

Filled Temperature-Sensitive Poly(vinyl methyl ether) Hydrogels

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ABSTRACT: Temperature-sensitive hydrogels based on poly(vinyl methyl ether) (PVME) with ferroelectric or ferromagnetic properties were synthesized by high-energy irradiation. Barium titanate and poly(vinylidene fluoride) (PVDF) were used as ferroelectric filler and Ni as ferromagnetic filler. The filled PVME hydrogels were synthesized by electron beam or γ -ray irradiation (of a suspension with 5–50 wt % of filler (with respect to polymer mass) in a 20 wt % aqueous PVME solution). Filling of the gel reduces the absolute swelling degree at low temperatures, but do not influence the phase-transition temperature of the gel. The particle distribution of the fillers inside the gel was visual-

ized by field emission scanning electron microscopy. The fillers were incorporated in the PVME network and fixed because of their size (inorganic particles), as well as by chemical bonds (PVDF). The ferroelectric or ferromagnetic properties of the filled gels were proved. Measurements in a corresponding alternating field provide the hysteresis loop, for both the ferromagnetic and ferroelectric gel. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2253–2265, 2005

Key words: hydrogels; stimuli-sensitive polymers; ferroelectricity; ferromagnetism; field emission scanning electron microscopy

INTRODUCTION

Temperature-sensitive hydrogels are showing a drastic change in volume and in mechanical properties as a result of a slight change in temperature.^{1–3} For the synthesis of these gels, several techniques can be used: physical, chemical, or radiochemical crosslinking reactions. Radiochemical crosslinking can be achieved by electron beam or γ -irradiation of a monomer or polymer solution in water or in aqueous solvent mixtures. Irradiation of a polymer solution above the overlapping concentration c^* leads to the formation of macroscopic networks, often designated as bulk gels. Variation of the radiation dose and the polymer concentration leads to a change in gel (g) and sol (s) contents.⁴ Irradiation of a diluted solution forms microgels or branched polymers.^{5–7}

Poly(vinyl methyl ether) (PVME) was used for investigations in this work. The phase-transition temperature of its gels corresponds to the lower critical solution temperature (LCST) of the noncrosslinked polymer^{8,9} in water. The LCST can be influenced by

the addition of various salts.¹⁰ PVME can be crosslinked by irradiation with electron beam or γ -rays of its aqueous solution,^{11,12} usually solutions with a polymer concentration of 10 wt % or 20 wt % and radiation doses between 20 and 120 kGy.^{13–16} Another possibility is the crosslinking of dry PVME films.¹⁷ The advantage of radiochemical crosslinking is that no additives (e.g., initiator, crosslinker) are required. Irradiation above the phase-transition temperature (electron beam) leads to porous gels and irradiation at room temperature (γ -rays) to homogeneous ones.⁹ Porous gels possess a faster swelling behavior.¹³ Using sodium alginate as template, it is also possible to synthesize PVME gel beads.¹⁸

The stimulation of deswelling of a temperature-sensitive gel causes the direct contact of the gel to a heat source or heating of the surrounding liquid phase. To avoid this, we filled the PVME gels with ferroelectric or ferromagnetic materials. An alternating electric or magnetic field causes a heating of these particles because of the hysteresis loss.

According to the literature, hydrogels were filled by ferroelectric substances to obtain electrorheological materials. Gao and Zhao¹⁹ investigated a barium titanate (BaTiO₃)-filled gelatin network under an electric DC field. Ferromagnetic temperature-sensitive networks were investigated by Kato et al.²⁰ They filled PNIPAAm networks with γ -Fe₂O₃ particles to heat

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these gels by alternating magnetic fields. Magnetic PNIPAAm gel beads were synthesized and characterized by Kuckling et al.²¹

The aim of this work was the synthesis of PVME gels filled with ferromagnetic and ferroelectric particles by radiation techniques. BaTiO₃ and poly(vinylidene fluoride) (PVDF) particles were used as ferroelectric fillers and Ni powder as ferromagnetic filler. The hydrogels are characterized with respect to their gel content, swelling behavior, phase- and glass-transition temperature, distribution of filler in the gel, as well as hysteresis loop. Field emission scanning electron microscopy (FESEM) was used for the study of the behavior and the fixation of the fillers influenced by swelling–deswelling processes. This method represents an indispensable and well-tried tool to study the structures of hydrogels at both the micrometer- and nanometer scale.²²

EXPERIMENTAL

Materials

PVME was obtained as a 50 wt % aqueous solution from BASF (Lutonal M40) and was used without further purification. The molecular weight of the polymer was determined by static light scattering on FICA 50 (SLS Systemtechnik G. Baur, Freiburg, Germany) in 2-butanone to $M_w = 57,000$ g/mol. The phase-transition temperature of PVME in aqueous solution (5 g/L) was determined by differential scanning calorimetry (DSC) with a 2920 Modulated DSC (TA Instruments) to 37°C (onset). PVME solutions of different concentrations were prepared by diluting the stock solution with deionized water. Ni powder (FLUKA), BaTiO₃ (FLUKA), and PVDF with a molecular weight of 534,000 g/mol (Aldrich) were used as received.

Synthesis

The inorganic particles were suspended under stirring in the aqueous polymer solution (20 wt %), with a total amount of filling particles between 5 and 50 wt % (with respect to the mass of polymer). The suspensions were degassed by blowing argon through the solution for about 4 h. Electron beam irradiation was carried out with an electron accelerator ELV-2 (Budker Institute of Nuclear Physics Novosibirsk, Russia). The energy of the electrons was 1.0 MeV at a beam power of 20 kW. The maximum value of beam current was 25 mA. At a constant value of beam current, the absorbed dose depends on the exposure time (typically < 1 min). Because of the high-energy absorption in a short time, the samples were heated above the phase-transition temperature, which results in porous hydrogels. For preparation of PVME by γ -irradiation, a ⁶⁰Co radiation source with a dose rate of 2 kGy/h was used.

The radiation dose was determined by a dosimeter based on alanine film. The generated alanine radicals were quantitatively analyzed by ESR spectroscopy with a high degree of accuracy (>99%). An advantage of γ -rays for crosslinking is their high penetration depth. The crosslinking reaction needs a longer time (15–40 h), and the sample temperature is not influenced by the radiation. Therefore, the gels are more homogeneously crosslinked. In either case, for electron beam and γ -ray irradiations, the doses varied between 60 and 120 kGy in steps of 20 kGy.

Characterization

X-ray diffraction analysis and scanning electron microscopy (SEM) on filler particles

Inorganic particles can change their properties by suspending in water and during irradiation. Degassed aqueous suspensions of 5 wt % BaTiO₃ and Ni, respectively, were irradiated by electron beam at a dose of 80 kGy. X-ray diffraction experiments (STOE IPDS, STOE and Cie GmbH Darmstadt, Germany) were carried out on the nontreated fillers and on the dried irradiated fillers. The angle was varied stepwise (0.5°) between 10 and 90°, with a measuring time of 30 s per angle.

SEM of filler particles was carried out on a DSM 982“Gemini” (Zeiss) using 2 kV as acceleration voltage. Samples were prepared by air drying the suspension on an aluminum surface.

