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Judith Meid

Fiete Dierkes

Jun Cui

Renate Messing

Alfred Crosby, *University of Massachusetts - Amherst*, et al.

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PAPER

Mechanical properties of temperature sensitive microgel/polyacrylamide composite hydrogels—from soft to hard fillers†

Judith Meid,^a Fiete Dierkes,^a Jun Cui,^b Renate Messing,^c Alfred J. Crosby,^b Annette Schmidt^c and Walter Richtering^{*a}

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In this study we investigated the mechanical properties of composite hydrogels based on a polyacrylamide (PAAm) matrix with embedded temperature sensitive poly(*N*-isopropylacrylamide) (PNiPAM) microgels. We analysed the mechanical properties of the composite material with tensile tests, shear and cavitation rheology. The results of the different experiments displayed an enhancement of mechanical stability with increasing concentration of incorporated microgels. The improved stability is related to an increase of physical cross-linking points due to the incorporation of the microgels. The incorporation of temperature responsive microgel particles introduces temperature sensitive mechanical behaviour of the composite hydrogels. The collapse of the microgels inside the polyacrylamide matrix leads to a change of the volume of the filler particles as well as to a change from a soft filler to a hard filler. The influence of the hard particles on the mechanical stability of the matrix is much stronger which leads to materials with enhanced mechanical properties at high temperatures.

Introduction

Hydrogels are three-dimensional hydrophilic polymer networks which are highly swollen in water. As a combination of solid and liquid components, hydrogels differ from both materials in their mechanical properties; they have a defined geometry and do not flow like a liquid, but at the same time soluble molecules can diffuse through the hydrogel matrix depending on the mesh size of the network and the level of interactions. In many respects, gels present qualitatively contradictory behaviour; they are commonly soft but also notoriously brittle. For the growing amount of applications, like food science, tissue engineering and contact lens material,^{1–3} it is important to know the mechanical behaviour of gels and to be able to influence it. Recently, great efforts have focused on developing gels with the required properties for applications.^{4–6}

One possibility to increase the mechanical stability of hydrogels is the preparation of hydrogels in the presence of nanoparticles such as silicates, metal nanoparticles or clay minerals.⁷ Haraguchi *et al.* investigated hydrogels in which Laponite, a hectorite clay, replaced the chemical cross-linker^{8,9} and showed that Laponite

acts as a multifunctional, physical cross-linker. This seems to be due to the strong interactions between the polymer and the clay-particle at the clay-surface. Oppermann and Okay showed by rheological measurements the influence of incorporated clay on the mechanical properties of macroscopic hydrogels.^{10–12}

A very interesting group of materials are stimuli sensitive polymers.¹³ Such materials show major changes in conformation in response to the change of external stimuli such as temperature, salt concentration or pH value. Poly(*N*-isopropylacrylamide) (PNiPAM) is one famous example for temperature sensitive polymers.^{14,15} It becomes much less soluble in water at temperatures above 32 °C. Water is a good solvent at temperatures below the volume phase transition temperature (VPTT) and the polymer chains exist as coils. The hydrogel bonds between water and amide groups of the polymer are disrupted, if the temperature rises above the VPTT. The chains collapse because attractive inter-segment interactions between the isopropyl groups dominate.¹⁶

It is also possible to prepare composite hydrogels based on poly(*N*-isopropylacrylamide). Banet *et al.* prepared a PNiPAM/SiO₂ hybrid gel in a one-step synthesis. They showed that the obtained hydrogel is an interpenetrating network with improved mechanical properties. The VPTT was slightly shifted to lower temperatures.¹⁷ Another way to influence the VPTT is the usage of clay nanoparticles as cross-linking units or by adding an inorganic salt or cationic surfactant.¹⁸ One method to prepare macroporous hydrogels is the cryotropic gelation.¹⁹ With this method it is possible to incorporate emulsion droplets within the hydrogel.²⁰ These droplets release the entrapped oil only during the collapse at the VPTT.

^aInstitute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany. E-mail: richtering@rwth-aachen.de

^bDepartment of Polymer Science and Engineering, University of Massachusetts Amherst, 120 Governors Drive, Amherst, Massachusetts 01003, USA

^cInstitute of Physical Chemistry, University of Cologne, Luxemburger Straße 116, D-50939 Cologne, Germany

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The swelling and deswelling of microgels in mixtures of alkali swellable microgel and linear PNiPAM chains are shown to change the rheological properties of the composite. This provides a unique way to tune the elastic properties of the material with a change of the temperature.²¹ Tieke *et al.* prepared temperature sensitive copolymer hydrogels based on NiPAM and cationic surfactant monomers by irradiation with γ -rays.²² While pure PNiPAM hydrogel is easily disrupted under low compression, this composite hydrogels can be reversibly compressed.²³

Microgels made of temperature sensitive polymers are so-called “smart nanoparticles” which show a great potential in a variety of applications, *e.g.* encapsulation/carrier systems, thickeners or chemical sensing.^{24–26} This is due to the fact that the swelling/shrinking response can be tailored to occur in response to specific environmental conditions.

