U.P.B. Sci. Bull., Series B, Vol. 72, Iss. 4, 2010 ISSN 1454-2331

THE STATES OF WATER IN HYDROGELS SYNTHESIZED FROM DIEPOXY-TERMINATED POLY(ETHYLENE GLYCOL)S AND ALIPHATIC POLYAMINES

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Au fost studiate prin DSC stările apei într-o nouă familie de hidrogeluri obținute din polietilenglicoli cu grupe terminale epoxi reticulați cu diverse poliamine alifatice. Au fost investigate influența masei moleculare a oligomerilor, a compoziției amestecului de oligomeri cu mase moleculare diferite, influența lungimii catenei, a functionalității și structurii aminei, respectiv raportului $H_{amină}$/grupări epoxidice asupra conținutului diverselor tipuri de apă din hidrogelurile gonflate la echilibru. S-a arătat că conținutul de apă care îngheață depinde în principal de structura şi dimensiunea ochiurilor rețelei, în timp ce cantitatea de apă care nu îngheață depinde de compoziția chimică a rețelei. Hidrogelurile descrise aici pot avea aplicații în domeniul eliberării controlate a medicamentelor.

The states of water within a novel family of hydrogels prepared from diepoxy-terminated poly(ethylene glycol)s of different molecular weights crosslinked with various aliphatic polyamines were studied by DSC measurements. The influence of PEG molecular weight, weight composition of the $DEPEG_{600}$-$DEPEG_{4000}$ mixtures, amine chain length, amine functionality and structure and amine/epoxy groups mole ratio upon the different types of water in hydrogels were investigated. It was shown that the freezing water amount depended mostly on the structure and size of the meshes of the polymer network, while the non-freezing water content was mainly affected by the chemical structure of the network. The hydrogels described here may find applications in the controlled delivery of drugs.

Keywords: hydrogels; poly(ethylene glycol); aliphatic polyamines; freezing water; non-freezing water

1. Introduction

Hydrogels are polymeric networks made up of hydrophilic polymers able to absorb and retain large amounts of water [1]. This field has been intensely researched during the last decades, since hydrogels have found important

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applications in medicine and pharmacy [2-5], agriculture [6] and many other fields. Agricultural applications of hydrogels include soil conditioners and controlled release of agrochemicals, while the main biomedical applications are in the field of biosensors, controlled drug delivery and tissue engineering.

As most applications of hydrogels are based on their water absorption, the water content of a hydrogel is one of the most important elements, affecting its quality and functionality. Moreover, as the blood compatibility is not necessarily a simple function of hydrogel water content, it is reasonable to suppose that the state of water in the hydrogels and at the hydrogel/water interface may also be important [7].

The states of water in a hydrogel are generally classified into three types: i) free water, which is the water that does not form hydrogen bonds with the polymer and behaves similarly with pure water as far as freezing and melting is concerned; ii) freezing bound water, which interacts weakly with the polymer chains and freezes/melts at temperatures shifted with respect to that of free water; and iii) non-freezing bound water, which is bound to the polymer chains through hydrogen bondings, and does not exhibit a detectable phase transition within the normal temperature range associated with pure water [8-11]. Therefore, besides the swelling behavior, and the mechanical and thermal properties, the determination of the various states of water in hydrogels is important for the understanding of the nature of the interactions between polymer and water on one hand, and on the other hand it is an important indicator for some of the characteristics of the hydrogel, like biocompatibility [12].