Sol–gel analysis

For determination of the sol (*s*) and gel (*g*) contents, the synthesized gels were dried in vacuum for several days, weighed, and extracted with water or acetone for 5 days using a Soxhlet extractor. The gel content *g* (eq. 1) is determined as the ratio of mass of the dry gel after extraction (m_{gel}) to initial mass of dry gel before extraction ($m_{\text{gel}} + m_{\text{sol}}$).

$$g = \frac{m_{\text{gel}}}{m_{\text{initial}}} = \frac{m_{\text{gel}}}{m_{\text{gel}} + m_{\text{sol}}} \quad (1)$$

The sol content *s* is defined as $s = 1 - g$.

The extraction with both the solvents provides the same sol and gel contents. Therefore, most of the extractions were performed with acetone (lower boiling point). The sol content was calculated from the weight loss of the dry gel. PVDF-filled gels were also extracted with *N,N*-dimethylacetamide, which is a good solvent for PVDF.

Swelling measurements

The mass degree of swelling with respect to the whole gel is given by eq. 2(a); and with respect to PVME, this is given by eq. 2(b).

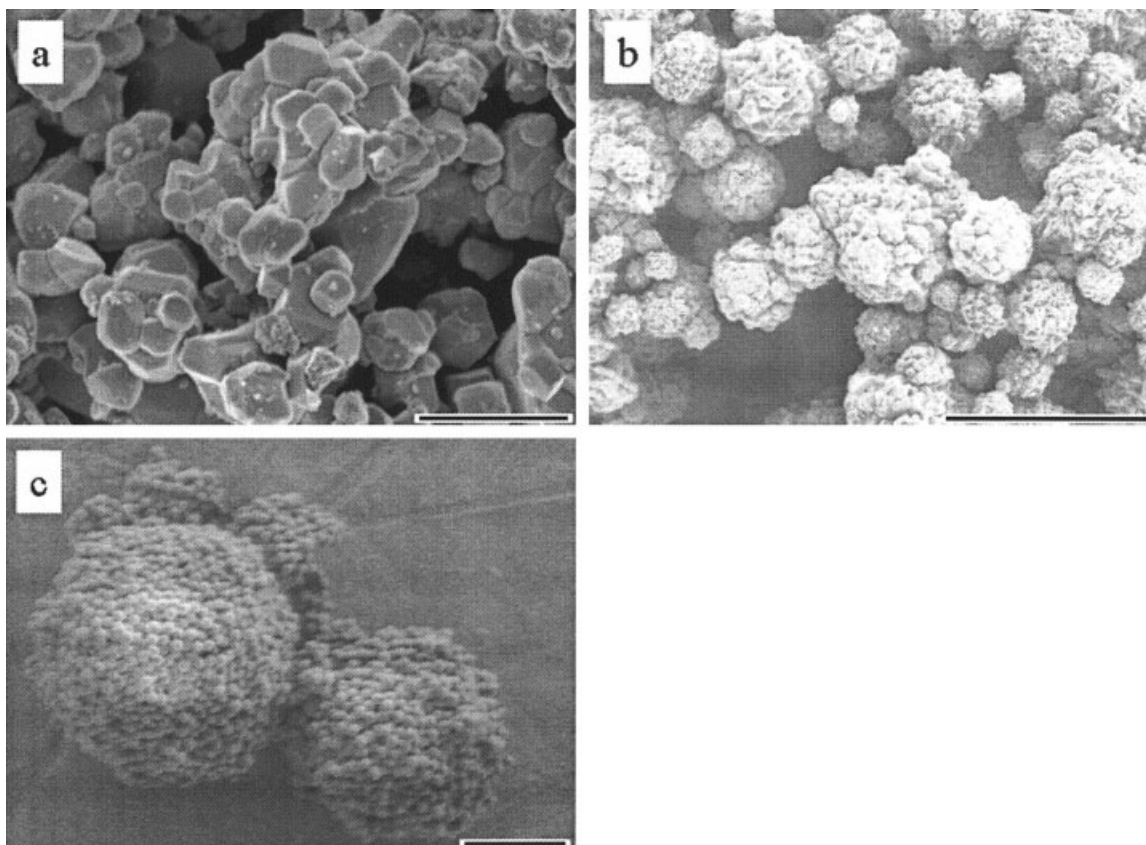


Figure 1 SEM micrograph of (a) BaTiO₃ powder ($d \leq 3 \mu\text{m}$), (b) Ni powder ($d = 1\text{--}5 \mu\text{m}$), and (c) PVDF powder (aggregates with $d = 3\text{--}5 \mu\text{m}$ of smaller spheres with $d \approx 250 \text{ nm}$). The bars correspond to (a) $1 \mu\text{m}$, (b) $10 \mu\text{m}$, and (c) $2 \mu\text{m}$.

$$Q_{m(\text{gel})} = \frac{m_{\text{PVME}} + m_{\text{water}} + m_{\text{filler}}}{m_{\text{PVME}} + m_{\text{filler}}} \quad (2a)$$

$$Q_{m(\text{PVME})} = \frac{m_{\text{PVME}} + m_{\text{water}}}{m_{\text{PVME}}} \quad (2b)$$

The dry gels ($m_{\text{dry}} = 20\text{--}50 \text{ mg}$) were swollen in water at room temperature for 3 days. After this, the gels were stored for 8 h at constant temperature in water and weighed (determination of m_{swollen}).

Thermogravimetry analysis (TGA) and DSC measurements

The absolute amount of filler in the gel after extraction was determined by using TGA (TG50, Mettler Toledo). Measurements on the dry samples were performed with a heating rate of 10 K/min from room temperature to 650°C in air atmosphere. The glass-transition temperatures (dry samples) and phase-transition temperatures (swollen samples) were determined with a 2920 Modulated DSC device (TA Instruments). In both the cases, the heating rates were 5 K/min .

Field emission scanning electron microscopy (FESEM)

The hydrogel structure and the distribution of the filling materials in the gel in different states were visualized by FESEM at low voltage. The sample preparation was as follows: 20 wt % PVME solution, containing 35 wt % (with respect to the dry mass of polymer) of the filling particles, was dropped onto a small piece of clean aluminum. The Al support was irradiated with a 1.0 MeV electron beam at a dose of 80 kGy. The gel-coated aluminum was immersed in distilled water for 15 min to remove noncrosslinked PVME. Secondary electron micrographs were taken on swollen samples (swollen at room temperature and at 40°C) with an "in-lens" FESEM S-5000 (Hitachi, Japan). The structure formed during swelling at different temperatures was fixed by rapid cooling to 77 K with liquid ethane. Under these conditions, the formed ice is in an amorphous state and do not destroy the network structure. The frozen water was removed by freeze-drying at 190 K for 6 h at about $5 \times 10^{-6} \text{ torr}$. The samples were rotary coated with 2 nm Pt/C at an elevation angle of 65° .