Sierra-Martin *et al.* were able to measure the bulk modulus of microgel particles by detecting the size of the particles *via* dynamic light scattering as a function of external osmotic pressure caused by different dextran solutions.²⁷ Another possibility to detect the modulus of a microgel is the investigation of the particles adsorbed on a solid surface with scanning force microscopy. Von Klitzing *et al.* showed with this technique that (PNiPAM-*co*-acrylic acid) microgels show their highest Young's modulus in the centre of the particles. The modulus increases with increasing cross-linker concentration and rising temperature.²⁸

Liu *et al.* prepared pH-sensitive macroscopic hydrogels consisting of singly cross-linked hydrogels, which are covalently linked to each other *via* free radical coupling of vinyl groups in the microgels. Such hydrogels are called doubly cross-linked hydrogels. Liu *et al.* showed that the doubly cross-linked microgels are able to swell strongly, have a low sol fraction and show a high elastic modulus in dynamic rheology experiments. The elastic modulus of the doubly cross-linked hydrogels is proportional to the degree of vinyl group functionalisation, the volume fraction of the particles and the pH.^{29,30}

In previous studies we showed that the presence of PNiPAM microgels during the formation of a polyacrylamide (PAAm) hydrogel leads to a shift of the gel point to longer reaction times and a higher number of long range heterogeneities.³¹ The incorporation of thermo-sensitive microgels leads to macroscopic temperature sensitive materials. This could be shown with light scattering and rheological experiments.³² Neutron scattering measurements revealed that the incorporated microgels are not aggregated and their swelling behavior is unaffected by the surrounding matrix if the cross-linker, acrylamide and microgel concentrations are low and the hydrogel polymerization is started *via* radical polymerization.^{33,34}

Lynch and Dawson synthesized similar, so-called “Plum-Pudding-Gels”, which consist of PNiPAM microgels embedded in a nontemperature sensitive hydrogel matrix.³⁵ Their research was mainly focused on the release of labelled tracer molecules, *e.g.* poly(ethyleneglycol) (PEG), and its diffusion through the hydrogel matrix. They showed that the incorporated microgels have hardly any influence on the diffusion of the PEG tracer through the matrix. This indicates a huge potential of this composite materials for medical application *e.g.* as drug-eluting material in stent coatings.^{36–38}

The incorporation of polymeric particles into a polymer matrix leads to a change in the mechanical properties of the macroscopic hydrogel. Gong *et al.* prepared tough hydrogel films by embedding densely cross-linked microgels with a size of about 5 μm (coefficient of variation was 28.6%) into a loosely cross-linked polyacrylamide matrix. Different microgels with different chemical compositions and different charges were used for the film synthesis. All microgel-reinforced hydrogel films showed an enhancement in mechanical strength in the performed tensile tests. Gong *et al.* assume that the increased mechanical stability mainly results from an interpenetration of chains of the polyacrylamide matrix and the embedded microgel particles.³⁹ At a first view, this observation is contradictory to our previous results. With neutron scattering measurements, we clearly showed that there is no interpenetration of the polyacrylamide matrix and the embedded microgels.³⁴ However one has to consider that the microgel particles we used were much smaller and prepared *via* dispersion polymerization. Gong *et al.* used W/O emulsion polymerization for the synthesis of their microgels. Both polymerization techniques can generate different surface structures of the resulting particles which lead to different interactions with surrounding polymer chains.

The incorporation of temperature sensitive PNiPAM microgels into a polymer matrix leads to a material with switchable porosities. The micro-scale structure can be easily manipulated by varying the temperature. This temperature induced change of the heterogeneities in the composite gel should lead to a change in the general mechanical properties of the bulk material.

In this contribution we systematically vary the amount of incorporated PNiPAM microgel and study the resulting mechanical properties with different techniques and at different temperatures.

A schematic drawing of gel formation is shown in Scheme 1. We characterize the samples in the swelling state directly after preparation and in the equilibrium swelling state with different techniques like tensile tests and shear rheology. Additionally we use the relatively new method of cavitation rheology for the characterization of soft materials.

