

Novel Poly(ethylene glycol) Composite Hydrogels with Hydrophilic Bentonite Nanoclay as the Filler

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Novel composite poly(ethylene glycol) hydrogels with hydrophilic bentonite as the filler were synthesized by the polyaddition reaction between diepoxy-terminated PEG of 2000 Da, 6000 Da and 10000 Da molecular weights and ethylenediamine in aqueous solution at 60°C, in the presence of the clay. The hydrogels prepared were tested from the point of view of their swelling behaviour and mechanical properties. The results showed that the clay practically did not affect both the water absorption by the crosslinked polymer and the storage modulus of the hydrogels. This seems to indicate that the interactions between the PEG chains and bentonite were very small or absent within the hydrogels in the presence of water, although they occurred in dry state, as proven by FTIR and XRD measurements upon xerogels.

Keywords: hydrogels; poly(ethylene glycol); bentonite; composite

Hydrogels are chemically or physically crosslinked hydrophilic polymer networks able to absorb and retain water or biological fluids up to several thousands times their dry weight [1]. Since their discovery in 1960 [2], the field has continuously expanded [3], as hydrogels have found numerous and important applications in medicine and pharmacy, industry, agriculture, etc. [4-6].

Besides many advantages, the conventional hydrogels display also some limitations, mainly poor mechanical properties and limited responsiveness to different external stimuli [7], that strongly impede their use in some applications. One of the methods employed to circumvent these drawbacks consists in the incorporation of various micro/nanofillers, like metallic/magnetic nanoparticles, clays, carbon nanotubes, silica, cellulose, etc., to form (nano)composite hydrogels [7-11]. Many hydrophilic synthetic and natural polymers, like for example: poly(ethylene glycol) (PEG) [12], poly(acrylamide)s [13-15], poly(vinyl alcohol) [16], chitosan [17] collagen [18], etc. have been employed for the preparation of (nano)composite hydrogels. Amongst them, PEG is very often used as a component of biohydrogels due to its remarkable properties like water solubility, biocompatibility, ability to control the bioactivity of surfaces, lack of toxicity, etc [19].

Recently, we developed a versatile class of hydrogels obtained by crosslinking low-polydispersity diepoxy-terminated poly(ethylene glycol)s with aliphatic polyamines [21,22], whose swelling and diffusion characteristics [21,22], mechanical [23], thermal [24] and drug-delivery [25] properties and states of water contained [26] can be easily adjusted by varying the molecular weight of PEG precursors, hydrocarbon chain length and functionality of the polyamine, the amine hydrogen/epoxy groups ratio, as well as by employing mixtures of oligomers with different MWs or mixtures of polyamines with various functionalities. Starting from this, the present work deals with the preparation and properties of some novel composite hydrogels with PEG chains of various lengths and different proportions of hydrophilic bentonite as the

filler. To the best of our knowledge, there is only one paper in literature describing some PEG – montmorillonite (MMT) hydrogels [20], obtained, nevertheless, in a different way and with a different structure, through the polymerization of poly(ethylene glycol) methyl ether acrylate in the presence of silane-modified sodium MMT, with no other crosslinking agent than MMT. Much larger research effort was devoted, however, to PEG nanocomposite hydrogels with Laponite, another layered silicate, as both crosslinker and filler [12,27-29].

Experimental part

Materials and methods

α,ω -Dihydroxy PEG with approximate molecular weights of 2000 Da (PEG₂₀₀₀, Fluka), 6000 Da (PEG₆₀₀₀, Scharlau) and 10000 Da (PEG₁₀₀₀₀, Fluka) were used as received. Diepoxy-terminated PEG (DEPEG_x) were synthesized through the reaction of the corresponding DHPEG_x and epichlorohydrin in benzene, in the presence of NaOH, as previously described [21,30]. Their functionality (\bar{f}) was 2.0 (DEPEG₂₀₀₀), 1.8 (DEPEG₆₀₀₀) and 1.7 (DEPEG₁₀₀₀₀) epoxy groups/molecule, as determined by the HCl addition method. The hydrophilic bentonite (B) nanoclay (Nanomer[®] PGV) was purchased from Aldrich and used as received. Its montmorillonite (MMT) content was over 98% according to the manufacturer (Nanocor[®], Inc.) specifications. Ethylenediamine (Scharlau, 99%) and all the other reagents were used as received. The surfaces of the glass plates employed for the preparation of hydrogels were made hydrophobic (silanized) by treating with Sigmacote[®] solution (Sigma). Distilled water was employed in all experiments involving water.