Hysteresis measurement

Ferromagnetic hysteresis was measured on a superconducting vibration magnetometer. The sample was

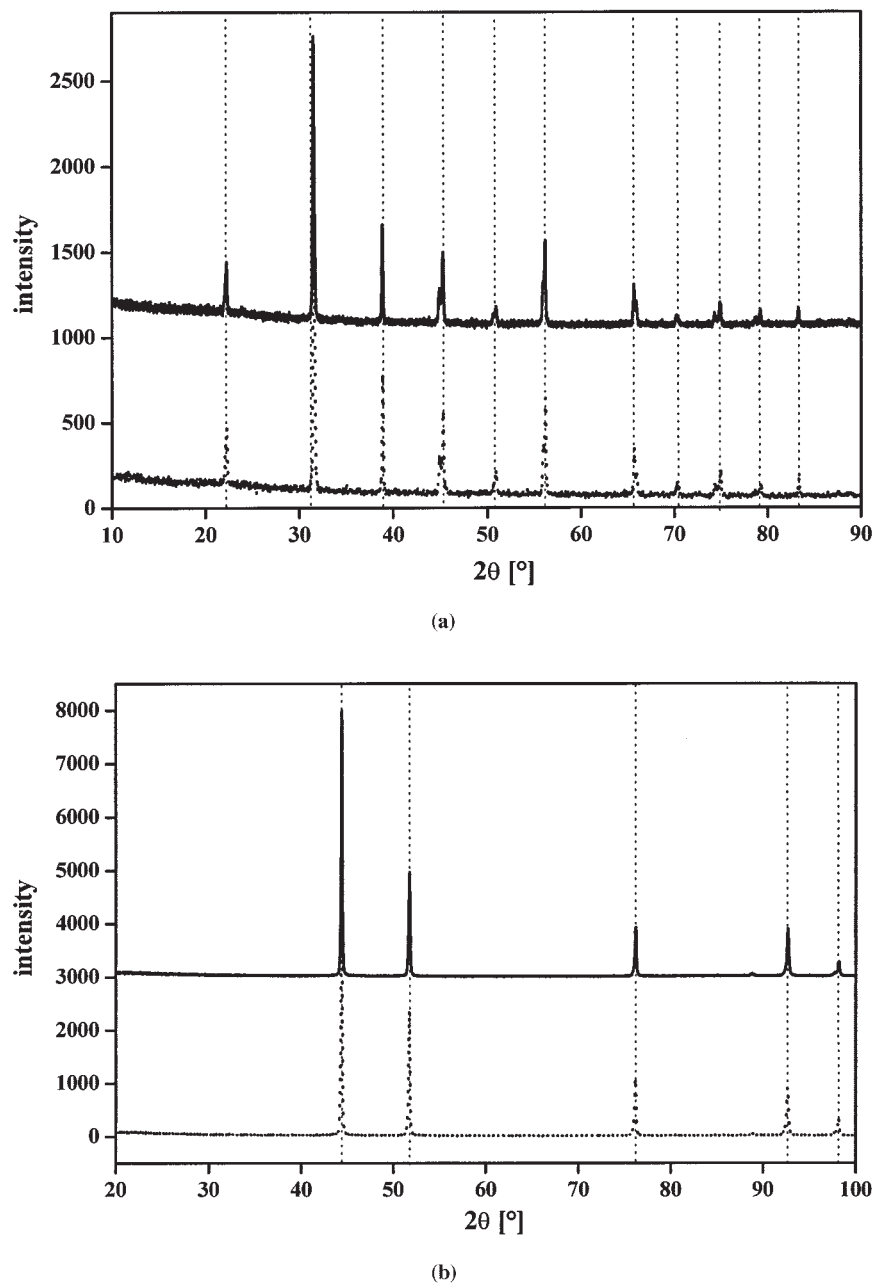


Figure 2 (a) X-ray diffraction of the nonirradiated (solid line) and with the 80 kGy electron beam irradiated (dashed line) BaTiO_3 particles. (b) X-ray diffraction of the nonirradiated (solid line) and with the 80 kGy electron beam irradiated (dashed line) Ni particles.

a dry 35.7 wt % Ni-filled gel with a volume of $2 \times 2 \times 2 \text{ mm}^3$. An alternating magnetic field (frequency of 30 Hz) was used at 300 K, with a $dB/dt = 0.1 \text{ T/min}$ in the range from $B = -1\text{T}$ to $B = 1\text{T}$.

Ferroelectric properties were determined at a custom-made measuring device. The samples were 2-mm thick dry cylindrical gels with a diameter of 13 mm. The samples were mounted between copper plates with a size of $20 \times 10 \text{ mm}^2$. A triangle-modulated voltage with a frequency of 10 Hz and field strength in the range of $-0.1\text{--}0.1 \text{ V}/\mu\text{m}$ was used.

RESULTS AND DISCUSSION

Influence of high-energy irradiation on filling materials

For both Ni and BaTiO_3 , no changes in particle sizes were observed after irradiation. Ni powder consists mainly of spherical particles with a diameter of some microns [Fig. 1(b)]. The size of the BaTiO_3 particles is smaller than $1 \mu\text{m}$ [Fig. 1(a)]. Figure 1(c) shows that PVDF spheres with a diameter of about 200 nm form spherical aggregates in a range of 2–5 μm . These aggregates are also stable during the irradiation with the electron beam in aqueous suspension.

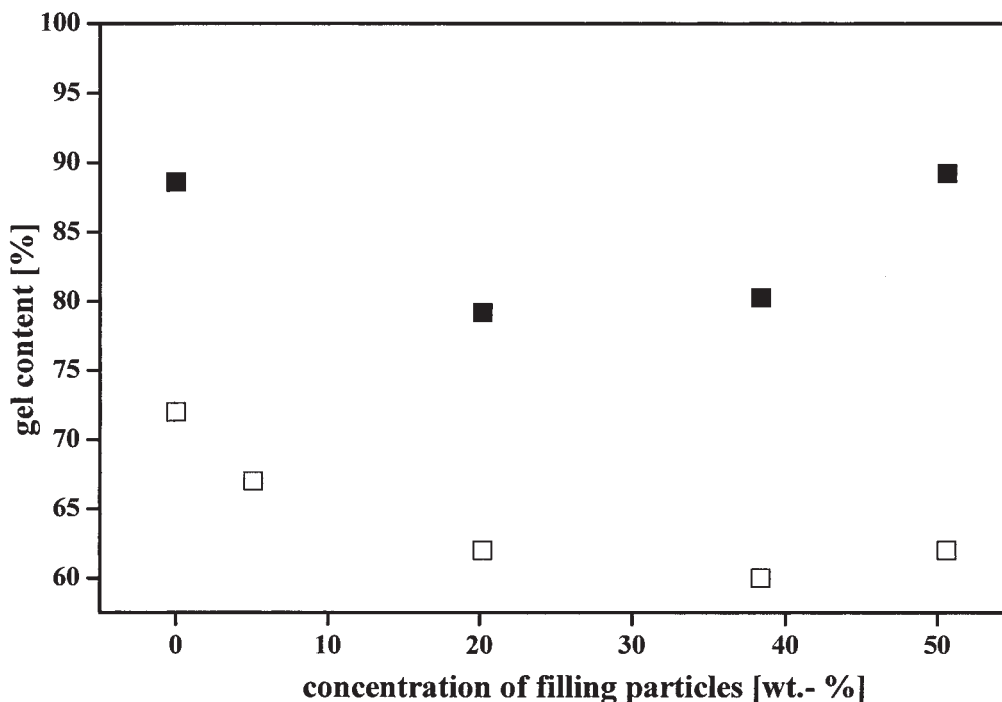


Figure 3 Gel content g of BaTiO₃-filled ((□) 80 kGy electron beam) and PVDF-filled ((■) 80 kGy γ -rays) gels as a function of the filler concentration c .