Experimental section

Materials

N,N'-Methylenebisacrylamide (BIS), *N,N,N',N'*-tetramethylethylenediamine (TEMED) and potassium peroxydisulfate (KPS) were obtained from Merck. *N*-Isopropylacrylamide (NiPAM)

Scheme 1 Schematic representation of the synthesis of composite hydrogels:⁴⁰ component 1: acrylamide (AAm, monomer); component 2: *N,N'*-methylenebisacrylamide (BIS, cross-linker). The reaction was performed at constant temperature (20 °C) and was initiated with radical starter.

was purchased from Acros. Acrylamide (AAm) was commissioned from Fluka/Serva. Rhodamine B was obtained from Polyscience Inc.

All chemicals were used without further purification. For all preparation and experiments doubly distilled water was used.

The PNiPAM microgel particles used for all measurements were synthesized and characterised by Berndt *et al.* In the microgels the molar ratio of cross-linker (BIS) to monomer (NiPAM) was 1 : 71. Details of the synthesis *via* dispersion polymerization are described in the literature.⁴¹

Hydrogel synthesis

The filled and unfilled hydrogels were prepared under argon atmosphere in a glove box. The hydrogels were prepared from a 50 g L⁻¹ acrylamide solution in water with BIS used as the cross-linker. The cross-linker to monomer ratio for all samples was 1 : 60. For the preparation of composite hydrogels microgels were redispersed in the pre-gel solution together with monomer and cross-linker. To start the polymerisation a drop of saturated KPS solution was added along with TEMED. All samples were prepared at 20 °C when the microgels were in the equilibrium swollen state. The compositions of all samples, directly after preparation, are shown in Table 1.

Swelling experiments

We performed swelling experiments to determine the swelling ability of the composite hydrogels depending on the concentration of the incorporated microgel. In our focus of interest is the difference in swelling of the composite gels at the two different temperatures above and below the VPTT of the PNiPAM microgels. Therefore we define the temperature dependent degree of swelling S_T as shown below. For the experiments, the hydrogels were prepared in a size of 100 mm × 10 mm × 3 mm and weighed afterwards (m_{prep}). These samples were immersed in water at room temperature (20 °C) until they were in the equilibrium swelling state. The water uptake was determined gravimetrically by weighing the samples ($m_{20^\circ\text{C}}$). The same samples were then exposed to thermostatted water at 40 °C until they reached the equilibrium swelling state at 40 °C and weighed again ($m_{40^\circ\text{C}}$). The temperature dependent degree of swelling S_T was calculated:

$$S_T = \frac{m_T - m_{\text{prep}}}{m_{\text{prep}}} \quad (1)$$

where m_T is the mass of the swollen gel at temperature T (20 °C or 40 °C). S_T was determined as a function of the concentration of incorporated microgels for both temperatures.

Calculation of the sol fraction

We dried and weighed the supernatant of the swelling experiments to determine the sol fraction w_{ex} . We used the following equation:

$$w_{\text{ex}} = \frac{m_{\text{ex}}}{m_{\text{m}}} \cdot 100 \text{ wt\%} \quad (2)$$

where m_{ex} is the mass of the extractable monomers and m_{m} is the mass of the inserted monomers.

Cavitation rheology

Even if there are numerous methods to measure the mechanical stability of materials *e.g.* rheology, tension-test, *etc.*, it is often difficult to implement these methods for soft materials. For example highly swollen PAAm-hydrogels already break under their own weight, so it is not possible to perform for example tension tests with these kinds of samples. However cavitation rheology is a very useful method to analyse these soft samples. This experimental technique was developed by the group of Prof. Crosby. It takes advantages of the simple relationship between the critical pressure for growing cavitation and the material properties of the surrounding material.^{42–44} With cavitation rheology every kind of weak material can be measured.

All cavitation rheology measurements were performed by the group of Prof. A. Crosby at the Department of Polymer Science and Engineering, University of Massachusetts Amherst (USA). Cavitation rheology involves quantifying the pressure dynamics of a growing cavitation or fraction within a soft solid. Cavity introduction is controlled and monitored with a custom-built, semi-automated instrument that consists of a syringe pump (New Era Syringe Pump NE1000), a pressure sensor (Omega Engineering PX26-001GV), syringe needle (Fisher Scientific and World Precision Instruments), microscope (Edmunds Optic), and personal computer to record the pressure and microscope pictures of cavity growth as a function of time. The pressure and image acquisition are controlled by a custom-written program within National Instruments LabView software. All experiments were performed at a syringe pump rate of 6.7 μL s⁻¹. All samples were measured with needle tips with a diameter of 110 μm, 30 μm, 10 μm and 5 μm. Water was used as the cavitating medium for all measurements.