Hydrogel preparation

The appropriate amounts of hydrophilic bentonite and distilled water were magnetically stirred at room temperature for 24 h. Alternatively, the dispersion of bentonite in water was sonicated in an ice-water bath at 60% amplitude and 1 cycle for 30 min. Then DEPEG_x was added to form a solution of 30 wt.% polymer concentration,

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Oligomer	\bar{f} (epoxy/molecule)	Bentonite (wt.%)			
		0	2.5	5	10
		Xerogel yield (%)			
DEPEG ₂₀₀₀	2.0	97.7	98.4	98.2	98.5
DEPEG ₆₀₀₀	1.8	96.9	96.3	96.7	96.5
DEPEG ₁₀₀₀₀	1.7	82.4	84.3	84.0	82.9

Table 1
INFLUENCE OF BENTONITE
CONCENTRATION AND DEPEG_x
FUNCTIONALITY UPON THE
XEROGEL YIELD

followed by the addition of the stoichiometric amount of EDA (amine hydrogen atoms/epoxy groups = 1). The reaction mixture was very well stirred, degassed under a small vacuum for a few minutes and transferred by means of a syringe into the space between two hydrophobic (silanized) glass plates separated by a 1.4-mm thick rubber spacer. The glass matrix was kept in an oven, at 60°C for 140 h. At the end of the reaction time, the matrix was cooled down, the glass plates were removed, and disks of 8 – 20 mm diameter were cut from the hydrogel. The disks were then swelled into an excess of distilled water for 7 days at room temperature. The water was changed daily in order to remove unreacted amine and oligomer. The swollen disks were dried first in atmosphere and then in a desiccator over anhydrous CaCl₂ until constant weight was obtained. For yield measurements, part of the hydrogel was first dried to constant weight (W_o), followed by the purification procedure described before. The final weight of the disks (W_{ext}) was recorded as well. The yield (Y) of the polymer crosslinking reaction was calculated according to eq. 1.

$$Y(\%) = (W_{ext} - W_B)/(W_o - W_B) \times 100 \quad (1)$$

where W_B stands for the amount of bentonite contained by the hydrogel part employed for yield determination.

The samples were denoted as Px-By, where x indicates the approximate MW of the PEG oligomer (i.e. 2 for 2 kDa; 6 for 6 kDa, etc), while y stands for the bentonite weight percentage based on PEG in the hydrogel preparation mixture. For example, P2-B10 is the code for the hydrogel with PEG₂₀₀₀ chains and 10 wt.% bentonite based on PEG₂₀₀₀ in the hydrogel preparation recipe.

Equilibrium Swelling Experiments

The swelling behaviour of the composite hydrogels was determined by placing a 5-mm diameter xerogel disk (W_x) into distilled water at 37°C. The swollen disk was removed from the water bath at certain time intervals, wiped superficially with filter paper, weighed (W_h) and sunk back into water. The measurements were carried out until the weight of the swollen gel reached a constant value, corresponding to the equilibrium swelling (ESD). The swelling degree at various time intervals (SD_t), expressed as amount of water absorbed by 1 g of polymer contained by the xerogel, was calculated according to eq. 2.

$$SD_t(\text{g water/g dry polymer}) = (W_h - W_x)/(W_x - W_B) \quad (2)$$

where W_B stands for the amount of bentonite contained by the hydrogel disk employed in the experiment.

Characterizations

The rheological measurements were carried out on a Kinexus Pro (Malvern Instruments, U.K., software 1.40) rheometer equipped with a Peltier element for temperature control, by employing a 20 mm parallel plate geometry. Frequency sweep experiments in the 0.1 – 10 Hz range were performed at 25°C on hydrogel samples of 20 mm diameter (1.5 – 2.5 mm thickness), swelled at equilibrium at the same temperature. A 0.1 % strain within the linear viscoelastic region was applied (“controlled strain” mode). A normal force of 0.3 N was applied on the hydrogel in order to avoid slippage. To prevent water evaporation a solvent trap was used.