The X-ray diffractograms of Ni and BaTiO₃ before and after the irradiation are shown in Figures 2 (a,b). The diffractograms of the irradiated Ni and BaTiO₃ suspensions are similar to those of the nonirradiated materials. The reflection angles correspond to the values given in the literature.^{23,24} There is no change in the crystal structure. It can be expected that the ferro-electrical and ferromagnetical properties of these materials are not changed.

The influence of high-energy radiation on the properties of PVDF was studied in the literature. Crosslinking is preferred to decomposition during irradiation.²⁵ The remanent polarization temporally increases because of the entrapped ions and electrons after irradiation. These changes are almost completely lost after subsequent annealing.^{26,27}

Modification of the surface of PVDF by grafting of vinyl monomers using electron beam was described by Fuehrer and Ellinghorst.²⁸ Furthermore, the surface modification of PVDF by grafting of acrylic acid to the polymer after irradiation was shown by Chlochard et al.²⁹

Sol-gel analysis

The sol content s at a constant radiation dose D depends on the filler concentration. After extraction of the BaTiO₃-filled gels, the sol was analyzed by TGA to obtain information about extractable BaTiO₃ particles. The residue at 650°C was less than 1 wt %. The particles are firmly locked inside the gel. The dependency

of gel content g on the concentration of BaTiO₃ and PVDF is shown in Figure 3.

In the case of BaTiO₃, the gel content decreases with increasing filler concentration. A possible reason for that is the absorption of radiation energy by the inorganic particles. Above a filling concentration of 20 wt %, the gel content is almost constant.

In the case of PVDF, the gel content increases at higher filler concentrations. It could be expected that the PVDF is directly involved in the crosslinking reaction. To prove this, after the extraction with acetone, PVDF-filled gels were extracted with *N,N*-dimethylacetamide (which is a good solvent for PVDF) to remove uncrosslinked PVDF. Only 50% of the PVDF could be removed, which means that the half mass of the PVDF is crosslinked or linked to the PVME network.

The gel content g of γ -irradiated samples is higher than that of the gels synthesized by electron beam. A reason is the different dose rate during the irradiation. Because of the high dose rate of the electron beam irradiation, the sample is heated above the phase-transition temperature of the polymer, leading to crosslinking. The synthesis of γ -irradiated gels is carried out at room temperature.

Swelling behavior

The influence of the filler concentration and temperature on the swelling behavior was investigated [Fig. 4(a,b)].

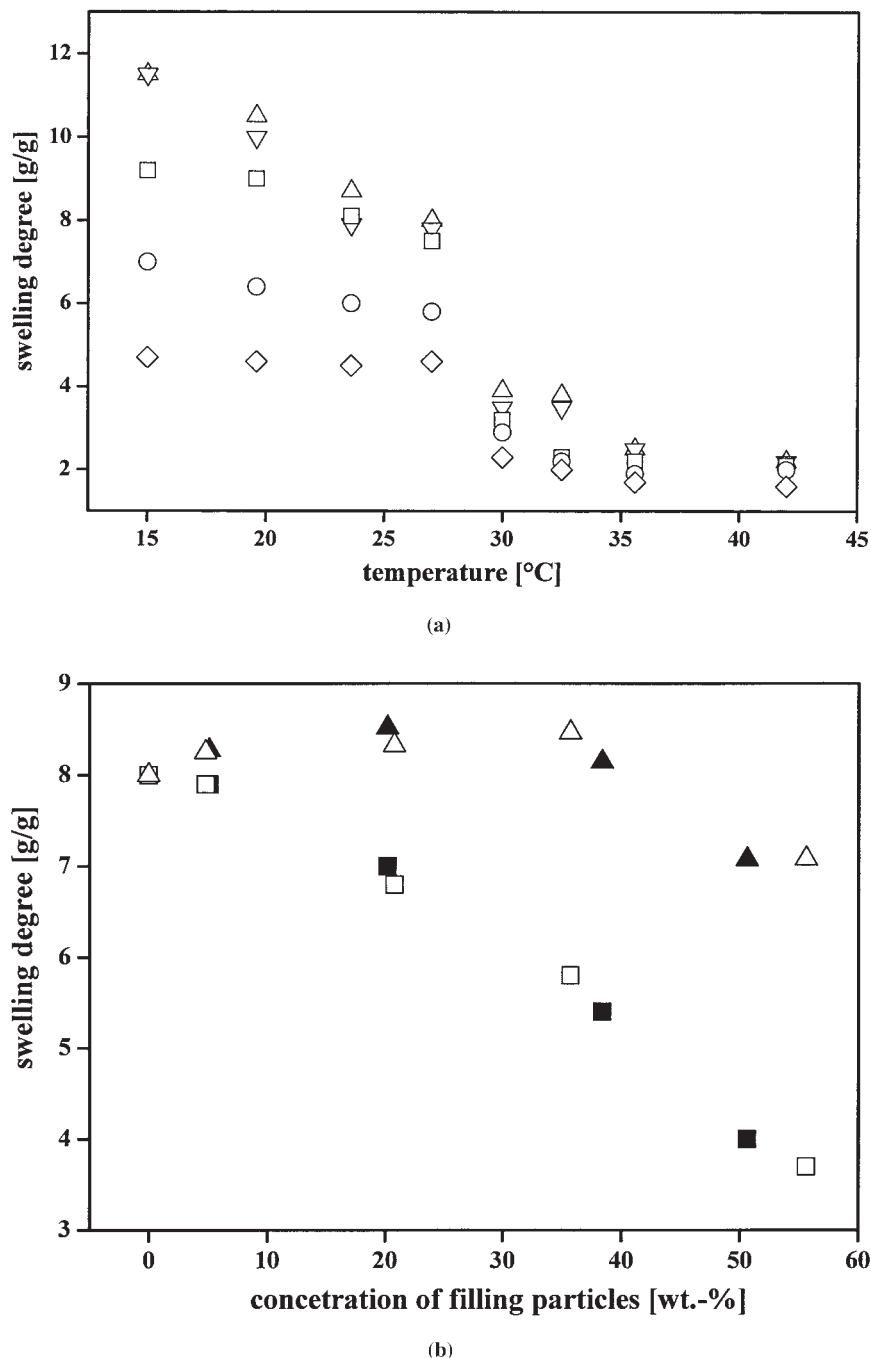


Figure 4 (a) Swelling degree $Q_{m(\text{gel})}$ of BaTiO₃-filled PVME gels as a function of the temperature T (Δ) 0 wt %; (∇) 5.1 wt %; (\square) 20.2 wt %; (\circ) 38.4 wt %; and (\diamond) 50.6 wt %). (b) Swelling degree of BaTiO₃-filled (solid symbols) and PVDF-filled (open symbols) PVME gels at $T = 23.6^\circ\text{C}$ as a function of filler concentration c (square, with regards to the whole gel $Q_{m(\text{gel})}$ and triangle, with regard to PVME $Q_{m(\text{PVME})}$).

