High Strength Thermoresponsive Semi-IPN Hydrogels Reinforced with Nanoclays

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ABSTRACT: Two series of nanoclay reinforced, thermoresponsive hydrogels were prepared, one based on poly(*N*-isopropylacrylamide) (PNIPA) and the other on semi-interpenetrating networks containing PNIPA and poly(*N*-vinyl pyrrolidone) (PVP), designated as SIPNs. The gels were crosslinked with 1, 3, and 5 wt % inorganic clay (hectorite) and SIPN gels additionally contained 1 wt % of PVP. The hydrogels were tested in the "as-prepared state," i.e., at 10 wt % PNIPA concentration in water and at equilibrium (maximum) swelling. Increasing the concentration of nanoclays increases crosslink density, modulus, tensile strength, elongation (except in equilibrium swollen gels), hysteresis and with decreases in the degree of swelling, broadening of the phase transition region, and a decrease in elastic recovery at high deformations. The presence of linear PVP in the networks increases porosity and the pore size, increases swelling, deswelling rates, and hysteresis, but decreases slightly lower critical solution temperature (LCST), tensile strength, elongation, and elastic recovery. The strongest hydrogels were ones with 10 wt % PNIPA and 5 wt % of nanoclays, displaying tensile strengths of 85 kPa and elongation of 955%. All properties of hydrogels at the equilibrium swollen state are lower than in the as-prepared state, due to the lower concentration of chains per unit volume, but the trends are preserved. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3024–3036, 2012

Key words: thermosensitive hydrogels; nanocomposite; semi-interpenetrating networks (semi-IPNs); swelling/deswelling kinetics; mechanical properties

INTRODUCTION

Polymer hydrogels that respond to external chemical and physical stimuli have been studied extensively from scientific and technical points of view. Due to their high water contents and soft consistency, hydrogels more than any other class of synthetic biomaterials resemble natural living tissue.[1,2] For this reason, polymer hydrogels were projected for a large number of various medical applications. Especially, stimuli-sensitive hydrogels offer great possibilities for different uses since the physicochemical and mechanical properties can be controlled by the change of some external parameters, such as pH, temperature, ionic strength, and electric field. However, their relatively low mechanical strength and low response rate, which mainly arise from restricted molecular motion of the chains caused by the high degree of crosslinking, limit their existing and potential applications. For example, fast responses are required for some specific applications, such as chemical sensors and artificial organs. Synthetic hydrogels used for artificial muscles have to exhibit moduli comparable to those found in living systems (0.2–1 MPa) for power generation, an extension to break of 100% and fast response rate (<10 ms). These target values of modulus and response rate could be achieved by molecular design and better understanding of the mechanical properties of hydrogels. Recently, the new classes of hydrogels with improved mechanical properties were designed, which included nanocomposite (NC) hydrogels,[3,4] double network (DN) gels,[5,6] and semi-interpenetrating gels.[7]

In 2002, Haraguchi et al.[8,9] reported novel polymer–clay NC hydrogels which exhibited remarkably improved mechanical properties as a result of incorporation of layered silicates. Incorporated clay such as hectorite clay Laponite XLG act as a physical crosslinker instead of traditional chemical crosslinkers.[8–12] The NC hydrogels were synthesized by free radical polymerization of *N*-isopropylacrylamide (NIPA) in an aqueous suspension of Laponite XLG. The exfoliated clay in water typically used in polymer–clay NCs are platelets 30 nm in diameter with a thickness of about 1 nm, carrying negative charge on the surface and positive charge at the edge. These NC gels exhibited high transparency, high deswelling rate, and excellent mechanical

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properties, e.g., elongation about 1300% was 50 times larger than that of the chemically crosslinked hydrogels. Tensile strengths were about 270–300 kPa for the gels which contain only 10 wt % of polymer. NC hydrogels could withstand high levels of deformation, not only in the extension and compression mode, but also bending, tearing, twisting, and knotting. It was found that mechanical properties of the NC hydrogels increased with increasing clay content. It was theorized that the network structure was formed by *in situ* free radical polymerization, in which the PNIPA chains were attached to the surface of clay sheets. It was confirmed by dynamic light scattering (DLS) and small-angle neutron scattering (SANS) measurements that clay platelets dispersed homogeneously in the polymer matrix and acted as multiple crosslinkers.[13,14] Clay particles acted as multifunctional crosslinkers with large effective functionality, through ionic or polar interactions with attached poly(*N*-isopropylacrylamide) (PNIPA) chains. Then, PNIPA–clay hydrogels with a high tensile strength of 1 MPa, elongation of 1400%, and complicated deswelling behavior were synthesized based on hectorite (Laponite XLS) modified by tetrasodium pyrophosphate.[15] Surprisingly, an extraordinary high surface hydrophobicity of the of PNIPA NC hydrogels was observed, with the water contact angle being greater than 100°. The high hydrophobicity of NC hydrogels is attributed to the effective alignment of *N*-isopropyl groups of PNIPA chains at the gel–air interface, which is also dependent on network structure, water content, and topological roughness.[16] Zhu et al.[17] reported the synthesis of high clay content Laponite XLS/poly(acrylamide) (PAAm) NC hydrogels with improved mechanical properties. The excellent resilience, low hysteresis, and ultrahigh elongation of these hydrogels are the consequence of better hydrophilicity and flexibility of the PAAm polymer chains.

Change in properties of hydrogels in a controlled way may be accomplished by adding linear polymers to the networks, i.e., by forming semi-interpenetrating networks (semi-IPNs or SIPNs). Recently, Ma et al.[18] reported a new pH/temperature-responsive semi-IPN hydrogel with improved swelling and mechanical properties, based on linear hydrophilic sodium carboxymethylcellulose (CMC), PNIPA, and inorganic clay as a multifunctional crosslinker. Also, a semi-IPN of the NC hydrogel, containing linear carboxymethyl chitosan (CMCS), was designed for dual, the temperature and pH response.[19] The SIPNs hydrogel was opaque due to the incompatibility of CMCS and PNIPA and exhibited lower mechanical properties compared to pure PNIPA NC hydrogels. Song et al.[20] showed the design of pH/temperature responsive semi-IPN NC hydrogels with superior mechanical and swelling/deswelling properties compared to chemically crosslinked PNIPA/PAA hydrogels, due to the hydrogen bonding interactions of polyacrylic acid (PAA) and the clay particles.

Thermally responsive gels may act as molecular machines capable of converting thermal to mechanical energy. Some potential uses include artificial muscles. The functional properties required from such gels are responsiveness, i.e., the fast rate of phase change upon the change of temperature, the magnitude of the response related to the dimensional change and the work carried out, elastic recovery, hysteresis, and mechanical strength. Usually swollen gels are weak and easily crushed upon application of pressure, but new strong gels have been reported recently. Since phase change in thermoresponsive gels involves diffusion of water in and out of a gel, the rate can be enhanced by reducing the diffusion path, i.e., using thin samples, either as sheets or fibers. Unfortunately, the mass of polymer chains in thin swollen gels is small resulting in relatively weak materials. Thus, increasing the strength of gels is an important goal. In this work, we are presenting fairly strong gels reinforced by nanoclays, capable of displaying highly reversible elongations. The gels are made from PNIPA, a well known thermoresponsive polymer. The polymer is bonded at both ends to nanoparticles of clay forming a tridimensional network. Thus, clay particles are behaving as effective crosslinks. Linear, hydrophilic chains of high molecular weight poly(*N*-vinyl pyrrolidone) (PVP) were added to enhance the rate and magnitude of response. PVP is weaved in the PNIPA network forming a semi-IPN.