The test begins with the controlled lowering of the syringe needle into the sample. An initial signal is recorded. The water in the syringe is compressed *via* the syringe pump. The pressure within the system is measured throughout the experiment. The critical pressure P_c at the point of mechanical instability is then plotted as a function of the inverse radius of the syringe needle and the data points were fitted linearly, thus all cavitations involve reversible deformation. The critical elastic modulus E_c was then calculated from:

$$P_c = \frac{2\gamma}{r} + \frac{5}{6}E_c \quad (3)$$

where γ is the surface tension between the injecting liquid and the surrounding fluid and r is the inner radius of the syringe needle.^{45,46}

Shear rheology measurements

The amplitude sweep measurements were carried out with a Bohlin C-VOR 150 rheometer equipped with a thermostat. For all measurements plate/plate tools (40 mm diameter) were used and the samples were measured directly after polymerization without further swelling. The amplitude sweep measurements were performed with a frequency of 0.7 Hz. The shear stress was varied between 1 and 600 Pa.

Tensile test

The experiments were performed with a Zwick 2.5 N Tensile Tester with temperature control. The samples were prepared with a size of 50 mm × 10 mm × 3 mm and were measured directly after preparation without further swelling. The samples were fixed with tailor-made clamps for the measuring of hydrogels. The samples were measured at 20 °C and 40 °C with a constant elongation rate of 10 mm min⁻¹. The elastic modulus E was determined as the slope of the stress–strain curve in the linear region.

All mechanical experiments were carried out three times, each time with a new sample. We calculated the average from all three measurements as the final result. The standard deviations are shown as error bars.

Cryogenic scanning electron microscopy images (cryo-SEM)

The cryo-SEM pictures were taken at the Institute of Technical and Macromolecular Chemistry of the RWTH Aachen University on a Hitachi S-4800 electron microscope equipped with a liquid-nitrogen cooled sample preparation and transfer unit. The hydrogel was prepared as usual. The incorporated microgels have a size of about 50 μm and their preparation is described elsewhere.³³ The hydrogels were cut into small pieces and fixed to a copper tip. The sample was frozen in liquid nitrogen and transferred into the cooled sample chamber (−140 °C). Then the top of the sample was cut away with a razor blade. Afterwards the temperature within the sample chamber was increased to −90 °C to sublime the water crystals from the surface of the sample and to excavate the polymeric structure of the hydrogels. After about 10 minutes the temperature was decreased again to −140 °C and the sample was transferred directly to the microscope.

Confocal scanning microscopy

The pictures were taken on a Fluorescence Lifetime Microscope Micro Time 2000 developed by Picoquant. The optical setup was an Olympus IX 71 microscope. The wavelength of the laser was 532 nm. The picture was taken at room temperature. The hydrogels were prepared as usual. The incorporated microgels were labeled with rhodamine B.

Results and discussion

The aim of our study is to determine the influence of embedded PNIPAM microgels in a PAAm hydrogel matrix on the mechanical properties of the macroscopic composite material at different temperatures. The collapse of the microgels inside the bulk polymer leads to a change of the volume of the filler particles as well as to a change from a soft filler to a hard filler.

Structure and microscopy

In previous studies, we showed with small angle neutron scattering (SANS) measurements that the incorporation of microgels into a hydrogel matrix leads to a homogeneous material. The incorporated microgels are able to swell and shrink unaffected by the surrounding matrix. The microgels are not aggregated and equally distributed within the hydrogel matrix, if the microgel concentration is low.³³ For composite hydrogels with microgel

concentrations near the crystalline region (about 2.5 wt%) the formation of the hydrogel matrix seems to squeeze the microgels together and leads to a partial aggregation. The dense package of the microgels is disturbed.³⁴

Fig. 1 Confocal scanning microscopy picture of PNIPAM microgels embedded into a hydrogel matrix.

Fig. 1 shows a cross-section of a composite gel sample. The image was taken with a confocal scanning fluorescence microscope. The incorporated microgels are labelled with rhodamine B and hence visible in the microscopy. Obviously, the microgels are equally distributed within the hydrogel without any visible structure. The microgels are not aggregated.

Fig. 2 Cryo-SEM picture of a PNIPAM-microgel particle embedded into a hydrogel matrix.