As expected, the swelling degree of the gels at lower temperature decreases with increasing filler concentration. The fillers do not swell in water. At higher temperature in the deswollen state, the swelling degrees show the same tendency. The cavities and inhomogeneities of the gels (gels synthesized by electron beam are porous), which can retain water in the deswollen state, are partially occupied

by the filling particles. The difference between the swelling degree in swollen and in deswollen state is smaller at higher filler concentration. The phase-transition temperature is about 36°C . Figure 4(b) shows the swelling degrees of BaTiO₃- and PVDF-filled gels at 23.6°C . With respect to the whole gel, the swelling degree decreases with filler concentration as expected. However, with respect to the

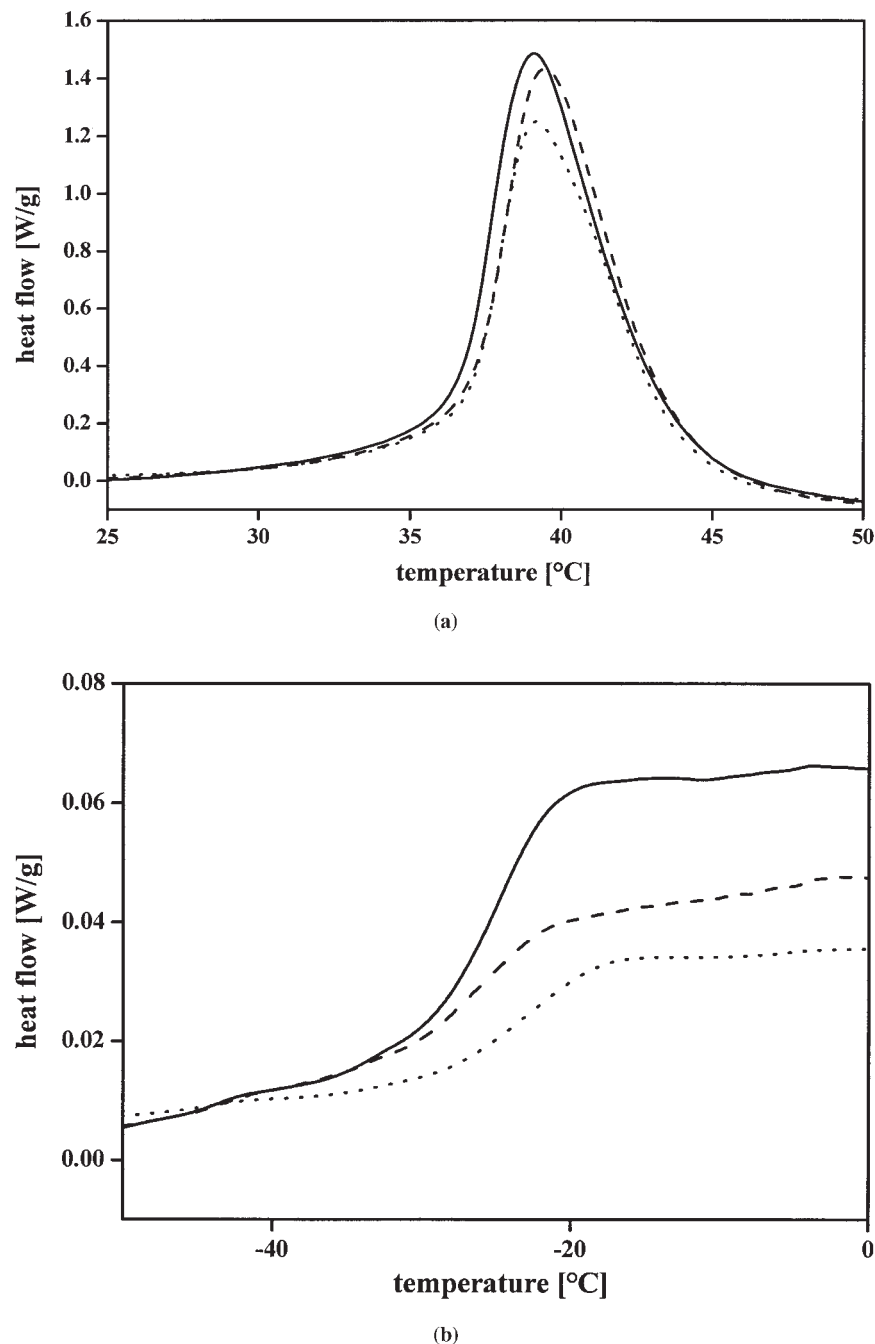


Figure 5 (a) DSC traces (phase-transition) of filled swollen PVME gels (solid line, PVME; dashed line, PVME + 35.7 wt % BaTiO₃; and dotted line, PVME + 35.7 wt % PVDF). (b) DSC traces (glass-transition) of filled dry PVME gels (solid line, PVME; dashed line, PVME + 35.7 wt % BaTiO₃; and dotted line, PVME + 35.7 wt % PVDF).

PVME matrix, the swelling degree decreases slightly at filler concentrations above 40 wt %. The fillers have only a small influence on the swelling behavior of the thermosensitive polymer matrix.

DSC measurements

Figure 5(a) shows the DSC traces of the filled gels. All gels are showing a phase-transition temperature of

about $(36.7 \pm 0.6)^\circ\text{C}$ (onset). The fillers have no influence on the temperature-sensitive properties. Only small differences could be observed, but there is no tendency in phase-transition temperature depending on the particle concentration. Similar results were obtained by analyzing the glass-transition temperature T_g of the dry gels [Fig. 5(b)]. Almost no changes in T_g were observed. The inorganic and polymer filling materials do not influence the thermal properties of the

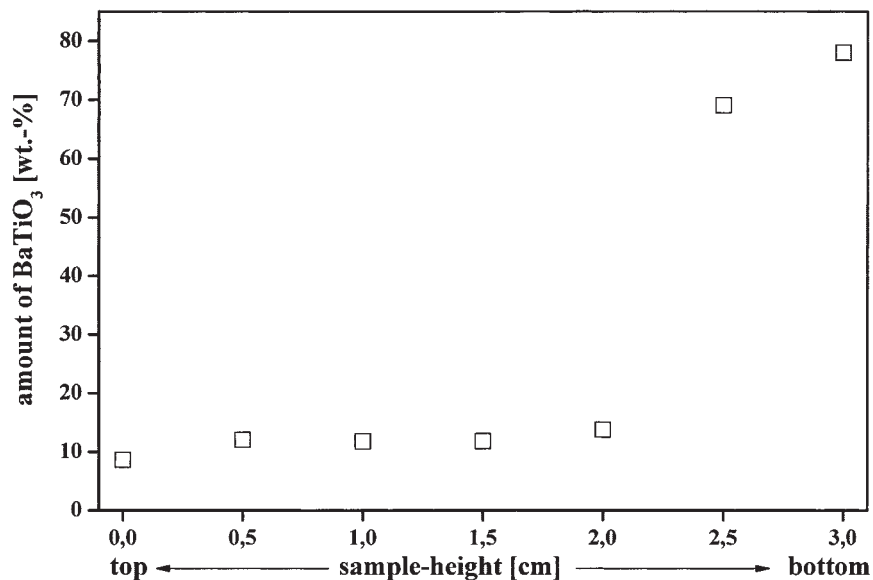


Figure 6 Distribution of BaTiO₃ in 20 wt % PVME solution (crosslinked by electron beam $D = 80$ kGy).