This study was carried out to optimize the structure of thermoresponsive hydrogels through the use of the nanoparticle reinforced SIPNs, to increase the tensile strength and modulus as well as to improve the swelling/shrinking thermal response. A series of SIPN gels with 1 wt % of linear PVP and with different crosslinking densities by varying the content of clay in the range 1–5 wt % was prepared within the frame of this study (Fig. 1). For comparison, a second series of hydrogels consisting of pure PNIPA reinforced with nanoclays was prepared. Linear PVP was used because it is highly hydrophilic, nonionic, and impart some useful properties, such as good physiological inertia and biocompatibility with the human body. Its high molecular weight allows it to form entanglements for further increase in mechanical properties. Recently, we reported that the addition of 2 wt % linear hydrophilic PVP into the chemically crosslinked PNIPA hydrogels improved thermal response and mechanical properties of the traditional PNIPA hydrogels.[21]

In this article, the mechanical properties of SIPN and PNIPA hydrogels are described and

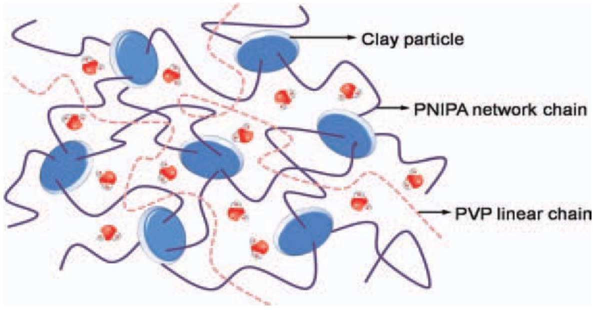

Figure 1 Schematic presentation of the structure PNIPA/clay network interpenetrated with linear PVP chains. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characterization of the gel structure is provided. Gels were prepared at 10 wt % of PNIPA polymer in water (as-prepared state) and then swollen to equilibrium. The equilibrium degree of swelling at 25°C, the dynamic shear modulus and the effective crosslinking density, tensile strength and elongation at the equilibrium swelling, and in the "as-prepared" state were determined. The phase transition temperature of hydrogels was determined by differential scanning calorimetry (DSC). Scanning electron microscopy (SEM) was used to investigate the morphology of the PNIPA and SIPNs hydrogels. Kinetics of swelling and deswelling was used to estimate the responsiveness of the gels. Viscoelastic behavior of the prepared hydrogels was analyzed by dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

NIPA was purchased from Acros Organics (NJ). It was purified by recrystallization from benzene/*n*-hexane (32/68 v/v) and dried under vacuum at 40°C. The synthetic clay hectorite "Laponite XLG" ($[Mg_{5.34}Li_{0.66}Si_8O_{20}{}^{-}(OH)_4]Na_{0.66}$, layer size 20–30 nm in diameter and a thickness of about 1 nm, cation exchange capacity 104 mequiv./100 g) from Rockwood, Ltd., TX, was used as received. Ammonium persulfate (APS) initiator was recrystallized from water. PVP, $M_w = 1.3 \times 10^6$ g mol^{-1} and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TEMED) accelerator were purchased from Fluka, ς-Aldrich (Germany), and used as received.

Synthesis of PNIPA hydrogels

Hydrogels based on PNIPA with different crosslinking densities were prepared by varying the content of clay from 1 to 5 wt %, with and without 1 wt % of linear PVP. PVP solutions (10 wt %) were prepared by mixing the appropriate amount of polymer and water at 80°C and stirring until the polymer was completely dissolved. As a typical example, the hydrogel SIPN-1 was-prepared by adding 2.5 g (0.0221 mol) NIPA, 0.25 g clay, and 2.5 g 10 wt % PVP solution to 22.25 mL of water. The reaction mixture was bubbled with nitrogen for 60 min at approximately 4°C in an ice-water bath. After the addition of 0.25 mL of APS (freshly prepared 10 wt % aqueous solution) and 6 μL of TEMED, the polymerization was carried out at 20°C for 24 h either in a glass tube (diameter = 3 mm), wide glass tubes, or glass molds (12.5 cm × 12.5 cm plates separated by a 2 mm thick rubber gasket). After polymerization, the hydrogels were taken from tubes and glass molds. One part of hydrogels was stored in as-prepared state and other part was soaked in a large amount of distilled water for at least 4 days, changing the water several times to remove residual unreacted monomer.

Sample designations

The samples are designated as SIPNs for semi-interpenetrating networks and PNIPA for hydrogels without PVP, each series having clay content 1, 3, and 5 wt %. The concentration of NIPA was kept constant at 10 wt %. The amount of PVP in SIPN gels was 1 wt % of PVP in water solution. The sample composition and designations of NC hydrogels are summarized in Table I.

TABLE I
Composition and Some Structural and Physical Characteristics of the PNIPA and SIPN Hydrogels in their Equilibrium Swollen State

Sample		Equilibrium degree of swelling, Q_e	Polymer content in the swollen state (wt %)	PNIPA in the swollen state (wt %)	Content of clay remaining in dried gel (wt %)	LCST	
PNIPA-clay	wt % PVP					Heating	Cooling
PNIPA-1	0	41	2.5	2.5	8.7 (95)[a]	32.4	29.7
PNIPA-3	0	18	5.6	5.6	15.5 (80)	31.9	28.1
PNIPA-5	0	12	8.4	8.4	26.4 (78)	34.7	29.7
SIPN-1	1	52	1.9	1.7	7.9 (95)	32.3	29.7
SIPN-3	1	28	3.6	3.3	21.5 (99)	33.1	29.8
SIPN-5	1	15	6.7	6.1	31.7 (87)	31.6	28.3

[a] Clay content (wt %) relative to the added amount in dried PNIPA hydrogels evaluated by TGA.

Characterization

Degree of swelling, Q, was measured on as-prepared round-shaped specimens of the same size (3.3 mm in diameter and 20 mm length) by immersing them in distilled water until equilibrium was reached (after at least 4 days at 25°C). The mass of the dry sample was obtained after drying in an oven until constant weight. The average value of five measurements was taken for each sample. The degree of swelling, Q, was calculated as:

$$Q = m_t/m_d \tag{1}$$

where m_t is the weight of the polymer specimen swollen at time t, and m_d is the weight of the dry hydrogel.

The kinetics of deswelling was investigated gravimetrically at 40°C with hydrogels previously swollen to equilibrium in distilled water at 25°C. The weight changes of the hydrogels were recorded at different times of the deswelling process. Water retention (WR) can be defined as:

$$\mathrm{WR}[\%] = 100 \times W_t/W_e = 100(m_t - m_d)/(m_e - m_d) \tag{2}$$

where W_t and W_e are the weight of water at time t and in the equilibrium swollen state, respectively, and m_e is the weight of the polymer specimen swollen in the equilibrium swollen state.

The volume phase transition temperature was analyzed using a DSC (model Q100 from TA Instruments). The DSC analysis of the swollen hydrogels in hermetic pans was performed by cycling from 15 to 50°C at a heating and cooling rate of 3 °C min^{-1} and with nitrogen flow rate of 50 mL min^{-1}. Distilled water was used as the reference in DSC measurements. The lower critical solution temperature (LCST) of NC hydrogels was determined as the maximum point of the endothermal peak.

Viscoelastic properties of the hydrogels were studied using a Rheometrics mechanical spectrometer, model RMS 605, operating in the shear mode, parallel plate geometry. The diameter of the plates was 25 mm. The storage modulus, G', the loss modulus, G'', and tan δ were analyzed as a function of frequency (varied from 0.1 to 100 rad s^{-1}) at a shear strain of 10% (samples were in the linear viscoelastic range at this strain) at 22°C.