FT-IR spectra were recorded on a Bruker Vertex 70 instrument equipped with an ATR device, with a resolution of 4 cm⁻¹ and accumulation of 32 scans.

X-ray diffraction (XRD) measurements were carried out on a Shimadzu 6000 X-ray diffractometer using CuK radiation under a voltage of 40kV and a current of 30 mA.

Results and discussions

To prepare composite hydrogels, DEPEG_x was reacted with EDA in the presence of bentonite. Stoichiometric ratios between the epoxy groups and amine hydrogen atoms were employed in order to obtain hydrogel networks with a structure as close as possible to an ideal one. As clay concentration increased, the viscosity of the PEG – bentonite – water mixture increased as well, so that above 10 wt.% concentration it was no longer possible to inject the mixture between the glass plates.

The addition of bentonite did not affect the crosslinking yield, which, however, depended on the molecular weight of DEPEG_x due to the different functionalization degree of the PEG oligomers (table 1).

Xerogel yield is a good indicator of the defects content (loops and pendant chains) of a network obtained by step-growth processes. A higher value denotes a lower network defects content, and therefore a higher degree of perfection of the hydrogel network [31]. Table 1 shows that very good xerogel yields were obtained in the case of DEPEG₂₀₀₀ and DEPEG₆₀₀₀, indicative for a high degree of perfection of the network, while in the case of DEPEG₁₀₀₀₀ the yield was much lower, suggesting a hydrogel network with many defects.

The composite xerogels synthesized were characterized by FTIR and XRD measurements, in order to check for the presence of PEG – bentonite interaction in solid state. Figure 1 shows the FTIR spectra of hydrophilic bentonite and PEG₂₀₀₀ xerogels with 0 – 10 wt.% bentonite. The spectra of the composite xerogels contained all the characteristic vibrations of the individual components, including the Si-O bond stretching vibration from bentonite that shifted from 1003 cm⁻¹ in the clay to 1034 – 1038 cm⁻¹ in the xerogel,

and the C-O bond stretching vibration belonging to the PEG chains, that shifted from 1105 cm⁻¹ in the neat PEG xerogel to 1103 cm⁻¹ in the composite ones. These band shifts in the composite xerogels suggested the presence of interactions, at least in solid state, among bentonite on one side and the PEG chains on the other side.

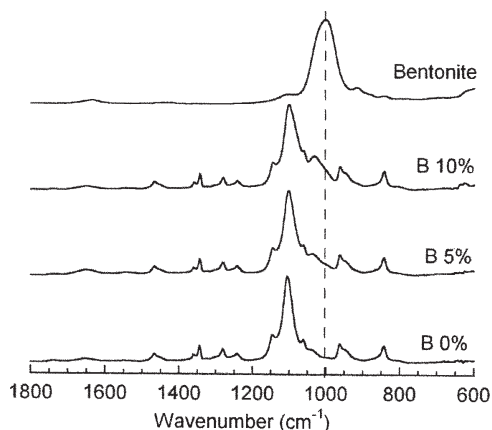


Fig. 1. FTIR spectra of hydrophilic bentonite and PEG₂₀₀₀ composite hydrogels with various amounts of clay

The occurrence of interactions in solid state among PEG chains and bentonite was also proved by XRD measurements (fig. 2). The X-ray diffractogram of bentonite contained the characteristic diffraction peak of MMT at 2θ = 6.6°, that shifted to a lower value (2θ ≈ 4.7°) and strongly decreased in intensity in the composite xerogel, indicative for a partial clay exfoliation and polymer intercalation within the intragallery space of MMT. This is in agreement with literature reports that showed that PEG chains intercalate easily into the interspace layer of sodium MMT [32-34]. One can notice as well that the crystallinity of the PEG xerogel, indicated by the sharp peaks at 2θ = 19.0° and 2θ = 23.18° was preserved in the composite xerogel.