PVME gel. Only a change in the specific heat capacity of the glass-transition was observed. This difference corresponds to the amount of filling particles, which do not show structural changes in this temperature range.

Sedimentation of filler

The period between suspending the fillers and crosslinking can influence the distribution of the filler because of the sedimentation. Therefore, it was necessary to prove the stability of the suspensions. BaTiO₃ (35.7 wt %) was suspended in a 20 wt % PVME solution. The suspension was kept without stirring for 2 days in a 3-cm high glass tube before irradiation. The sample was irradiated with a dose of 80 kGy. In distances of 0.5 cm, slices were taken parallelly to the surface of the gel. The concentration of BaTiO₃ in these slices was determined by thermogravimetry. The BaTiO₃ content as function of sample height is shown in Figure 6.

Above 1 cm from the bottom of the gel, the amount of BaTiO₃ is almost constant. At the bottom of the sample, the concentration is very high (above 60 wt %). Possibly the larger particles sedimentate and smaller particles form a suspension that is stable for several days. Therefore, all further investigations were performed on filled PVME gels, which were synthesized by irradiation of stirred solutions.

FESEM measurements

The localization of Ni, BaTiO₃, and PVDF particles inside of the filled gels was studied by two different

modes of FESEM. Secondary electron imaging was used to illustrate the morphological features of the gels [Fig. 7(a,c,e)]. On the other hand, backscattered electron imaging provides a better contrast between materials with different mean atomic numbers and a higher depth of information concerning the distribution of the particles [Fig. 7(b,d,f)].

The BaTiO₃-filled gel consists of clusters of the particles that are randomly distributed inside the gel. The domains without BaTiO₃ are not larger than 2–4 μm . These images were taken on samples prepared in swollen state. Because the gel is synthesized above the phase transition temperature, these distances are caused by the swelling process. In deswollen state, distance between the clusters would be smaller.

The Ni-filled gel shows a similar structure. The Ni rich clusters are greater in comparison to BaTiO₃, which can be simply explained by the larger particle size. The particles are hardly visible using secondary electron imaging, but there is a high contrast in backscattered electron imaging.

In the case of PVDF-filled gels, the material contrast given by backscattered electron imaging is very low, because the mean atomic numbers do not vary so much. Nevertheless, it is easy to recognize the aggregates of PVDF particles. The PVME network spans over the aggregates but also between the particles. Like in other cases, the PVDF particles are statistically distributed.

We were also interested in the structure of the hydrogels in swollen and shrunk state. Therefore, the accordingly prepared samples were investigated at higher magnifications [Fig. 8(a–f)].

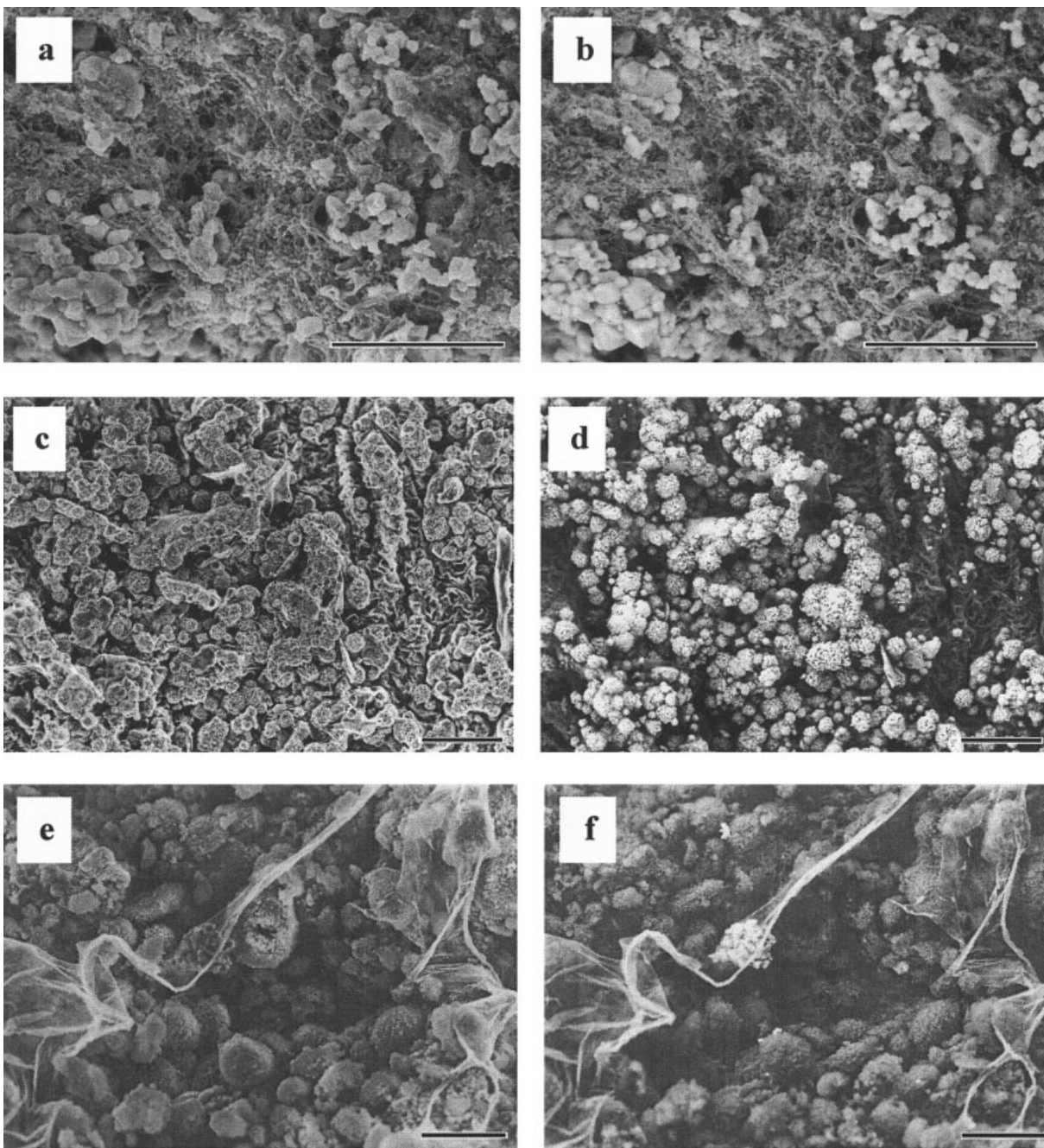


Figure 7 FESEM micrographs (secondary(SE) and backscattered(BSE) electron imaging) of PVME hydrogels filled with BaTiO₃ particles SE (a) and BSE (b); with Ni particles SE (c) and BSE (d); and with PVDF particles SE (e) and BSE (f). The bars correspond to (a, b) 5 μm , (c, d) 20 μm , and (e, f) 10 μm .

The investigated gels have a porous structure (caused by high-energy electron beam irradiation), which is characterized by a pore size of less than some 100 nm. This structure is obvious in swollen and in shrunk state. At high resolution, chains of the gel “docked” to the filling particles were observed, in particular, in the case of BaTiO₃. For Ni-filled gels, this effect is not so prevailed. As a reason for that, we expect hypothetical hydrogen bonds or other interactions at the interface between PVME

and the oxidized particles. Using much smaller particles could lead to a shift in phase-transition temperature, because the larger interphase between PVME and the filler could also influence the interaction between the temperature-sensitive polymer and the water.