In previous articles we have described the synthesis and swelling behavior [13,14], the compression properties [15] and the thermal properties [16] of some novel crosslinked poly(ethylene glycol) (PEG) hydrogels prepared from linear diepoxy-terminated PEGs (DEPEG) and aliphatic di- and polyamines as crosslinking agents, in water/aqueous solutions. The results showed that, under constant environmental and synthesis conditions, the swelling characteristics and the compression and thermal properties depended on the molecular weight of PEG oligomers, number of carbon atoms within the amine chain, amine structure and functionality and amine/epoxy groups mole ratio. The equilibrium swelling degree (ESD) was additionally tuned by employing mixtures of oligomers of different molecular weights, i.e. $DEPEG_{600}$ and $DEPEG_{4000}$ [14]. The present work aims at investigating the influence of the same factors upon the various states of water within the resulting DEPEG – polyamine hydrogels. In order to do this, hydrogels with various structures, crosslinking degrees and properties were synthesized from diepoxy-terminated poly(ethylene glycol)s of different molecular weight and various aliphatic polyamines of different chain length, functionality and structures: ethylenediamine (EDA), 1,6-hexamethylenediamine (HMDA), 1,8-octanediamine (ODA), 1,12-dodecanediamine (DADD), diethylenetriamine

(DETA), triethylenetetramine (TETA), tris(2-aminoethyl)amine (TREN) (fig. 1). As additional means to adjust the ESD of the hydrogel, mixtures of DEPEGs of different molecular weights were employed.

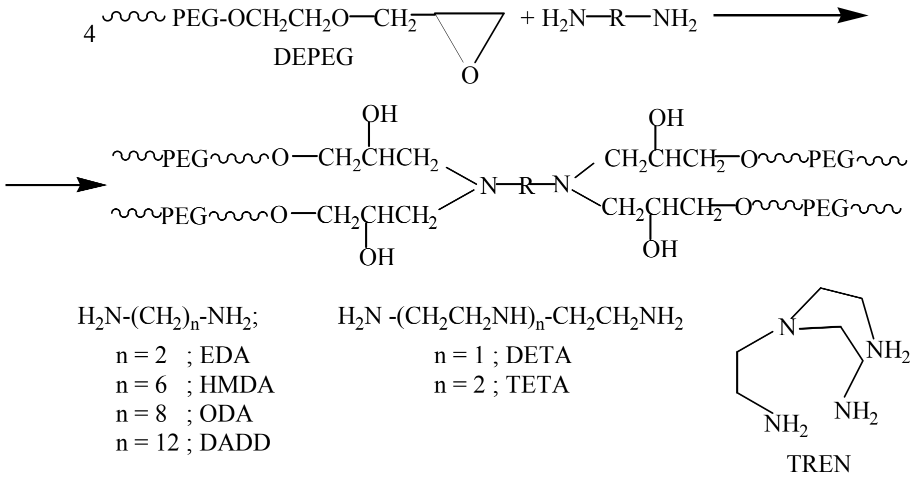

Fig. 1. Synthesis of hydrogels

2. Experimental part

2.1. Materials

α,ω-Dihydroxy PEG ($DHPEG_X$, Fluka) with an approximate molecular weight of 600 ($DHPEG_{600}$), 1000 ($DHPEG_{1000}$), 2000 ($DHPEG_{2000}$) and 4000 mol/g ($DHPEG_{4000}$) were used as received. Their hydroxyl numbers, determined by the phthalation method, were 185.52, 114.44, 54.55 and 27.99 mg KOH/g, respectively, corresponding to number average molecular weights ($M_{n,\ PEG}$) of 605, 982, 2060 and 4010 Da, respectively, calculated presuming the presence of two hydroxyl groups within each PEG macromolecule. Diepoxy-terminated PEGs ($DEPEG_x$) were synthesized from the corresponding $DHPEG_x$ and epichlorohydrin, in benzene, as previously described [12]. Their functionality ($\bar{f}$) is shown in table 1. Ethylenediamine (EDA, Scharlau, 99%), hexamethylenediamine (HMDA, Merck, 99%), 1,8-octanediamine (ODA, ACROS, 99%), 1,12-dodecanediamine (DDDA, Aldrich, 98%), diethylenetriamine (DETA, 99%, Alfa Aesar), triethylenetetramine (TETA, Fluka, 97%), tris(2-aminoethyl)amine (TREN, 96%, ACROS) and all the other reagents were used without further purification.

Amine solution of known concentrations were prepared in volumetric flasks by employing bidistilled water or 75/25 v/v ethanol-water mixture, in the case of DADD.

