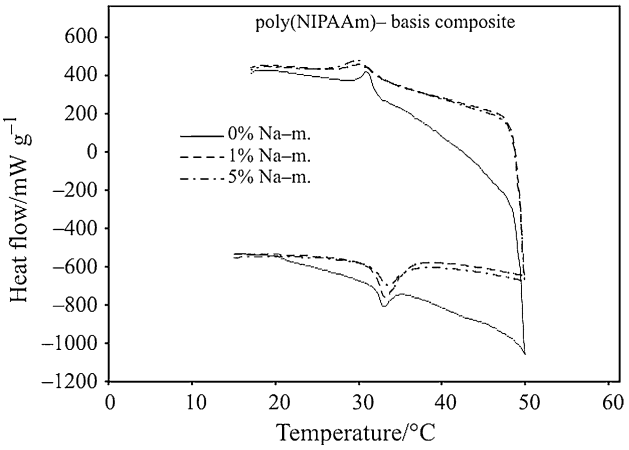

Fig. 7 Volume phase transition (VPT) of poly(NIPAAm)-based composites containing Na-m

Conclusions

The swelling properties of poly(NIPAAm-*co*-AAm)-based composite hydrogels of various compositions were studied. It was established that the extent of swelling increases with increasing the molar ratio of the hydrophilic AAm monomer. It was demonstrated by DSC measurements that increased swelling is due to an increase in the so-called free water content, because desorption enthalpy peaks appeared with increasing water content even at relatively low temperatures (75–80 °C). It was also shown that these gels bind water by strong interactions, since even in the case of poly(NIPAAm) the value of desorption enthalpy is as high as 98.41 kJ/mol, more than twice the value measured in pure water (41.74 kJ/mol).

Differences between the hydrophilicities of the fillers used were demonstrated by TG and DSC measurements and the water content of clay minerals and the strength of the interactions between clay and water molecules were shown to decrease with decreasing hydrophilicity. The water contents of clay minerals swollen under identical conditions varied in the range of 86.92% (Na-m)–67.54% (C_{18}-m) and desorption enthalpies also decreased with increasing hydrophobicity: 41.27 kJ/mol (Na-m), 39.41 kJ/mol (C_4-m), 37 kJ/mol (C_{12}-m) and 32.37 kJ/mol (C_{18}-m).

It was shown for composites containing fillers of different hydrophilicities that swelling increases at lower filler contents; in the case of poly(NIPAAm), swelling of the sample containing C_{18}-m, and in the case of poly(AAm), that of the sample containing Na-m exceeded swelling of the corresponding pure gel by nearly 60%. It was also demonstrated by DSC measurements that these samples bind their water content by stronger interactions than do gels without filler: in both cases gels containing C_{12}-m had the highest desorption enthalpy values. The results of our swelling and thermoanalytical measurements lead us to assume that in the case of the hydrophobic poly(NIPAAm) the relationship between the polymer matrix and the lamellae of the filler is dominated primarily by hydrophobic association interactions, whereas in the case of the hydrophilic poly(AAm) hydrophilic interactions are predominant.

It is demonstrated that the presence of fillers also increases the thermal stability of the samples: for example, in the case of poly(NIPAAm) supplemented with Na-m filler, decomposition temperatures are shifted to increasingly higher values, namely 343.2 °C (1% Na-m), 402.58 °C (5% Na-m) and 408.25 °C (10% Na-m). In the course of DSC measurements it was also shown that, in the case of poly(NIPAAm), filler content has no significant effect either on the position of the peaks associated with swelling/shrinking or on their magnitude, i.e. on desorption enthalpies.

The prepared nanocomposite hydrogels with controllable swelling can be used as skin expanders or tissue implants in the plastic and reconstructive surgery.

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