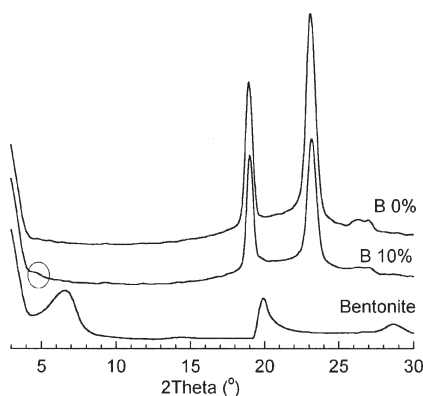


Fig. 2. XRD patterns of bentonite and PEG₂₀₀₀ composite hydrogels with various amounts of clay

The swelling behaviour of the resulted composite xerogels was tested by immersion in distilled water at 37°, and the water intake was followed gravimetrically at certain time intervals until a constant weight was reached (equilibrium swelling). The swelled hydrogels were completely transparent in the absence of bentonite, while they became increasing cloudy as the bentonite concentration increased (fig. 3).

The swelling degree (SD) was calculated by taking into account only the polymer part of the hydrogel and excluding the clay, according to eq. 2. From the SD - time plots obtained, the equilibrium swelling degree (ESD) was determined as the value corresponding to the curve plateau (fig. 4, table 2). The numbers displayed in table 2 shows

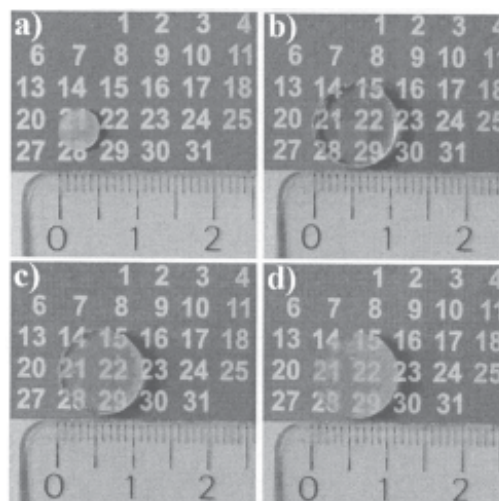


Fig. 3. PEG₂₀₀₀ hydrogel disks swelled at equilibrium: a) xerogel; b) 0 wt.% bentonite; c) 2.5 wt.% bentonite; d) 5 wt.% bentonite

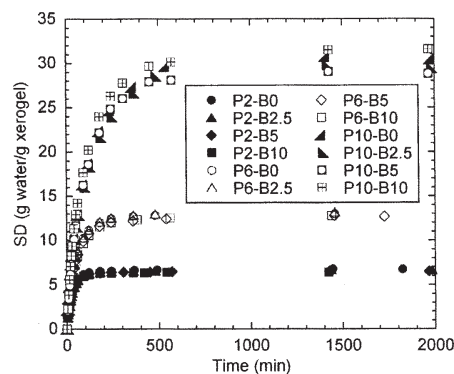


Fig. 4. Swelling degree – time plots for the hydrogels prepared

that ESD increased with the MW of the PEG chains, as expected [21], and it was practically independent on the bentonite concentration in the hydrogel. If the apparent equilibrium swelling degree (ESD_{app}) is taken into account, which is calculated considering bentonite as a participant to the swelling process (table 2), one can notice that this one decreased with the clay concentration. However, we consider that ESD_{app} is not correct because the clay did not swell in water, leading to an apparent decrease of the equilibrium swelling degree. The results also show that sonication of the clay – water dispersion, instead of magnetical stirring, before DEPEG addition, had no effect upon ESD.

The independence of ESD on the bentonite content of hydrogels suggested that the clay did not produce any additional crosslinking of the gels, and therefore its interaction with PEG chains was low in the presence of water, although these interactions were present in the xerogel, as shown before.