Table 1

Functionality of the DEPEG$_x$ prepared

Oligomer	$M_{n,DHPEG}$[a] (g/mol)	$\bar{f}_{DEPEG}$ [b] (epoxy groups/molecule)
DEPEG$_{600}$	605	2,00
DEPEG$_{1000}$	982	1,98
DEPEG$_{2000}$	2060	1,99
DEPEG$_{4000}$	4010	1,91

[a] Determined by the phthalic anhydride/pyridine method
[b] determined by HCl addition method

2.2. Hydrogel preparation

A 30 wt.-% DEPEG$_X$ solution was prepared by dissolving 0.5g oligomer into the appropriate amount of bidistilled water, followed by the addition of the calculated volume of the aliphatic polyamine solution of known concentration. In the case of DDDA, whose solubility in water is very low, a 75:25 v/v ethanol-water mixture was used instead water. The reaction mixture was very well stirred and transferred by means of a syringe into a 10 mm diameter glass tube, which was sealed by a rubber septum and kept in an oil bath at 60ºC for 140 hours. At the end of the reaction time, the glass tube was removed from the bath, cooled, broken and the resulting hydrogel rods were cut into small disk-shape pieces 1.5-2 mm thick. The disks were then placed into an excess of bidistilled water for 7 days at room temperature. The water was changed daily in order to remove the unreacted amine and oligomer. The swollen disks were dried initially under air and then in a desiccator over anhydrous $CaCl_2$ until constant weight was reached. Hydrogels were swelled to equilibrium in bidistilled water at 34ºC before the DSC measurements were carried out.

2.3. Equilibrium swelling degree (ESD) determination

The ESD of the synthesized hydrogels was determined by placing a weighed xerogel disk (W_x) into bidistilled water, at 34ºC. The swollen disk was removed from the water bath at certain time intervals, wiped superficially with filter paper, weighed and sunk back into water. The measurements were carried out until the weight of the swollen gel reached a constant value (W_h), corresponding to the equilibrium swelling. ESD, expressed as amount of water absorbed by 1 g of xerogel, was calculated according to the following equation:

$$\text{ESD (g water/g dry polymer)} = \frac{W_h - W_x}{W_x} \tag{1}$$

2.4. Characterization

The functionality ($\bar{f}$) of the synthesized DEPEG$_X$ was titrimetrically determinated by the addition of HCl to the epoxy ring, in dioxane, at room temperature [17].

Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH DSC 204 F1 Phoenix instrument operating under nitrogen flow at 5ºC/min heating rate.

The hydrogel samples swelled to equilibrium were quickly frozen inside the DSC instrument chamber to -50ºC, kept for 5 minutes to equilibrate, and heated to 40ºC.

3. Results and discussion

The DSC heating curves of all hydrogel samples displayed some endothermic peaks due to the melting of the various forms of water which freeze during the cooling stage (fig. 2). The endothermic peak around 0-10ºC was split into two peaks, which have been ascribed previously to the freezing bound water (the sharp one) and free water (the broad one) [9,11]. Because of the overlapping of the two peaks, their quantitative analysis was not possible, and thus the amounts of these two kinds of water in hydrogels were only qualitatively compared. The free water and freezing bound water represent forms of water that are not structured or slightly structured, respectively, in the presence of the polymer chains. As shown in figure 2, the DEPEG$_{2000}$- and DEPEG$_{4000}$- based hydrogels displayed also a smaller peak at temperatures below -15ºC, whose position differed from a hydrogel to another. These small peaks may be assigned to the melting of a small amount of PEG trihydrate complex that crystallized during the cooling step [18,19]. The water contained by the PEG trihydrate represents a form that interacts strongly with the polymer and obviously does not freeze during the cooling process. Therefore, it can be included into the same category with the non-freezing water, i.e. the water strongly bound to the polymeric chains.