Tensile measurements were carried out on the Table tensile tester, model Q-test 2 from MTS (Eden Prairie, MN) on hydrogels having diameter $d = 3.3$ mm in the as-prepared state (10 wt %) and in their equilibrium swollen state (variable diameter). Gauge length was 30 mm. A 100 N load cell was used with the strain rate set at 30 mm min^{-1}. The hydrogel samples were mounted on a plastic film frame and inserted in the jaws of the tensile tester. The initial dimensions and length of the hydrogel were measured to obtain cross-section area and the percent of strain. The tensile strength, elongation, and elastic modulus of the NC hydrogels were measured on at least five specimens. The elastic recovery and hysteresis of hydrogels was measured at 50, 100, and 200% elongations.

Morphology of hydrogel samples was examined with a scanning electron microscope (SEM, JEOL JSM-5800). To conserve the structure of the hydrogel without collapse, each sample was rapidly frozen and subsequently freeze-dried for 24 h under vacuum at −40°C. The freeze-dried pieces were plunged into liquid nitrogen and carefully cut with a scalpel to observe the interior morphology of the gels. Finally, the samples were coated with a thin layer of Pd-Pt alloy and the microstructure was imaged in the SEM at an acceleration voltage of 20 kV.

Thermogravimetric analysis (TGA) was carried out on TA instrument TGA, model 2050. Dried samples were heated in air from 30 to 1000°C at a heating rate of 10 °C min^{-1}. The clay content in the dried SIPN and PNIPA gels was evaluated from the residual weight at 850°C. Assuming that the conversion of NIPA monomer to the crosslinked network is complete, the theoretical clay content in PNIPA dried gels ranged 9–33.3% and in SIPNs series were between 8.3 and 31.2%. Extent of the incorporation of clay was calculated from TG measurements.

X-ray diffraction (WAXS) patterns of the powder of dried NC gels and the powder of the clay Laponite XLG were obtained with Diffractometer system APD 2000 from X-Ray Associates (UK) scanning from 3° to 60° at 0.02 degree s^{-1}. The voltage and current of the X-ray tubes were 40 kV and 30 mA.

RESULTS AND DISCUSSION

Synthesis and structure of PNIPA and SIPN NC hydrogels

The NC hydrogels were prepared by free-radical polymerization of NIPA in aqueous suspension of Laponite XLG with or without linear PVP. The initial concentration of the monomer NIPA was 10 wt % or 0.885 mol dm^{-3}, while the Laponite XLG concentration in the reaction mixture varied from 1 to 5 wt %. Laponite XLG behaves as a multifunctional crosslinker. NC hydrogels were in the form of either 3 mm thick fibers (cylinders) or sheets.

The clay content in the dried PNIPA gels relative to the added amount, estimated from TGA measurements, varied from 78 to 88%, indicating loss of some Laponite XLG particles from the gel network. The content of clay remaining in dried network was higher in the SIPNs series and was in the range from 87 to 99% of the added quantity. The higher content of Laponite XLG clay in SIPN hydrogels was attributed to the presence of linear hydrophilic PVP, which suppresses extraction of clay particles from hydrogels. Similar observations, reported for PAAM hydrogels/Laponite XLS, showed that above 3 wt % of clay some particles were extracted, while in PNIPA and poly(*N*,*N*-dimethylacrylamide) (PDMA) hydrogels with the same concentration range of clay particles, they remained inside, bound to polymer chains.[22]

It was reported that clays in the NC gels can be substantially exfoliated and that the clay platelets dispersed uniformly throughout the sample.[8–10] The conclusion was based on the high transparency of hydrogels, as well as on TEM and SEM analysis on the thin films and powders of dried NC gels, respectively. To reveal the extent of exfoliation in prepared PNIPA and SIPN hydrogels WAXS analysis was carried out. The WAXS patterns for clay and powders of dried PNIPA and SIPNs gel samples were compared. The clay powder shows XRD peaks at $2\theta = 5.94$, 19, and 35°, corresponding to a basal spacing of 1.49 nm between clay sheets. The peaks at $2\theta = 5.94°$ and 35° corresponding to a layer of 1.49 nm for regularly stacked clay sheets, were reduced in the pattern of dried SIPN and PNIPA gels indicating that the layered structures of clay were partially destroyed, i.e., the clay platelets were not completely exfoliated and dispersed randomly in the hydrogels. The results showed that the fraction of clay which was not exfoliated but retained its own form increases with increasing the clay content.

Degree of swelling of PNIPA and the SIPN NC hydrogels

The equilibrium degree of swelling of PNIPA and the SIPN hydrogels as a function of the clay content and incorporation of linear hydrophilic PVP in water at 25°C, is shown in Table I. The SIPN hydrogels had higher swelling ratios than the PNIPA hydrogels at temperatures below the LCST. The equilibrium degrees of swelling of NC hydrogels were 41, 18, and 12 for PNIPA hydrogels with 1, 3 and 5 wt % clay, respectively, whereas Q values for corresponding SIPNs were 52, 28, and 15, respectively. Thus, in both series of PNIPA and SIPN NC hydrogels, the swelling ratio gradually decreased with increasing content of clay. The degree of swelling of the SIPNs series increased 25–55% with incorporation of linear hydrophilic PVP. Also, the degree of swelling of these NC hydrogels was higher than that in chemically crosslinked SIPNs with the NIPA/MBA (NIPA/*N*,*N*′-methylenebisacrylamide) molar ratio 100/1, in which the degree of swelling was 15.[21] In the equilibrium swollen state, the content of crosslinked PNIPA in hydrogels varied from 2.5 to 8.4 wt %, while the concentration of semi-IPNs in water including linear PVP was in the range from 1.9 to 6.7 wt %, depending on the clay content (Table I).

Morphology of PNIPA and SIPN NC hydrogels

The interior matrix structure of freeze-dried samples of the PNIPA and SIPNs with linear PVP chains was analyzed by SEM. The SEM micrographs of the hydrogels, presented as a function of the clay content and linear PVP incorporated in the hydrogels, are shown in Figure 2. The porous structure of the samples in the swollen state was preserved by employing the freeze-drying method. It has been reported that the freeze-drying process could generate the honeycomb structure of the hydrogels, formed through hydrophobic interaction between polymer chains.[12,23] It can be seen from the micrographs that PNIPA and SIPN hydrogels had similar morphologies, characterized by a broad distribution of pore sizes and very thin pore walls. However, SEM micrographs revealed that the pore size of the SIPN networks increased significantly in the presence of added linear PVP chains and modestly changed with increasing clay amounts. The pore sizes of the prepared SIPNs hydrogels were in the range from 80 to 100 μm and irregular, while the pore size in the PNIPA–clay hydrogels were in the range 38–50 μm. The heterogeneous and irregular structure of the SIPN hydrogels is evidenced by the large standard deviation, in the range from 22 to 26 μm (coefficient of variation, CV~ 26%) compared to PNIPA hydrogels which varied from 12 to 16 μm (CV ~ 32%).

It is well established that the main factor controlling the rate of water diffusion during deswelling is the structure of the matrix, i.e., the number and size of the channels out of which water diffuses. The structure of the PNIPA-1 hydrogel with the lowest degree of crosslinking was completely irregular, consisting of areas with very large channels and other areas with a very large number of small pores. These networks exhibited a very fast response to the temperature change, manifested as the rapid volume shrinkage during the deswelling process.