A close view of a microgel embedded into a hydrogel matrix is shown in Fig. 2.

Tensile tests

We performed tensile tests of the composite gels at different temperatures in order to obtain the mechanical stability of the material at temperatures below and above the VPTT. The obtained elastic moduli are plotted as a function of the concentration of the incorporated microgels and of the resulting hydrogel composition. The total polymer concentration $c_{\text{tot-poly}}$ was calculated by addition of the acrylamide concentration c_{AAm} and the concentration of microgels c_{microgel} :

$$c_{\text{tot-poly}} = c_{\text{microgel}} + c_{\text{AAm}} \quad (4)$$

From static neutron scattering experiments we know that the swelling behaviour of the incorporated microgels is uninfluenced by the surrounding polyacrylamide matrix.³³ Neither the cross-linker concentration nor the acrylamide concentration shows any influence on the swelling of the microgels. We assume that the volume fractions of the microgels incorporated into the gel matrix are the same as the ones in aqueous solution.³³ Furthermore we know from SANS experiments that there is hardly any interpenetration of microgels and the polyacrylamide matrix.³⁴ Thus we calculate the theoretical polyacrylamide concentration of the matrix c_{matrix} which we assume in the free volume outside the microgels:

$$c_{\text{matrix}} = \frac{m_{\text{AAm}}}{V - \Phi \cdot V} \quad (5)$$

with V being the volume of the sample and m_{AAm} the mass of acrylamide in the sample.

For example the sample with 10 g L⁻¹ incorporated microgel has a volume fraction of 0.342; a third of the overall volume is occupied by microgels. This leads to a polyacrylamide concentration in the matrix of 76.0 g L⁻¹. The sample with a microgel concentration of 25 g L⁻¹ has a volume fraction of 0.855. Only about 15% of the complete volume is left for the formation of the PAAm matrix. This leads to a polyacrylamide concentration in the matrix of 344 g L⁻¹. The polyacrylamide concentration in the matrix is about 5 times higher as for the sample with 10 g L⁻¹ microgel. This increase of the polyacrylamide concentration in the matrix leads to more entanglements, which changes the swelling behavior of the composite material. The compositions of all samples are given in Table 1.

Fig. 3 shows the results of the tensile tests at temperatures below (20 °C) and above (40 °C) the VPTT for composite hydrogels prepared at 20 °C. In both diagrams we see the same behaviour of the samples. The elastic modulus increases with increasing amount of incorporated microgels. This increase of the modulus is caused by an increase of entanglements of the polyacrylamide matrix. In earlier experiments we showed that there is hardly any interpenetration of the microgels by the surrounding polymer matrix.³⁴ We assume that the polymerisation of the acrylamide takes only place in the free volume outside the microgels. This leads to a change of the structure of the polyacrylamide matrix especially at high microgel concentration. The increase of the polymer concentration in the matrix leads to formation of a larger number of entanglements and thus to a stronger physical cross-linking. From the literature it is well known that stronger cross-linked hydrogels show a higher elastic modulus.⁴⁸

We show linear fits for the results of our measurements in Fig. 3. This is the simplest approach to fit the data points with minor deviation. However other fitting models are also described in the literature. For example Horkay *et al.* show for the dependence of the shear modulus on the polymer concentration a power law behaviour with $G \propto \varphi^n$, $n = 0.34 \pm 0.03$.⁴⁹ We also show this plot in Fig. 3 on the left side. This model fits well with the result of the collapsed microgels at 40 °C, but not with the results measured at 20 °C. To decide which fit is the best one, more data points are required. Fig. 3 shows that at 40 °C the elastic modulus is even higher than that at 20 °C. Since all samples are prepared at 20 °C and afterwards heated to measure them at temperatures above the VPTT, all entanglements which are created during the sample preparation remain at elevated temperatures, even if the volume, which is occupied by the

Fig. 3 Elastic modulus E as a function of the concentration of the incorporated microgels (left side) and the total polymer concentration (right side) at 20 °C (black squares) and 40 °C (red circles). All samples were measured directly after synthesis without further swelling.