The pore size, both in swollen and shrunk state, is smaller than the particle size of both Ni and BaTiO₃. Therefore, the particles cannot be removed from the gel by extraction.

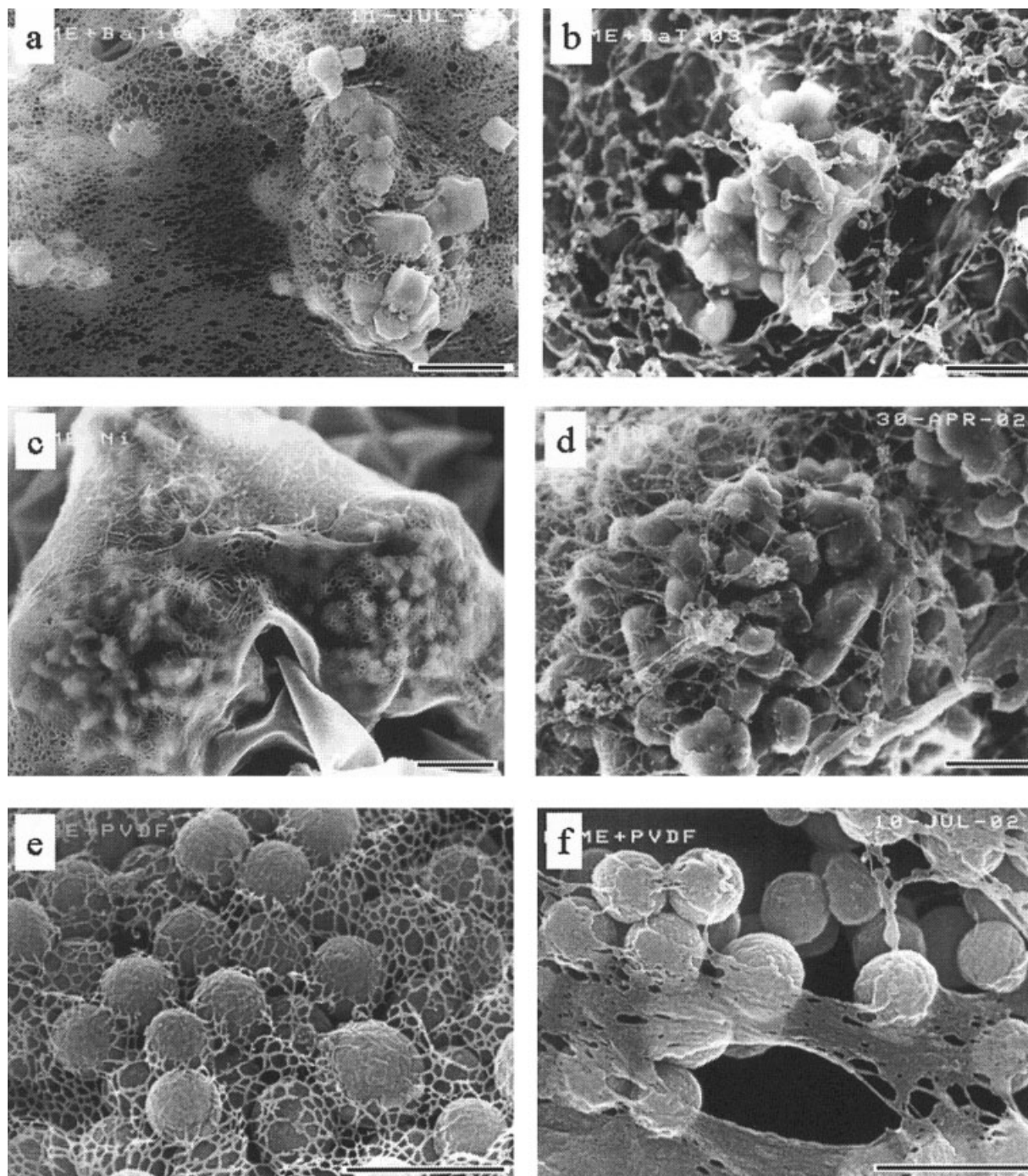


Figure 8 FESEM micrographs of the PVME hydrogels filled with BaTiO₃ particles in swollen (a) and in the shrunken state (b); with Ni particles in swollen (c) and in the shrunken state (d); and with PVDF particles in swollen (e) and in the shrunken state (f). The bars correspond to (a–d) 1 μm and (e, f) 500 nm.

In the case of PVDF-filled gels, the PVME network seems to be “coated” on the surface of the PVDF particles. In swollen state, some kind of regular structure was observed, which is characterized by a net of PVME with a pore size of about 50 nm. The PVME chains are docked to the surface of the PVDF particles. This effect agrees with the results of the extraction experiments and suggests that PVDF is directly crosslinked with PVME.

Ferroelectric/ferromagnetic hysteresis

Measurements were carried out on a Ni-filled gel with a particle concentration of 40 wt %. The sample behaves like soft magnetic Ni. The saturation magnetic moment of ~40% of the saturation magnetic moment of pure Ni corresponds to the filling amount. The ferromagnetic properties of the Ni particles are not influenced by the crosslinked polymer in any way.

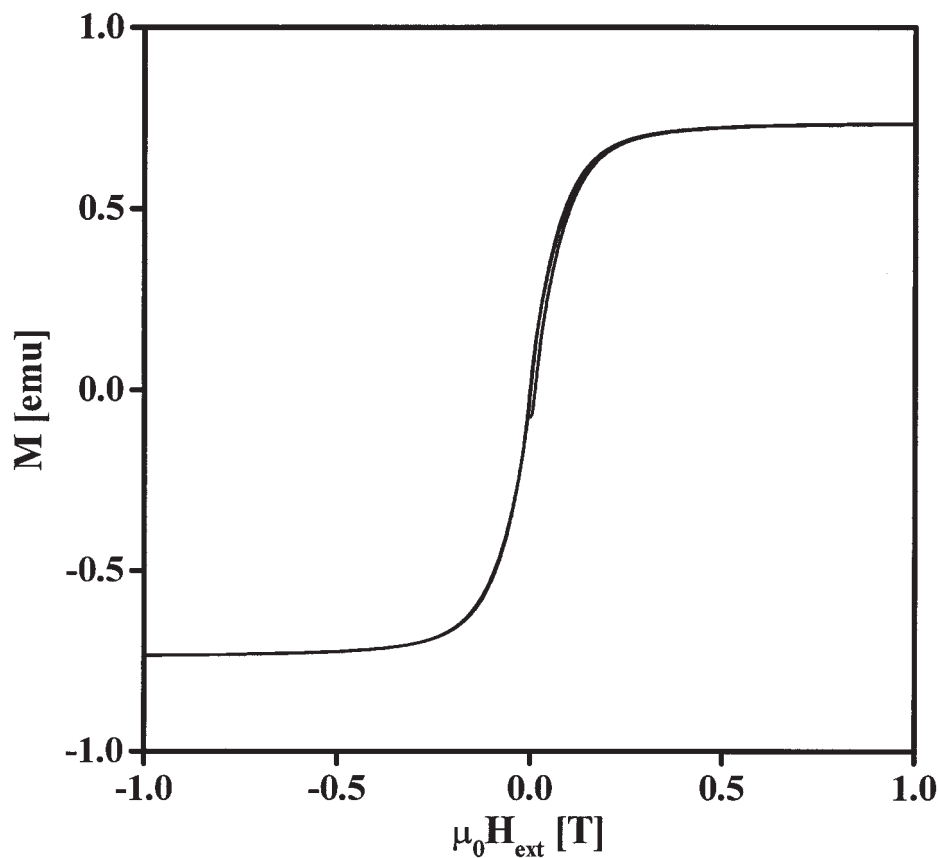


Figure 9 Virgin curve of an Ni-filled gel in magnetic field.