The gels synthesized were also investigated from the point of view of the water diffusion process, i.e. mechanism of water transport within the hydrogel and kinetics of the swelling process. The mechanism of water diffusion through hydrogel was determined by applying eq. 3 [16,35] to the swelling degree vs. time values recorded. Only the data fulfilling the condition $SD_t/ESD \leq 0.6$ were taken into account.

$$M_t/M_\infty = SD_t/ESD = kt^n \quad (3)$$

M_t represents the amount of water absorbed at time t (min), M_∞ is the water uptake at equilibrium, k is a constant depending on the characteristics of both gel and solvent,

Hydrogel	ESD (g/g)	ESD _{app} ¹⁾ (g/g)	n	k·10 ²	ESD _{calc} (g/g)	K·10 ⁴ (g/(g·min))	R
P2-B0	6.78	6.78	0.63	8.19	6.80	125	0.99998
P2-B2.5	6.64	6.48	0.66	6.59	6.69	98	0.99997
P2-B5U ²⁾	6.56	6.25	.069	6.57	6.62	108	0.99998
P2-B5	6.57	6.26	0.68	7.34	6.58	131	1.0000
P2-B10	6.45	5.86	0.68	7.42	6.48	122	0.99998
P6-B0	12.85	12.85	0.71	4.36	12.89	35.9	0.99996
P6-B2.5	13.10	12.78	0.73	3.79	13.17	30.1	0.99997
P6-B5	12.87	12.26	0.73	3.73	12.94	26.2	0.99999
P6-B10	13.19	11.99	0.73	3.49	13.22	13.3	0.99996
P10-B0	30.27	30.27	0.72	2.23	30.40	5.47	0.99983
P10-B2.5	29.25	28.54	0.70	2.50	29.33	6.09	0.99983
P10-B5	28.81	27.44	0.73	2.46	29.02	6.15	0.99986
P10-B10	31.45	28.59	0.72	2.32	31.64	5.72	0.99992

¹⁾apparent ESD, calculated including bentonite in the hydrogel; $ESD_{app}=(W_h-W_x)/W_x$

²⁾bentonite was dispersed into water by sonication

and n is the swelling exponent, whose value depends on the transport mechanism. For disk-shaped xerogel samples, n = 0.5 indicates a Fickian diffusion mechanism, n = 1 shows a Case II transport, while intermediate values of n indicate a non-Fickian or anomalous transport. The constants k and n were determined from the intercept (lgk) and slope (n) of the lg(SD/ESD) vs. lg(t) plots, as illustrated in figure 5. The results (table 2) indicated an anomalous transport in all cases and also the independence of n and k on the clay content of hydrogels.

A second order kinetics was proposed for the swelling process of the composite hydrogels, which can be described by eq. 4 [36,37]:

$$d(SD_t)/dt = K(ESD - SD_t)^2 \quad (4)$$

where K is the swelling rate constant. After integration, eq. 4 becomes:

$$t/SD_t = A + Bt \quad (5)$$

where A is the reciprocal of the initial swelling rate or 1/(K×ESD²) and B is the inverse of the equilibrium swelling degree (1/ESD) [36,37]. The validity of the kinetic model

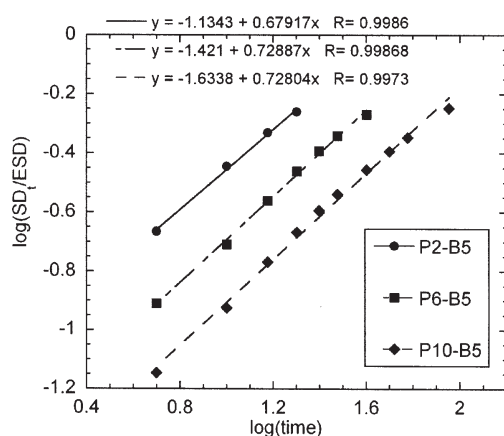


Fig. 5. Determination of n and k constants

Table 2
SWELLING CHARACTERISTICS OF THE
COMPOSITE HYDROGELS SYNTHESIZED

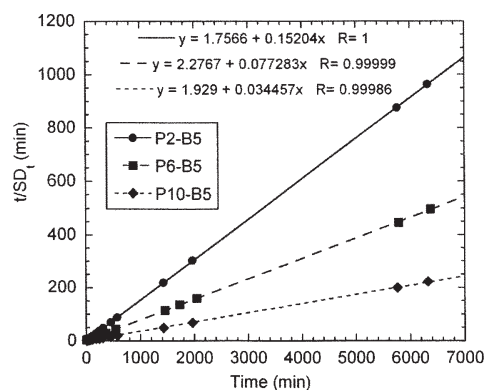


Fig. 6. Examples of second order kinetic plots for the composite hydrogels prepared

suggested was tested by constructing t/SD_t versus t plots based on the experimental swelling data (fig. 6), from which the kinetic parameters were determined (table 2). One can see that the experimental data fitted very well a straight line, proving the second order kinetics proposed, and the equilibrium swelling degrees calculated from these plots (ESD_{calc}) agreed well with the ESD measured experimentally. In general, the swelling rate constant was relatively independent on the bentonite amount in the hydrogels.