Table 1 Compositions of the composite gels after preparation. The effective volume fraction Φ was detected by capillary viscosimetry measurements.⁴⁷ The concentration of the amount of total polymer $c_{\text{tot-poly}}$ was calculated from eqn (4) and the concentration of the polyacrylamide in the matrix c_{matrix} was calculated from eqn (5)

#	20 °C				40 °C		
	$c_{\text{microgel}} / \text{g L}^{-1}$	Φ	$c_{\text{tot-poly}} / \text{g L}^{-1}$	$c_{\text{matrix}} / \text{g L}^{-1}$	Φ	$c_{\text{tot-poly}} / \text{g L}^{-1}$	$c_{\text{matrix}} / \text{g L}^{-1}$
1	0	0	50	50.0	0	50	50.0
2	1.0	0.034	51	51.8	0.003	51	50.2
3	10	0.342	60	76.0	0.034	60	51.8
4	25	0.855	75	344	0.085	75	54.6

Fig. 4 Results of the tensile tests: the elastic modulus E is plotted *versus* the polyacrylamide concentration within the matrix (left side) and *versus* the volume fraction of the embedded microgels (right side). The measurements were performed at temperatures below (20 °C; black squares) and above (40 °C; red circles) the VPTT. All samples were measured directly after synthesis without further swelling.

microgels, is much lower. Additionally we have a change of the volume and density of the PNIPAM microgels. At 40 °C the particles are collapsed and show a hard and spherical form. In this state they are similar to well known filler particles like silicate, clay or polystyrene particles, from which it is well known, that they increase the mechanical stability of a polymer matrix.^{50,51} Thus we see two effects which enhance the mechanical stability of the composite materials: the increase of the number of entanglements during preparation and the effect of the collapsed and thus hard embedded microgels at temperatures above the VPTT.

Fig. 4 shows the elastic modulus as a function of the calculated polyacrylamide concentration in the matrix (left side) and of the volume fraction of incorporated microgels (right side). Both values are directly calculated from the concentration of the incorporated microgels (compare Table 1). In both diagrams the elastic modulus increases with rising polyacrylamide concentration in the matrix, respectively with rising volume fraction of incorporated microgels. Again we see that the increase of the elastic modulus is stronger at high temperatures.

However both diagrams are not well suited for the comparison of the samples at 20 °C and 40 °C, because the values of the x -axes depend strongly on the temperature of the sample. Thus we use the microgel concentration for all further diagrams as x -axis. These plots give the clearest and most valuable information about the temperature and concentration dependent properties of the samples.

Fig. 5 Stress at break as a function of microgel concentration at 20 °C (black squares) and 40 °C (red circles). All samples were measured directly after synthesis without further swelling.

Fig. 6 Strain at break as a function of microgel concentration at 20 °C (black squares) and 40 °C (red circles). All samples were measured directly after synthesis without further swelling.

The incorporation of microgels leads to a strong temperature dependent enhancement of the mechanical properties of the composite material (compare Fig. 5 and 6). We observe not only an increase of the elastic modulus, but also the strain and stress at break are enlarged. The composite material is more stable than the pure polyacrylamide gel. This result is more pronounced at higher temperatures, too. Fig. 5 shows for example that the stress at break at 40 °C is about four times higher for the hydrogel with 25 g L⁻¹ incorporated microgel compared to the pure polyacrylamide. At 20 °C the stress at break is doubled by the incorporation of microgels. In Fig. 6 the strain at break is plotted *versus* the microgel concentration. At 40 °C we see an almost linear increase of the maximum strain with the raise of the microgel concentration, while at 20 °C the change is within the error bars. It is well known that the incorporation of filler particles enhances the tear strength of polymer materials, *e.g.* carbon black in rubber materials.⁵⁰ On the other hand the literature shows that the increase of monomer concentration in homopolymer hydrogels increases the stress at break, whereas the strain at break is hardly influenced.⁵²

We conclude that PNIPAM microgels act like hard filler particles at temperatures above the VPTT. The composite material behaves like a polymer-/hard-filler-composite material.

At temperatures below the VPTT the microgels are swollen and soft. The cross-linker concentration in the microgels and in the surrounding polymer matrix, respectively, is comparable. The composite material behaves similar to homopolymers with an increased monomer concentration.

Fig. 7 The plateau value of the storage modulus G' as a function of the microgel concentration at 20 °C (black squares) and 40 °C (red circles), obtained in amplitude sweep measurements. The black cross shows the plateau value of G' of a pure PAAm hydrogel with a total polymer concentration of 75 g L⁻¹. All samples were measured directly after synthesis without further swelling.