The fraction of the freezing water (W_f, free water and freezing bound water) within the hydrogel was determined from the area under the corresponding endothermic peak (ΔH_{endo}) according to Eq. 2:

$$W_f(\%) = \frac{\Delta H_{endo}}{\Delta H_W} \times 100 \tag{2}$$

where ΔH_w is the heat of fusion of pure water (333,3 J/g [10]).

Non-freezing bound water content (W_{nf}) was determined (Eq.3) by subtracting W_f from the equilibrium water content of the hydrogel (W_∞) calculated from the ESD of the corresponding hydrogel according to Eq. 4.

$$W_{nf} = W_\infty - W_f \tag{3}$$

$$W_\infty(\%) = \frac{ESD}{ESD+1} \times 100 \tag{4}$$

Also, the xerogel content of the hydrogel was calculated according to Eq.5:

$$X(\%) = 100 - W_\infty \tag{5}$$

We will present below the influence of the following factors upon the states of water within the hydrogels: molecular weight of the DEPEG oligomer, weight composition of a mixture of oligomers with different molecular weights, amine chain length, amine functionality and structure, and amine/epoxy groups mole ratio.

3.1. Influence of PEG molecular weight upon the state of water in $DEPEG_X$-EDA hydrogels

Fig.2 shows the DSC heating curves of the $DEPEG_X$-EDA hydrogels at equilibrium swelling. As the molecular weight of the PEG chains increased, the intensity of the free water peak increased by comparison to that of the freezing bound water, suggesting that the proportion of free water in hydrogel became increasingly important as the water absorption increased.

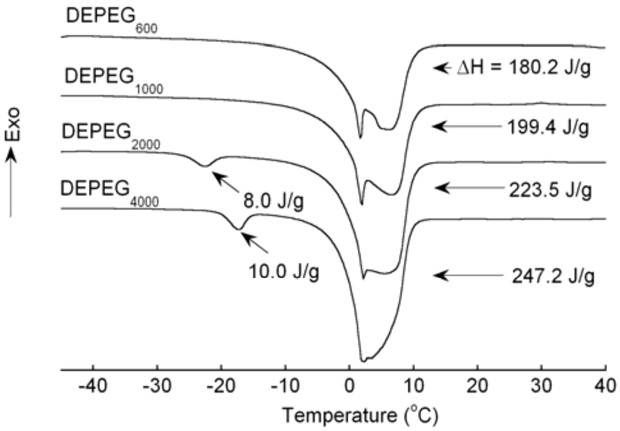

Fig. 2. DSC heating traces of $DEPEG_X$-EDA hydrogels at equilibrium swelling

The freezing bound water peak decreased very much in the case of PEG_{2000}- and PEG_{4000}-based hydrogels, which displayed in exchange at temperatures below -15ºC the peak assigned to the melting of the PEG trihydrate complex, whose position differed from a hydrogel to another, because of the different molecular weight of the PEG chain [18].

Table 2 shows the amounts of the various forms of water in $DEPEG_X$ – EDA, calculated from the DSC measurements. Also, for an evaluation of the polymer network influence upon the structuration of water within the hydrogel, the amount of each kind of water was divided by the polymer amount (equal to the xerogel amount) of the hydrogel. One can see that the amount of freezing water increased, while the proportion of non-freezing water decreased, as both the molecular weight of the PEG chains and the swelling degree increased.

Table 2

Influence of the molecular weight of $DEPEG_X$ upon the various states of water in $DEPEG_X$-EDA hydrogels

$DEPEG_X$	$M_{n,DEPEG}$*	ESD	W_∞(%)	W_f(%)	W_{nf}(%)	**X**(%)	W_f/X	W_{nf}/X	W_f/W_{nf}
$DEPEG_{600}$	717	4.15	80.6	54.1	26.5	19.4	2.78	1.37	2.04
$DEPEG_{1000}$	1093	5.17	83.8	59.8	24.0	16.2	3.69	1.48	2.50
$DEPEG_{2000}$	2171	6.90	87.3	67.1	20.3	12.7	5.30	1.60	3.31
$DEPEG_{4000}$	4117	10.15	91.0	74.2	16.9	9.0	8.27	1.88	4.40

*Molecular weight of $DEPEG_X$

As the molecular weight of the oligomer $DEPEG_X$ increased, the ESD of the resulting hydrogels increased as well due to the formation of a network with a lower crosslinking density, as previously shown [13]. In consequence, at higher ESD values, obtained when longer PEG chains were involved, the xerogel content of the hydrogel decreased.