Dynamics of water swelling and deswelling of PNIPA and SIPN NC hydrogels

The capacity of swelling is considered to be one of the most important parameters to evaluate the properties of hydrogels. Figure 3 shows the swelling behavior of PNIPA and SIPN NC hydrogels with different clay content as a function of time. The

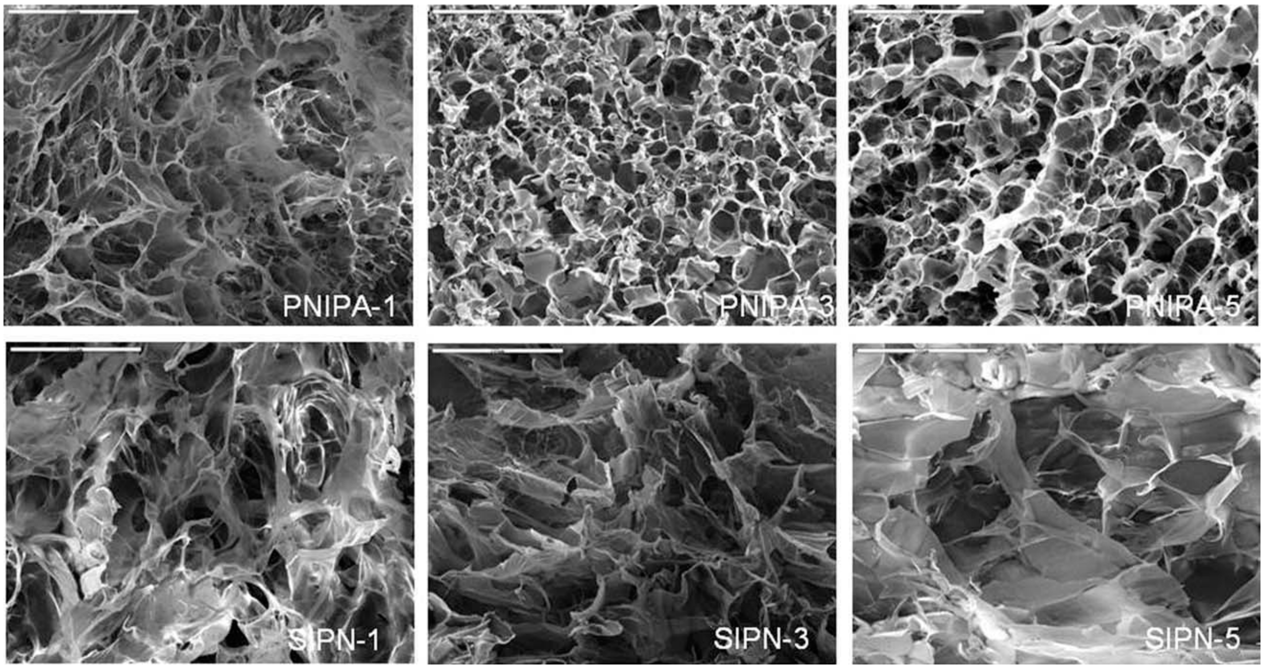

Figure 2 SEM images of the freeze-dried PNIPA gels with 1, 3, and 5 wt % clay (upper row) and SIPN gels with 1 wt % PVP and different content of the clay (bar = 200 μm) (lower row).

SIPN hydrogels swell faster than corresponding PNIPA hydrogels. Four days are needed for PNIPA hydrogels to reach their equilibrium swollen state while only two days were sufficient for the SIPN hydrogels. Higher rates of swelling are attributed to the presence of the hydrophilic PVP.

The kinetics of swelling of hydrogels are frequently formally described as a process controlled by diffusion or as a first order chemical reaction.[24–26] The swelling kinetics of NC hydrogels has been investigated and it was found that they followed non-Fickian diffusion.[27,28] In the present study, the influence of clay content as well as the presence of PVP in NC hydrogels on the swelling kinetics was analyzed by using the initial swelling rate. The initial swelling rate, ν_{in}, is defined as the ratio of the swelling degree and time, corresponding to the linear part of the swelling curve: $\nu_{\mathrm{in}} = (Q - 1)/t_{\mathrm{in}}$

The initial swelling rates thus obtained are 0.141, 4.3×10^{-2}, 2.66×10^{-2} (min^{-1}) for PNIPA-1, PNIPA-3, and PNIPA-5, respectively. It can be concluded that initial swelling rates of NC hydrogels decreased with increasing clay content as a consequence of the increase in crosslinking densities of the hydrogels, which restrict the mobility of polymer chains. In the series of SIPN hydrogels, the initial swelling rates were 0.225, 8.43×10^{-2}, 4.58×10^{-2} (min^{-1}) for SIPN-1, SIPN-3, and SIPN-5, respectively. The results confirmed that the swelling rates of NC hydrogels interpenetrated with PVP are higher than that of NC hydrogels with same clay content.

The deswelling tests were performed on samples that had been previously equilibrated at ambient temperature and then quickly transferred into distilled water at 40°C. The deswelling behavior of PNIPA and SIPN hydrogels above the volume phase transition temperature (Fig. 4) is characterized by the decreasing rate for both series of PNIPA and SIPN hydrogels with increasing content of clay as well as by faster deswelling of SIPN compared to PNIPA. The hydrogels with 3 and 5 wt % clay

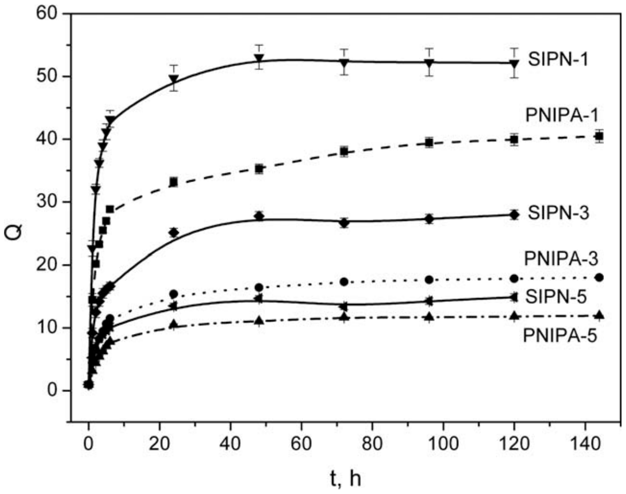

Figure 3 The degree of swelling of PNIPA and SIPN hydrogels with different amount of clay as a function of time at 25°C.

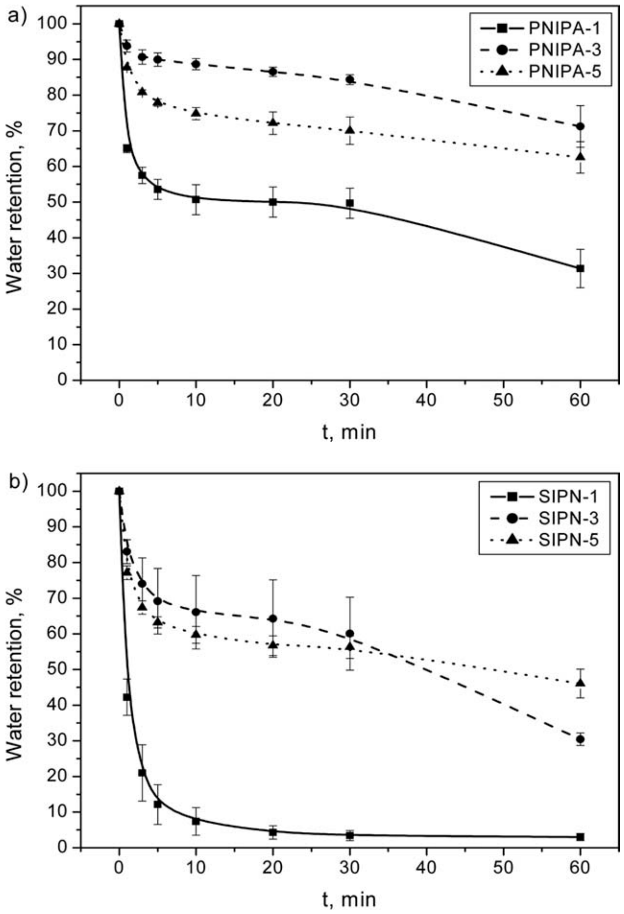

Figure 4 Deswelling kinetics of PNIPA and SIPN hydrogels in water at 40°C as a function of clay content.

exhibited a quite low deswelling rate because of the formation of highly crosslinked polymer network structure, which restricts the collapse of hydrogels during deswelling and resulted in rate decrease. PNIPA-1 hydrogel loses 50% of water within 5 min and SIPN-1 lost more than 70% water in 1 min. Hydrogel reinforced with 1wt % clay (PNIPA-1) exhibits large pores (channels) as observed by SEM, allowing faster diffusion of water from the hydrogel.