The fully swelled hydrogels were also rheologically tested from the point of view of their viscoelastic properties through strain controlled frequency sweep measurements. All of them displayed a gel character, i.e. the storage modulus G' was larger than the loss modulus G'' and they were independent on the frequency interval investigated, as expected due to their crosslinked character. In the case of hydrogels without clay, G' was larger for shorter PEG chains (fig. 7), because of the lower swelling degree and the inverse proportionality between G' and the average molecular weight between crosslinks [17].

The addition of bentonite did not improve the mechanical properties in the case of PEG₆₀₀₀ and PEG₁₀₀₀₀ composite hydrogels (fig. 8, A,B, table 3), as G' values practically did not change with clay concentration. In the case of PEG₁₀₀₀₀ hydrogels, a small decrease of G' may actually be observed as bentonite concentration increased,

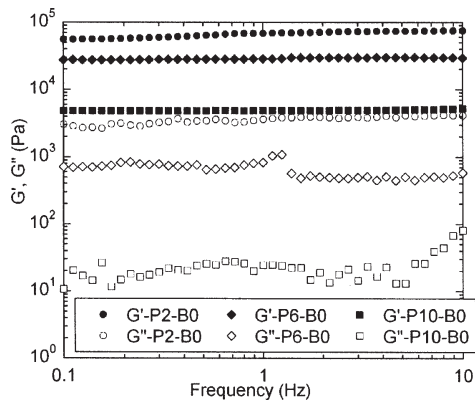


Fig. 7. Frequency sweep measurements for hydrogels without bentonite

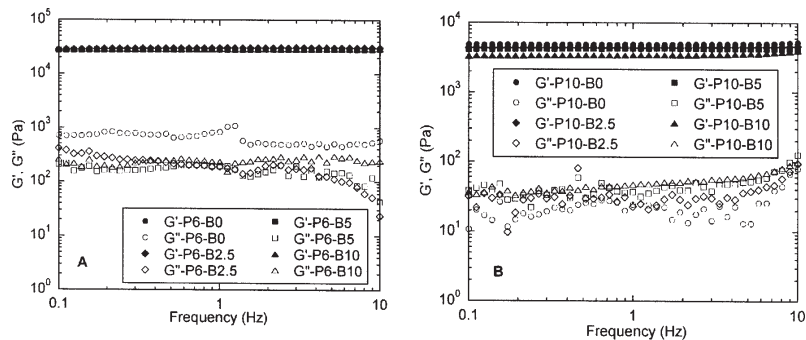


Fig. 8. Frequency sweep tests for the PEG₆₀₀₀ (A) and PEG₁₀₀₀₀ (B) composite hydrogels

Hydrogel	G' (Pa)	G'' (Pa)
P2-B0	69160	3630
P6-B0	28700	829
P6-B2.5	30150	190
P6-B5	28040	194
P6-B10	28800	232
P10-B0	4740	18
P10-B2.5	4380	23
P10-B5	4290	37
P10-B10	3420	46

Table 3
G' AND G'' VALUES AT 1 HZ FOR THE HYDROGELS SYNTHESIZED

but the differences were very small. For the PEG₂₀₀₀ composite hydrogels, the G' and G'' moduli could not be reliably determined because of the slippage of the rheometer measuring upper plate on the hydrogel surface.

Conclusions

Diepoxy-terminated PEG was crosslinked with EDA in aqueous solution in the presence of hydrophilic bentonite in order to prepare composite hydrogels. The hydrogels prepared were tested from the point of view of their swelling behaviour and mechanical properties. The results showed that the clay practically did not affect both the water absorption by the polymer and the storage modulus of the hydrogels. This seems to indicate that the interaction between the PEG chains and bentonite were very small or absent within the hydrogels in the presence of water, although they occurred in dry state, as proven by FTIR and XRD measurements upon xerogels.

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