In relation to the xerogel content of the hydrogel, both the fraction of slightly structured freezing water (W_f) and the content of non-freezing water (W_{nf}), structured around the polymeric chains, increased with the molecular weight of DEPEG, a much larger increase being noticed in the first case. This conclusion resulted from the comparison of the W_f /X and W_{nf}/X ratios (table 2) and also from the increasing and greater than 1 values of the ratio freezing water/non-freezing water (W_f/W_{nf}). Hence, the most part of the water absorbed by the hydrogel consisted of slightly structured water, whose freezing occurs in a temperature range close to that associated with pure water. The increase of the freezing water content of the hydrogel with the molecular weight of the oligomer may be explained through the enhancement of the water amount absorbed at equilibrium due to the increase of the size of the hydrogel network meshes.

One should also remark that the structured water content increased by rapport to the polymer amount as the molecular weight of DEPEG oligomer raised. This tendency may be explained by a larger number of water molecules binding to the PEG chain through hydrogen bonds due to the increase of the ratio between the length of the ethylene oxide chain, able to form hydrogen bonds, and the hydrophobic endgroups.

3.2. Influence of the weight composition of the DEPEG$_{600}$-DEPEG$_{4000}$ mixtures

The states of water within the hydrogels prepared from mixtures of DEPEG$_{600}$ and DEPEG$_{4000}$ in various ratios crosslinked with EDA were studied by DSC measurements (fig.3, table 3). As expected, both ESD and freezing water content increased with increasing equivalent molecular weight of the oligomer mixture. Also, the free water peak increased with the equivalent molecular weight of the oligomer mixture, as revealed in fig. 3. For oligomer mixtures where DEPEG$_{4000}$ prevailed, the DSC curves indicated the presence of the PEG-trihydrate complex in a different position from a hydrogel to another, depending on the DEPEG$_{4000}$ amount.

Both freezing and non-freezing water amounts of the mixed oligomers hydrogels progressively changed in-between those corresponding to the pure oligomers i.e. DEPEG$_{600}$ and DEPEG$_{4000}$ (table 3). Also, in relation to the xerogel amount, the slightly structured water increased much more than the strongly structured one with the equivalent molecular weight of the mixed oligomers hydrogels, in agreement with the tendency of pure oligomers hydrogel series.

As shown above, the variation of the different states of water amount was almost similar in the case of DEPEG$_{600}$ – DEPEG$_{4000}$ oligomer mixtures to that of the equivalent monooligomer hydrogel series.

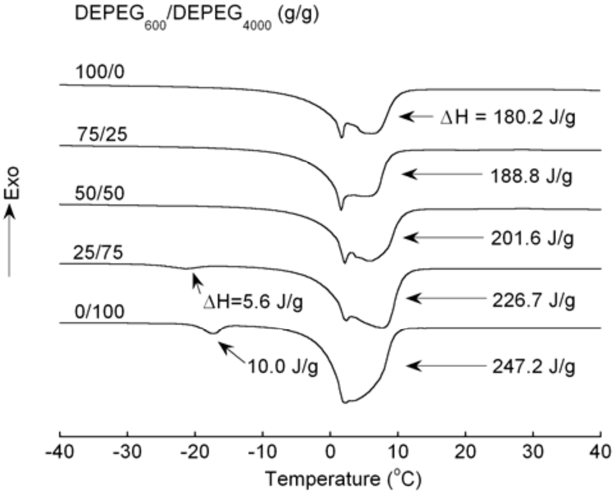

Fig. 3. DSC heating traces for the hydrogels prepared from DEPEG$_{600}$-DEPEG$_{4000}$ mixtures crosslinked with EDA at equilibrium swelling