Swelling and deswelling or gel collapsing are diffusion controlled processes. Their kinetics strongly depends on the size of the gels as well as on the gel structure. Additives may be used to enhance diffusion. It was reported that the swelling and collapsing rate could be increased by introducing a surfactant into PNIPA hydrogels.[29] We have achieved considerably faster deswelling and volume shrinkage of SIPN hydrogels by the addition of 1 wt % PVP. The sample of SIPN hydrogels with the lowest crosslinking density (1 wt % of clay) shrunk rapidly and lost more than 70% water within 1 min and deswelling equilibrium was achieved within the next 20 min. Other SIPN samples required a few hours to reach the equilibrium state.

To monitor the thermal response of the SIPNs and PNIPA hydrogels, the length contraction in water at 40°C of these gels under a load of 2 g was recorded with a camera. The photographs of the contraction of PNIPA-1 and SIPN-1 hydrogels, physically crosslinked with 1 wt % clay, recorded during 30 min, are given in Figure 5. PNIPA and SIPN gels with the lowest crosslinking density contracted rapidly, within 1 min, from 5 to 29%, and after 30 min they reached the equilibrium contraction at 16 and 42%, respectively. The contraction of PNIPA and SIPN hydrogels with 3 and 5 wt % of clay decreased and reached the values of 23–14% after 30 min, respectively. These results are opposite to the ones obtained on conventional chemically crosslinked hydrogels, which shrink faster as the crosslinking density increases.

Thermoresponse of PNIPA and SIPN NC hydrogels

Hydrogels based on chemically crosslinked PNIPA are known to exhibit a volume transition at about 34°C.[30,31] This is slightly higher than the (LCST ≈32°C) of the linear PNIPA polymer in the aqueous solution. Linear PNIPA polymers exhibit a sharp conformation transition in water by releasing structured water molecules around the polymer chains. In PNIPA hydrogels, the volume transition is

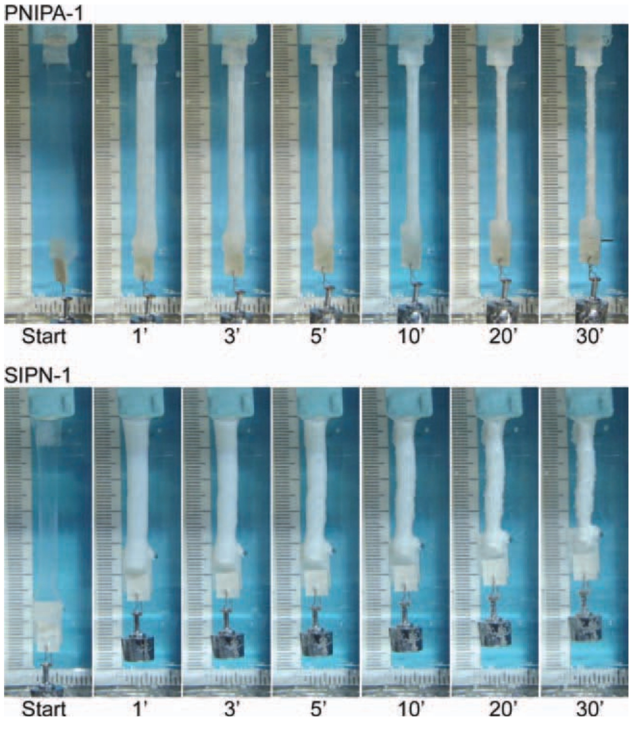

Figure 5 Photographs of the contraction of hydrogels in water at 40°C under a load of 2 g. Upper row: PNIPA-1 and lower row: SIPN-1. Numbers designate time in minutes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

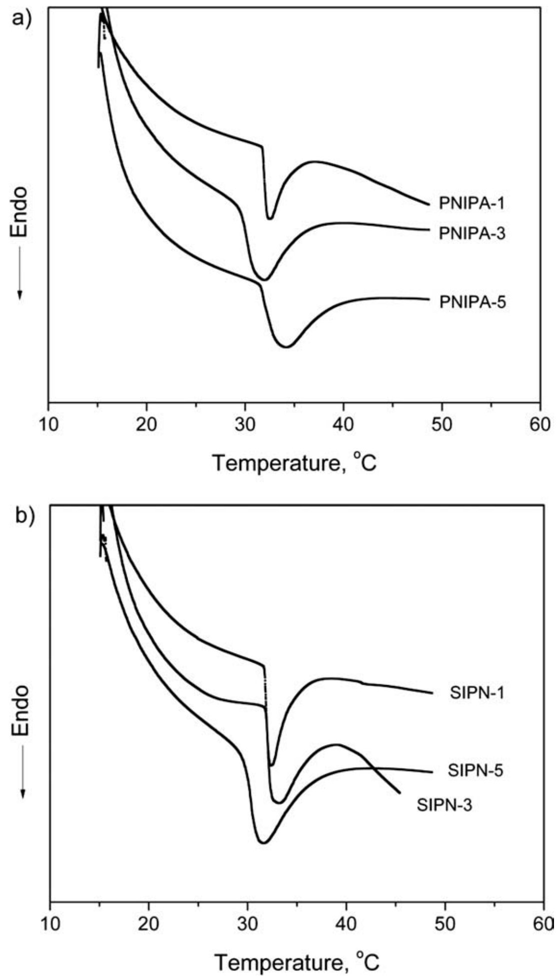

Figure 6 DSC thermograms of PNIPA and SIPN hydrogels in the temperature range from 15 to 50°C (second run).

induced by the cooperative dehydration of the hydrophobic isopropyl groups in the main chain, coupled with the entropic force of the chains, which shrinks the gel. The volume transition of PNIPA depends on the ratio of the hydrophilicity of the amide groups and the hydrophobicity of the isopropyl groups, which changes with temperature. Different strategies have been used for enhancing the temperature sensitivity of PNIPA hydrogels, increasing volume change, and accelerating deswelling. NC PNIPA hydrogels were reported to exhibit large volume change and high deswelling rate with decreasing clay content (crosslink density), which is opposite from the behavior exhibited by chemically crosslinked PNIPA hydrogels.[21] With increased clay content, swelling and deswelling rates of NC hydrogels were both depressed and furthermore NC hydrogels with clay content above 12 wt % did not deswell but swelled above LCST, losing their thermosensitivity.

Figure 6 illustrates the phase change and LCST of PNIPA and SIPN hydrogels as observed by DSC. Temperatures of the endothermic peaks of PNIPA and SIPN hydrogels, referred to as LCSTs, vary from 32 to 34°C (Table I). The change in LCST of NC hydrogels could be attributed to restrictions of the thermal molecular motions of PNIPA chains attached to the hydrophilic surface of clay particles or hindered by their proximity, as was previously reported.[32] Increasing clay content causes broadening of DSC peaks due to the decreased response rate, increased hydrophilicity of NC hydrogels, and the presence of hydrophilic PVP. The clay surfaces are highly hydrophilic and the conformational transition of polymer chains to the hydrophobic state could be partially hindered in polymer chains situated between clay sheets.[4] A faster response for PNIPA hydrogels was reported to result in sharper and narrower DSC peaks.[33] Our DSC analysis suggests that the incorporation of hydrophilic PVP into the PNIPA network of NC hydrogels did not have a distinct and significant effect on the LCST, although it is determined by the hydrophilic/hydrophobic balance of PNIPA chains. It was also observed that the lower clay content gave faster response rates, as was confirmed by the deswelling kinetics measurements.