Shear rheology

Fig. 7 presents results from shear measurements. The plateau values of storage modulus G' are plotted as a function of the weight concentration of incorporated microgels. Additionally we show the storage modulus of pure polyacrylamide hydrogel with a total polymer concentration of 75 g L⁻¹. This equates to the total polymer concentration of a composite hydrogel with 25 g L⁻¹ incorporated PNIPAM microgel. The storage modulus of the pure polyacrylamide hydrogel with a polymer concentration of 75 g L⁻¹ is about twice as high as that of the sample with a polymer concentration of 50 g L⁻¹. The results are comparable with the results of Zhang *et al.* They showed that the increase of the monomer concentration of pure polyacrylamide hydrogels from 50 g L⁻¹ to 100 g L⁻¹ (cross-linker to monomer ratio: 1 : 37.5) leads to an increase of the storage modulus from about 2 kPa to about 8 kPa.⁵²

The shear rheology measurements of the composite hydrogels show the same trends as the tensile tests. The storage modulus increases with increasing microgel concentration. Below the VPTT the incorporation of 25 g L⁻¹ microgels leads to a storage modulus that is about twice as high as that of pure polyacrylamide with a total polymer concentration of 75 g L⁻¹. At temperatures above the VPTT the incorporation of 25 g L⁻¹ microgels leads to a storage modulus that is almost ten times as high as the one of pure PAAm hydrogel with the same total polymer concentration. This strong influence of the incorporated particle is similar to other filler materials, for example latex particles. Gauthier and Munam observed that the

incorporation of latex particles into a matrix of linear polyisoprene increases the complex viscosity and the storage modulus of the blend material compared to the pure matrix material.⁵¹

Fig. 8 Results of the swelling experiments: the temperature dependent degree of swelling of the composite gel is plotted *versus* the microgel concentration embedded. S_T was obtained for temperatures below (20 °C; black squares) and above (40 °C; red circles) the VPTT.

Swelling experiments

It is important to know the swelling capability of different gel compositions at different temperatures. This knowledge helps us to analyse the results of mechanical measurements in swollen and unswollen hydrogels. Additionally, we determined the sol fraction for all samples. It lies between 5.7 wt% and 8.3 wt% and no clear trend is visible. The addition of microgels to the pre-gel solution shows no obvious effect on the reactivity of the monomers.

Fig. 8 shows results of swelling experiments at 20 °C and 40 °C. Compared to a pure PAAm-hydrogel, the addition of a small amount of microgels (1.0 g L⁻¹) leads to an increase of the temperature dependent degree of swelling at 20 °C. The microgels are in an equilibrium swollen state during hydrogel formation. This was expected, because the total mass of polymer was increased, which leads to a higher swelling capability of the composite hydrogel. Contrary to this, S_T decreases when the amount of incorporated microgels is raised. The incorporation of more microgels leads to a higher polyacrylamide concentration in the matrix which causes more entanglements in the polymer matrix, as explained above. It is well known that hydrogels with a higher cross-linking density cannot swell as strong as hydrogels with a lower cross-linking density.⁵³ All samples are able to take up more water if they are heated to 40 °C. However if we calculate the difference between the degree of swelling at 20 °C and 40 °C, we observe that the increase of the swelling degree at the higher temperature is the stronger and the more microgel is incorporated into the hydrogel matrix (compare Fig. 9).

Fig. 9 Difference of the temperature dependent swelling degree at 20 °C and 40 °C plotted as a function of the microgel concentration.

This is a rather surprising result because microgels are collapsed at 40 °C and thus they release water in the composite gel. One would expect that this amount of water is absorbed by the hydrogel matrix and no further water from the surrounding should be uptaken by the hydrogel matrix. However we observe that the swelling degree, and thus the uptake of water, of the composite gel with the high amount of incorporated microgel increases even more at 40 °C. We assume that the water, expelled by the collapse of the microgels, is not absorbed by the surrounding matrix. Instead the collapse of the microgels leads to

the formation of pores in which the water remains. The polyacrylamide matrix absorbs water from the surrounding to reach its equilibrium swollen state.

Due to the increased amount of water in the swollen samples all concentrations are changed. For a better overview the new calculated concentrations for the equilibrium swollen composite gels are shown in Table 2. For the interpretation of the mechanical measurements carried out in the swollen state we use the values shown in Table 2.

Cavitation rheology

From cavitation rheology we obtain the critical elastic modulus E_c at the point of mechanical instability, as described above. Fig. 10 shows the results of cavitation rheology of the composite hydrogels in the equilibrium swollen state. Thus the moduli are not comparable with the one shown in Fig. 3 which were measured without further swelling.