Table 3

Influence of the weight composition of the $DEPEG_{600}$-$DEPEG_{4000}$ mixtures crosslinked with EDA upon the various states of water in the resulting hydrogels

$DEPEG_{600}$/ $DEPEG_{4000}$ (g/g)	Equivalent molecular weight (${M_{n,amestec\ DEPEG}}$)[a]	ESD	W_∞(%)	W_f(%)	W_{nf}(%)	X(%)	W_f /X	W_{nf}/X	W_f/W_{nf}
100/0	717	4.15	80.6	54.1	26.5	19.4	2.78	1.37	2.04
75/25	829	4.96	83.2	56.6	26.6	16.8	3.38	1.58	2.13
50/50	1227	6.30	86.3	60.5	25.8	13.7	4.42	1.88	2.34
25/75	1873	8.20	89.1	68.0	21.1	10.9	6.26	1.94	3.22
0/100	4117	10.15	91.0	74.2	16.9	9.0	8.27	1.88	4.40

a) $M_{n,DEPEG\ mixture} = n_{DEPEG600} \times M_{n,DEPEG600} + n_{DEPEG4000} \times M_{n,DEPEG4000}$; n_{DEPEGi} = mole fraction of $DEPEG_i$

3.3. Influence of the amine chain length

The hydrophobic character, the ESD values and, in consequence the different states of water from the structuration point of view, at the equilibrium swelling, [13] can be tailored by varying the chain length of the crosslinking agent.

Thus, amines with 2 (EDA), 6 (HMDA), 8 (ODA), and 12 (DADD) carbon atoms, respectively, were employed as crosslinking agents. In order to record and investigate better the influence of the chain length upon the various states of water in hydrogels, $DEPEG_{600}$ oligomer was employed because of its smallest ethylene oxide chain/hydrophobic crosslinking points ratio, which allows for a stronger effect to be recorded as the hydrophobic character of the amine changes.

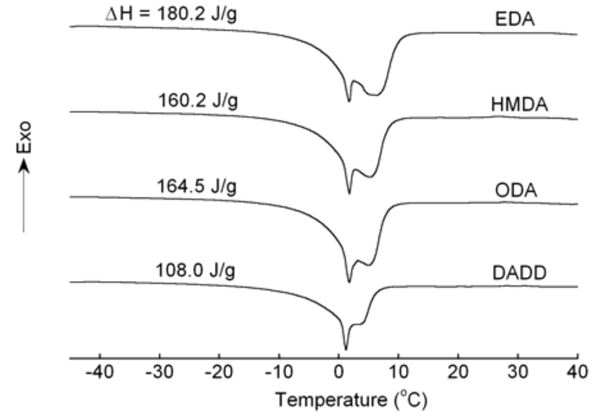

Fig. 4. DSC heating traces of hydrogels prepared from $DEPEG_{600}$ and diamines of various chain length, at equilibrium swelling

Table 4

Influence of the amine chain length upon the various states of water in DEPEG$_{600}$-diamine hydrogels

Diamine	ESD	W_∞(%)	W_f(%)	W_{nf}(%)	X(%)	W_f /X	W_{nf}/X	W_f/W_{nf}
EDA	4.15	80.6	54.1	26.5	19.4	2.78	1.37	2.04
HMDA	3.51	77.8	48.1	29.8	22.2	2.17	1.34	1.61
ODA	3.30	76.7	49.4	27.4	23.3	2.12	1.18	1.80
DADD	1.90	65.5	32.4	33.1	34.5	0.94	0.96	0.98