Mechanical properties of PNIPA and SIPN NC hydrogels

Tensile strength and elongation at break of PNIPA and SIPN NC hydrogels were measured in the stretching mode. The hydrogels in the form of thick cylinders were deformed uniformly without necking. The fracture usually occurred at a point close to the holder.

Haraguchi et al.[8–11] reported high ultimate tensile strength (about 70 kPa) and elongation at break (around 1300%) of NC hydrogels of low crosslinking density in the as-prepared state with Laponite. They attributed the unusual behavior of Laponite hydrogels to the uniform distribution of the clay particles within the hydrogel samples. Also, the near to complete recovery on release of the stress is consistent with extension and contraction of the flexible polymer chains. Shibayama and coworkers[34,35] attributed good mechanical properties of NC hydrogels with Laponite to the "plane crosslinking effect." In the deformed state, the clay platelets were highly aligned with their surface perpendicular to the stretching direction while the PNIPA chains were elongated parallel to the stretching direction. From tensile experiments, Xiong et al.[36] revealed that the high deformability of NC hydrogels is a consequence of their low effective network density and moderate relaxation of polymer chains.

Tensile strengths of PNIPA and SIPN NC hydrogels containing 1 wt % of clay were relatively low

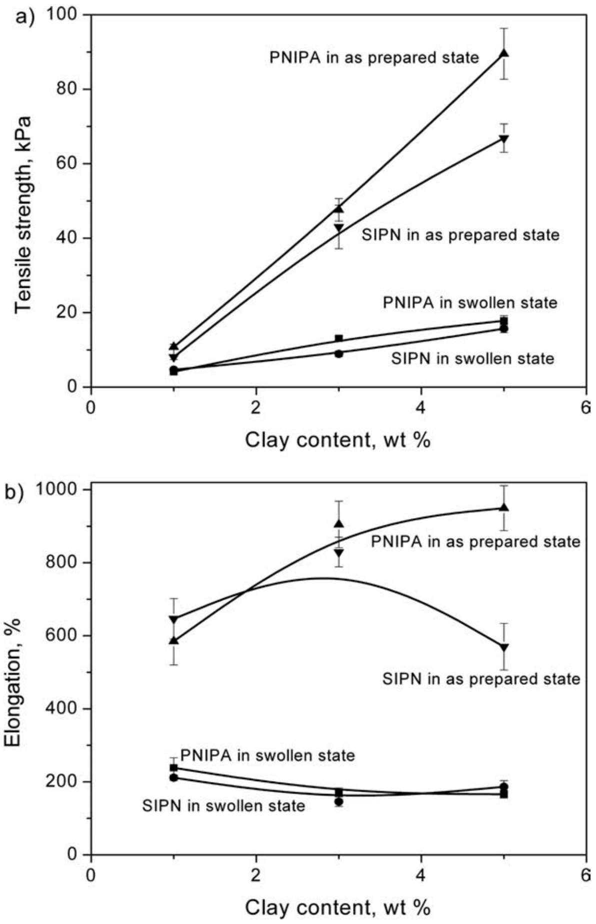

Figure 7 Tensile strength and elongation of PNIPA and SIPN hydrogels in as-prepared and equilibrium swollen state as a function of clay content.

(8–10 kPa) in the as-prepared state, and around 4 kPa in the swollen state, but elongations were high (600% in the as-prepared state versus 200% in the equilibrium swollen state). Figure 7 shows increasing tensile strength and elongation of PNIPA and SIPN hydrogels with increasing clay content in the as-prepared state, i.e., containing 10 wt % of PNIPA polymer chains. PVP presence did not improve mechanical properties of NC hydrogels at higher clay contents as SIPN samples displayed similar but somewhat inferior strengths and elongations to PNIPA gels. Tensile strengths of the equilibrium swollen gels were unaffected by the presence of PVP but they increased several fold with the addition of clay nanoparticles while elongation decreased mildly. Usually, increasing strength is associated with decreasing elongation, but in the case of the as-prepared gels, both increased with increasing content of nanoclays. This indicates improved network structure and mending of loose chain ends with increasing clay concentration. Elongation of PNIPA and SIPN hydrogels in the as-prepared state varied from 600 to 950% and decreased to around 200% in the equilibrium swollen state. As was expected, the modulus of PNIPA and SIPN hydrogels, determined from the tensile measurements, increases with increasing clay content. For example, the elastic modulus of PNIPA and SIPN hydrogels with 5 wt % clay in the equilibrium swollen state exhibited values of 12 kPa and 9 kPa, respectively. The elastic modulus of the SIPN hydrogels in the as-prepared state increased 1.12–1.7 times in the presence of the linear PVP polymer as a consequence of entanglement contribution, and with 5 wt % clay in the equilibrium swollen state approached the value of 28 kPa (Table II).

Also, the energy to break NC hydrogels slightly increases from 3 N mm for PNIPA and SIPNs with 1 wt % clay in equilibrium swollen state to 6.2 N mm for hydrogels with 5 wt % clay. Therefore, the

TABLE II
Mechanical Properties of the PNIPA and SIPN Hydrogels in their As-Prepared and in Equilibrium Swollen State

Sample		Equilibrium degree of swelling, Q_e	Tensile strength (kPa)	Elongation (%)	Modulus, E^a(kPa)	Hysteresis, at 200% I and II cycle^b (%)	Elastic recovery, at 200%
PNIPA-clay	wt % PVP						
PNIPA-1	0	41	4.1	238	1.9	7 (2)	90
PNIPA-3	0	18	13.1	168	7.3	10 (4)	96
PNIPA-5	0	12	17.8	166	12	–	–
SIPN-1	1	52	4.7	211	2.2	9 (2)	91
SIPN-3	1	28	8.9	146	5.9	16 (5)	98
SIPN-5	1	15	15.7	186	9.3	33 (12)	96
PNIPA-1s	0	10	10.8	583	1.3	14 (12)	95
PNIPA-3s	0	10	45.0	894	8.9	23 (12)	93
PNIPA-5s	0	10	85.1	955	25	42 (23)	95
SIPN-1s	1	10	8.4	638	1.1	23 (13)	96
SIPN-3s	1	10	45.6	818	15	59 (37)	83
SIPN-5s	1	10	63.3	604	28	59 (37)	81

s, standard preformed hydrogels in the as-prepared state (10 wt %)
[a] Young's modulus obtained from initial slope of the stress–strain curve.
[b] Hysteresis of the first and second cycle in the parenthesis.