For both temperatures we observe an increase of the critical elastic modulus E_c . From the literature we know that pure polyacrylamide hydrogels show an increase of E_c with increasing volume fraction of the polymer.⁴⁴ This fits very well with our results as shown in Fig. 10 on the left side. The critical elastic modulus increases with increasing polymer concentration. The incorporation of microgels leads to a higher concentration of total polymer. This is enhanced even more in the equilibrium swollen state, because hydrogels with a high amount of incorporated microgels are not able to swell as much as pure polyacrylamide gels. The increased concentration of total polymer gives rise to a stiffer hydrogel.

Table 2 Composition of the composite gels after swelling at 20 °C and 40 °C. The degree of swelling S was calculated from eqn (1) and the microgel concentration $c_{\mu\text{-gel}}$ was related to the total mass of water after swelling. The nominal effective volume fraction Φ was detected by capillary viscosimetry measurements.⁴⁷ The concentration of the amount of total polymer $c_{\text{tot-poly}}$ was calculated from eqn (4) and the concentration of the polyacrylamide in the matrix c_{matrix} was calculated from eqn (5)

#	20 °C					40 °C				
	S	$c_{\mu\text{-gel}} / \text{g L}^{-1}$	$\Phi_{\mu\text{-gel}}$	$c_{\text{tot-poly}} / \text{g L}^{-1}$	$c_{\text{matrix}} / \text{g L}^{-1}$	S	$c_{\mu\text{-gel}} / \text{g L}^{-1}$	$\Phi_{\mu\text{-gel}}$	$c_{\text{tot-poly}} / \text{g L}^{-1}$	$c_{\text{matrix}} / \text{g L}^{-1}$
1	7.2	0	—	6.90	6.9	8.4	0	—	5.98	5.95
2	8.5	0.1	0.004	6.06	5.9	9.1	0.1	0.0004	5.59	5.49
3	7.1	1.4	0.048	8.45	7.4	8.9	1.1	0.0038	6.73	5.64
4	5.0	5.0	0.170	13.3	12	7.8	3.2	0.0110	11.1	6.48

Fig. 10 Left side: critical elastic modulus E_c as a function of the microgel concentration after preparation; right side: critical elastic modulus E_c as a function of the total polymer concentration in the swollen hydrogel; both at 20 °C (black squares) and 40 °C (red circles).

Again we observe that the increase of E_c is stronger with higher temperature. This indicates that the hard and collapsed microgels enhance the tear strength of the composite materials.

The samples with 1.0 g L^{-1} embedded microgel show a different behavior, if E_c is plotted *versus* the microgel concentration (Fig. 10, left side). Its critical elastic modulus is lower than that of pure PAAm hydrogel at both temperatures. This sample showed already a different trend in the swelling experiments, where it reached a higher swelling degree as all other samples.

Conclusions

Composite hydrogels with temperature sensitive PNIPAM microgels embedded into a non-temperature sensitive polyacrylamide matrix were studied concerning their mechanical stability depending on the microgel concentration and the temperature. This study shows that the incorporation of microgels leads to stiffer hydrogels. The stability of the composite gels is even higher if the temperature is increased above the VPTT and the microgels collapse.

Tensile tests and shear rheology measurements showed an increasing elastic modulus and storage modulus with increasing microgel concentration. We conclude that the incorporation of microgels leads to an increase of the number of entanglements due to the fact that the formation of the polyacrylamide matrix takes place mainly outside the PNIPAM particles. The enhancement of mechanical properties is more pronounced for temperatures above the VPTT. At 40°C the microgels are collapsed hard spheres. They act like hard filler particles *e.g.* carbon black or silica particles from which it is well known that they increase the mechanical stability of rubber polymers.

Swelling experiments showed that the incorporation of microgels leads to a decrease of the swelling capacity of the composite material. As explained before the incorporation of microgels increases the number of entanglements, which reduces the possibility of the material to absorb water. Surprisingly the composite gels were able to absorb more water at 40°C than at 20°C , especially with high amounts of incorporated microgels. This indicates that the collapse of the microgels creates pores that are filled with water.

With cavitation rheology we measured the properties of the polyacrylamide matrix in the completely swollen composite gels. The incorporation leads to an increase of the tear strength. Again we observe that the collapsed particles have a stronger influence on the stability of the hydrogels compared to the weak and swollen microgels at room temperature.

We conclude that the incorporation of PNIPAM leads to an enhancement of the mechanical stability of a polyacrylamide matrix. At temperatures below the VPTT this effect is caused by an increase of the number of entanglements and can be compared to samples with increased cross-linker concentration. At temperatures above the VPTT the microgels are collapsed and can be compared to hard filler particles. The influence on the mechanical properties is much stronger.

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