The dependency of the magnetic moment M on the magnetic flow density $B = \mu_0 \times H_{\text{ext}}$ is shown in Figure 9.

Hysteresis loops of the BaTiO₃- [Fig. 10(a)] and PVDF-filled [Fig. 10(b)] gels are shown.

The filled gels are showing ferroelectric properties. Because of the small field strengths, the saturation field strength is not achieved. The hysteresis losses were calculated by integrating the hysteresis loops. For the BaTiO₃-filled gel (35.7 wt %), the calculated hysteresis loss was $P_V = 4.8 \times 10^{-5} \text{ J/cm}^3$. For the PVDF-filled gel (55.6 wt %), a hysteresis loss of $P_V = 7.4 \times 10^{-5} \text{ J/cm}^3$ was obtained. From these experimental data, the increase of temperature in the filled PVME gels due to the energy loss of hysteresis can be estimated. Applying an electric field with the field strength of 1 kV/cm and a frequency of 875 kHz on a gel (swelling degree of 10, adiabatic conditions) should theoretically result in a heating rate of 1 K/s. However, it is only a rough approximation, because the hysteresis loss depends on the frequency and field strength of the electric field.

CONCLUSIONS

In this work, we synthesized BaTiO₃-, Ni-, and PVDF-filled PVME hydrogels by electron beam or γ -ray ir-

radiation of an aqueous PVME solution containing suspended particles. Using these methods, we are able to synthesize thermosensitive gels with ferroelectrical or ferromagnetical properties.

First, the influence of high-energy radiation to the chemical properties and the particle size of the inorganic filling materials was investigated. The inorganic particles do not show structural changes after the irradiation treatment. The filler particles were suspended under stirring in aqueous PVME solutions (20 wt %) and subsequently irradiated. The resulting hydrogels are mechanically stable, even at filling amounts up to 50 wt %. The gel content g of these gels decreases with increasing filler concentration in case of the inorganic filling particles. For PVDF, g is increasing at high filling amounts. The swelling degrees are decreasing with higher particle concentration, but the swelling behavior of the gel matrix is only influenced at very high particle concentrations ($c > 40 \text{ wt } \%$). There is no influence on the phase-transition as well as the glass-transition temperature. A statistical distribution of the particles was observed using FESEM measurements in the swollen and shrunk state. The inorganic particles are incorporated into the gel caused by their particle size, which is larger than the mesh size of the network. For PVDF, a covalent bonding of the PVDF to the PVME gel matrix was

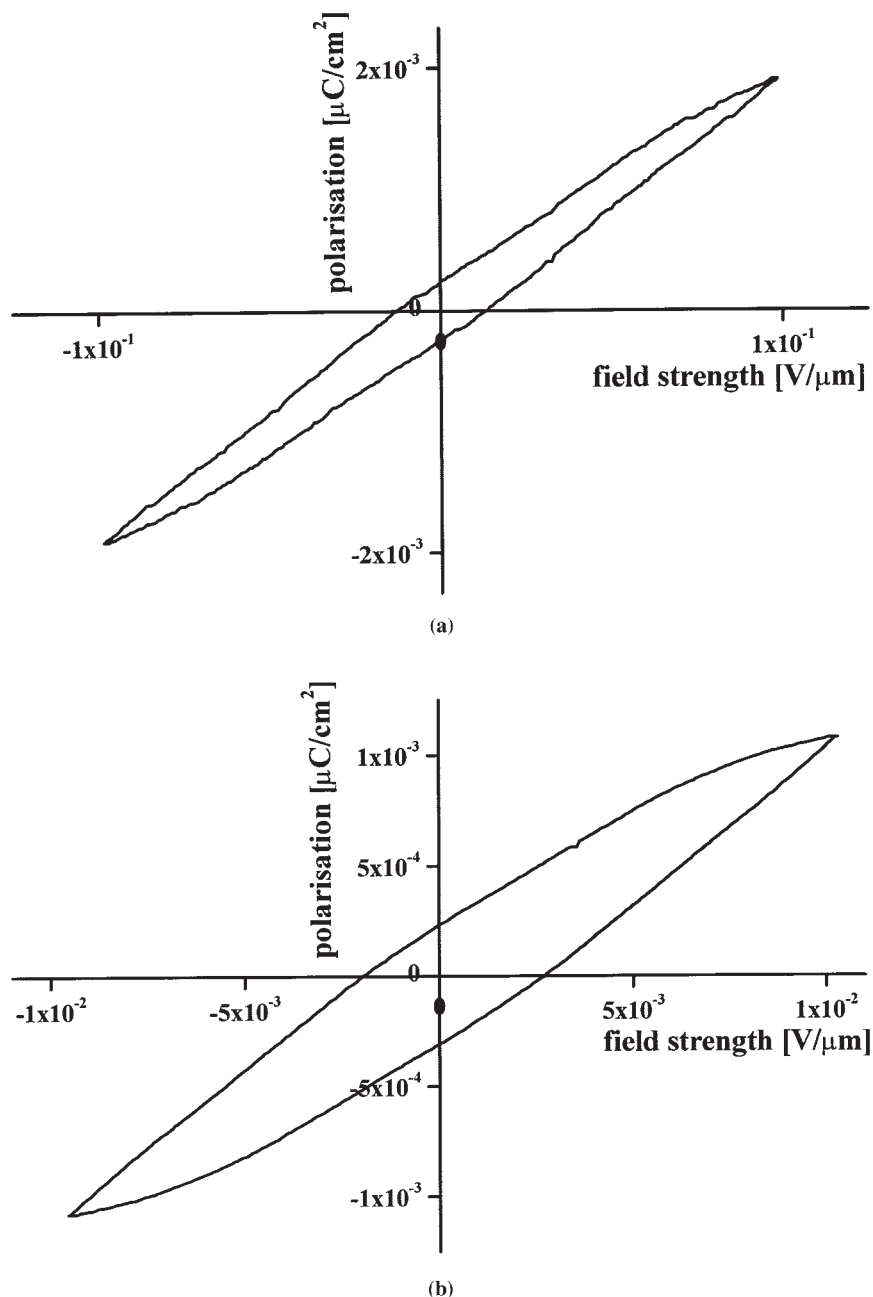


Figure 10 Hysteresis loop of the (a) BaTiO₃-filled gel and (b) PVDF filled gel.

shown. Furthermore, the ferroelectrical and ferromagnetic properties of the filled PVME gels were investigated. The filled gels are showing ferroelectric or ferromagnetic hysteresis, which depends on the filler amount.

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