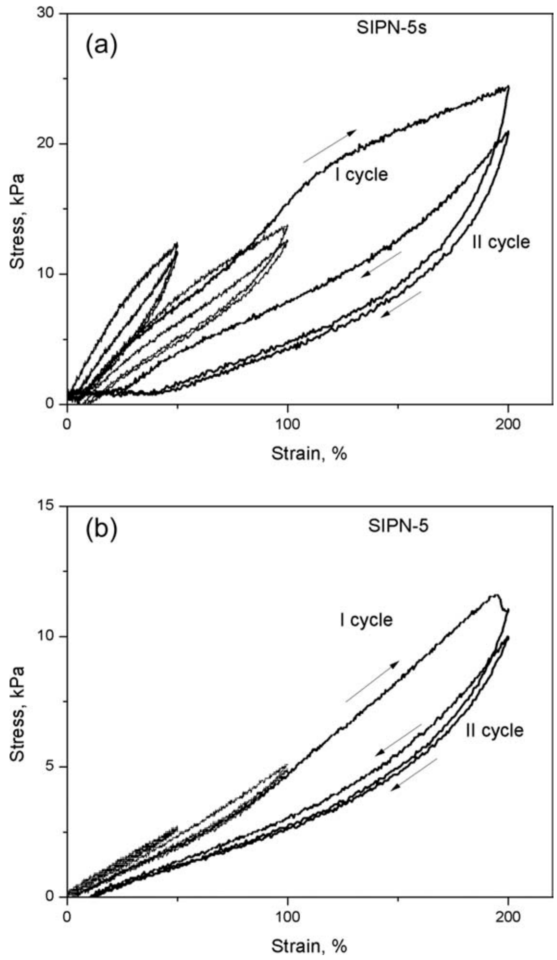

Figure 8 Hysteresis and elastic recovery in cyclic tests of SIPN hydrogels in as-prepared state SIPN-5s (a) and equilibrium swollen state SIPN-5 (b) as a function of strain.

energy to break hydrogels in the equilibrium swollen state increases 3.8–7.8 times compared to chemically crosslinked PNIPA hydrogels and 1.5–3 times compared to chemically crosslinked semi-IPNs.[7]

Elastic recovery and hysteresis of the hydrogels PNIPA and SIPN hydrogels

The series of loading–unloading experiments at elongations of 50, 100, and 200% were carried out on both equilibrium swollen and as-prepared state (10 wt % PNIPA) hydrogels to measure elastic (strain) recovery and hysteresis. Mullins effect (stress softening),[37] i.e., higher stresses in the first cycle than in subsequent cycles, was found in all gels. Some polymer chains attached to the particles are stretched while the others are relaxed. By stretching the samples the "prestretched chains" may be detached from the particles and rebonded in the new state causing equilibration of stresses. Hysteresis in the first cycle is large and it is significantly reduced in repeated cycles as shown in Figure 8. This means that the elastic properties of gels can be improved by prestretching. Higher extensions resulted in larger hysteresis in both PNIPA and SIPNs series. When extension in tensile measurements increased from 50 to 200% the values of hysteresis of PNIPA and SIPN hydrogels increased 1.5–5 times in the as-prepared state and 3–10 times in the equilibrium swollen state. The hysteresis loop, represented by the enveloped area increased with increasing clay content, as well as with increasing polymer concentration, i.e., it was higher in the as-prepared state (10 wt % PNIPA) than in the equilibrium swollen state, Figure 9. For example, hysteresis of the SIPN-5s hydrogels in the as-prepared state was 59% in the first cycle and 36% in the second cycle. Hysteresis in the swollen state of SIPN-5 is 33% in the first and 12% the second cycle. Hysteresis was higher for SIPN hydrogels than PNIPA hydrogels (Table II). It appears that PVP chains increase the internal friction and slow down relaxation processes. However, hysteresis of the PNIPA-1 and SIPN-1 hydrogels with 1

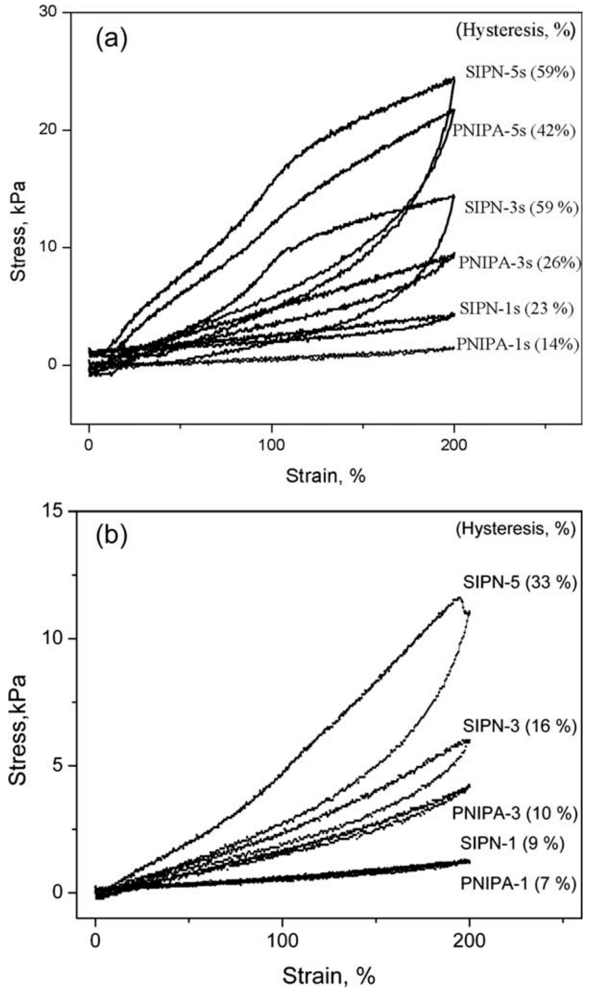

Figure 9 Cyclic stress–strain curves of PNIPA and SIPN hydrogels in the as-prepared state (a), and equilibrium swollen state (b), as a function of clay content.

wt % clay in both swollen and in the as-prepared state was very small, below 20%.

Elastic recovery for PNIPA and SIPN hydrogels in the equilibrium swollen state in the first cycle, after elongation from 50 to 200%, was high (90–98%), showing no dependence on clay content and the extent of elongation (Table II). It can be rationalized that in the highly swollen state the chains are disentangled and internal friction forces are reduced, implying little dissipation at the molecular level. This leads to low stress loss and high elastic recovery. Elastic recovery of PNIPA in the as-prepared state was about 95%, while SIPN hydrogels with higher concentration of the clay displayed a lower recovery of 81–87% at 200% elongation. PVP chains seem to increase the internal friction and viscous dissipation of energy, and slow down relaxation processes. Highly elongated hydrogels cannot recover immediately to the original length when the stress is released, but in time they recover completely, i.e., no permanent set was observed. They recovered their initial length typically within a few minutes. The results suggest that the interaction between polymer chains and clay particles are not permanently broken and that network structures can be easily restored.

SIPN hydrogels which exhibited a pronounced first cycle hysteresis, resembling some filled elastomeric materials. The toughness in these materials is attributed to a significant first cycle hysteresis.[38,39] As in elastomeric materials, the interaction between particles and polymers in SIPNs NC hydrogels are not permanently broken.

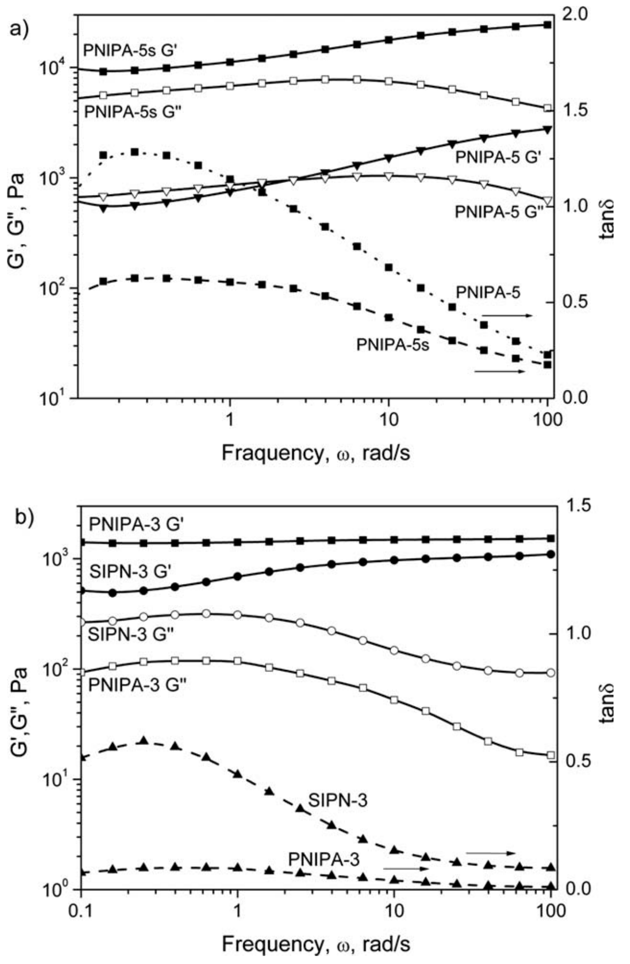

Figure 10 Storage G', loss G'' modulus and tan δ as a function of frequency of PNIPA-5 in as prepared and swollen state (a) and PNIPA-3 and SIPN-3 in equilibrium swollen state (b). See Table III.

Dynamic–mechanical measurements of PNIPA and SIPN hydrogels

The storage modulus G', loss modulus G'', and tan δ were determined from dynamic mechanical measurements in the shear mode (Fig. 10). The measurements were carried out on hydrogels in the as-prepared state as well as in the equilibrium swollen state at 22°C. The results showed that an increase in content of clay from 1 to 5 wt % resulted in an increase of 23–35 times the shear storage modulus G' of the PNIPA and SIPN hydrogels in the equilibrium swollen state, respectively. The PNIPA and SIPN hydrogels in the as-prepared state exhibited similar shear moduli from 5 to 16 kPa, indicating that clay nanoparticles acted as a multifunctional crosslinkers and controlled the rubber elasticity of these hydrogels. The loss factor, $\tan \delta = G''/G'$, which represents the ratio of dissipated to stored energy during one deformation cycle, and modulus measured at 1 Hz are presented in Table III.

Previously, it was reported that viscoelastic measurements showed that elastic storage modulus G' of PAAm/clay hydrogels increase three orders of magnitude with increased clay content and the loss factor tan δ was found to be around 0.1. This shows that the NC hydrogels are much more viscous than the conventional hydrogels.[40] For chemically crosslinked hydrogels, tan δ is around 0.01, indicating negligible viscous response. Our experiments showed that the addition of clay nanoparticles into hydrogels leads to an increase in tan δ, in both PNIPA and SIPN series, and in both the as-prepared and the equilibrium swollen state. In both series, tan δ increases from 0.10 to 0.79 with increasing clay content, meaning that the viscous response becomes comparable to the elastic response. The tan δ, markedly higher than 0.1, is related to a strong dissipation mechanism and is in agreement with the large hysteresis present in the tensile experiments. This could be one of the reasons for their excellent mechanical properties. Large tan δ values of PNIPA and SIPN hydrogels, as previously reported, indicate long relaxation times and a broad relaxation time

TABLE III
Dynamic Mechanical Properties of the PNIPA and SIPN Hydrogels in their As-Prepared and in Equilibrium Swollen State

Sample[a]									
PNIPA-clay	wt % PVP	Equilibrium degree of swelling, Q_e	G' (Pa)	G'' (Pa)	tan δ	G'_e (kPa)	G'_{red} (kPa)	N_e[a] (mol m^{-3})	M_c (g mol^{-1}) 10^{-4}
PNIPA-1	0	41	55	5.2	0.09	0.55	22.3	9.2	12.0
PNIPA-3	0	18	1480	67.6	0.05	1.48	26.6	11.0	10.0
PNIPA-5	0	12	1310	1040	0.79	1.31	15.6	6.4	17.1
SIPN-1	1	52	43	4.3	0.10	0.44	22.9	9.4	11.7
SIPN-3	1	28	934	182	0.19	0.93	26.2	10.8	10.2
SIPN-5	1	15	1530	1100	0.72	1.53	22.8	9.4	11.8
PNIPA-1s	0	10	900	195	0.21	0.90	9.0	3.7	29.8
PNIPA-3s	0	10	8040	585	0.07	8.04	80.4	33.0	3.33
PNIPA-5s	0	10	16,200	7780	0.48	16.2	162	66.7	1.65
SIPN-1s	1	10	–	–	–	–	–	–	–
SIPN-3s	1	10	4680	696	0.15	4.68	46.8	19.2	5.73
SIPN – 5s	1	10	11,660	4805	0.41	11.7	117	48.0	2.29

s, standard preformed hydrogels in the as-prepared state (10 wt %).

[a] The effective network chain density determined from G'_e with Eq. (3).

spectrum, influencing the large hysteresis of these hydrogels.

The storage modulus G' was used to evaluate the effective chain density of these PNIPA and SIPN hydrogels. The effective network chain density N_e of hydrogels, assuming an affine network, is related to the equilibrium shear modulus G_e given with following equation[41]:

$$G_e = \phi \frac{\rho}{M_c} R T \tag{3}$$

where, G_e was taken as plateau modulus or at low frequency, at G' versus ω curves. R and T are the gas constant and absolute temperature, respectively, ϕ is the volume fraction of the polymer in the swollen network and M_c is the molecular weight of network chains. The estimated values of crosslinking density in the unswollen state, N_e, and M_c are given in Table III, together with the G'_{red} (the storage shear modulus in the dry i.e., unswollen state) values. As the clay content is increased from 1 to 5 wt %, the molecular weight M_c decreased from 30×10^4 to 1.6×10^4 g mol^{-1} for the polymer network. The results of molecular weight of the crosslinked chains M_c determined from tensile (not presented here) and dynamic shear experiments confirmed good agreement between the two sets of experiments for PNIPA and SIPN hydrogels.

The values of the elastic modulus, E, determined from tensile measurements are higher than corresponding given by the relationship: $E = 2(1 + \nu)\ G_e$ (G_e, taken as the plateau modulus at G' versus ω curves and ν is the Poisson's ratio). The Poisson's ratio could be assumed to equal to one-half, since hydrogels as rubber-like materials usually exhibit Poisson's ratio close to 0.5. However, swollen gels were shown to exhibit Poisson's ratio lower from [1/2] by a number of researchers.[42,43] If we assume the Poisson's ratio to be equal $\nu = 0.5$ for our NC hydrogel there is also discrepancy between values of the elastic and the equilibrium shear modulus. It is probably attributed to deviation from the affine deformation and the volume compression of hydrogels, predominantly caused by stretching of the gel network, as was previously reported.[44] The strain used in tensile measurements (100%, $\alpha = 2$) is much larger than deformation used in the shearing measurements ($\gamma = 10\%$), which seems to cause a deviation from the affine deformation and the volume compression.

CONCLUSIONS

Novel strong, temperature responsive gels based on SIPN reinforced with nanoclays were prepared and characterized. Hydrophilic linear PVP modified the morphology of gels by increasing pore size and contributed to the higher equilibrium swelling ratio and higher swelling–deswelling rates. Tensile strengths of the SIPNs and PNIPA hydrogels increased linearly with the clay content, approaching 60 kPa and 80 kPa, respectively, for gels with 5 wt % clay. Tensile strength of PNIPA and SIPN equilibrium swollen hydrogels dropped to 4–18 kPa. The elongation to break of PNIPA and SIPN hydrogels in the as-prepared state varied from 600 to 950% with increasing clay content, but fell to around 200% in the equilibrium swollen state. The gels display excellent elastic recovery even at high elongations.

SIPN hydrogels with improved mechanical properties and thermal response could find various potential applications as biomedical materials but are still insufficiently responsive for applications as artificial muscles. Their useful application areas could be in controlled release of drugs, different actuators or as comfort materials in orthopedics or sports, due to their highly viscoelastic behavior and elastic properties.

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