The results showed that as the amine chain length increased the intensity of the free water peak decreased, while the freezing bound water peak areas remained approximately the same, indicating that the free water content decreased (fig.4). By increasing the chain length of the amine employed, a reduction of ESD was obtained as a consequence of the increased hydrophobic character of the hydrogel. This effect predominates over that of the decreasing crosslinking density, as previously shown [13]. This effect explains also why the freezing water content strongly decreased as the diamine carbon atoms number increased (table 4). Also, in the case of the non-freezing water, the number of hydrogen bonds formed between the PEG chains and the water molecules decreased due to decreasing amount of PEG in hydrogel as the amine/PEG$_{600}$ chains ratio increased with the diamine chain length. At first sight, this effect should lead to a lower non-freezing water content. However, this type of water slightly increased as the diamine carbon atoms number increased. This behavior may be explained through the strong decrease of the freezing water content, which determined, through the equation 3, an apparent increase of the non-freezing water amount by rapport to the freezing water content. In relation to the xerogel content, both slightly structured water and structured water decreased, as explained above, but the free water amount decreased much more, as can be seen from the W_f/W_{nf} ratio. The non-freezing water amount increased with the amine chain length, so that in the case of hydrogels crosslinked with DADD the non-freezing water content was approximately equal to the freezing water content.

3.4. Influence of amine functionality and structure

The amine functionality equals its number of hydrogen atoms involved in the addition reaction to the epoxy ring (H_{amine}), reaction which is responsible for the formation of the network. Thus, the functionality of the amines employed to synthesize the hydrogels was 4 in the case of diamines (EDA, HMDA, ODA and DADD), while for DETA, TETA and TREN it was 5, 6 and 6, respectively.

As it can be seen from Figure 1, TETA has a different structure in comparison with TREN: TETA is a linear polyamine with 2 primary and 2 secondary amine groups, whereas TREN is a branched polyamine with 3 primary and one tertiary amine groups. Networks with higher crosslinking degree were obtained by increasing the functionality of the amine. As in the situation of the investigation of amine chain length influence, only DEPEG$_{600}$ oligomer was employed, as, due to the shorter PEG chain length, the effect of the functionality and structure of the amine used upon the various states of water in hydrogels should be higher, and therefore easier to record.

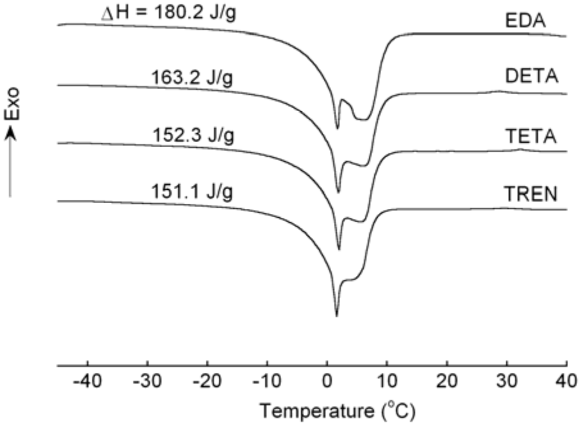

Fig. 5. DSC heating traces of hydrogels prepared from DEPEG$_{600}$ and polyamines of various functionalities and structures, at equilibrium swelling

The DSC measurements revealed the decrease of the intensity of the free water peak while the intensity of the sharper peak, which have been ascribed before to the freezing bound water, remained relatively constant as the functionality of the amine increased from 4 to 6, which is indicative for a reduction of the proportion of the free water within the hydrogel. The different structure of the crosslinking agent (TETA vs. TREN) had a relatively small influence upon the free water and freezing bound water peaks, as indicated by the DSC curves in fig. 5. It can be noticed that ESD decreased as the functionality of the amine increased, as a consequence of the formation of a polymer network with a higher degree of crosslinking (table 5), in agreement with the previously reported results [14]. Because of the ESD decrease, the freezing bound water (slightly structured) decreased by rapport to the xerogel content of the hydrogel. In the same time, the non-freezing water (structured water)/xerogel ratio remained practically constant because the amine hydrophilicity does not substantially change from EDA to TETA due to the specific polyamine structure, in contrast to the EDA-DADD amine series. The slightly structured water/structured water ratio decreased as the functionality of the amine increased, in agreement with both freezing bound water and non-freezing water content evolution (table 5).

One can see also that both the freezing water and non-freezing water contents were not influenced by the structure of the crosslinking agent (TETA vs. TREN).

Table 5

Influence of the polyamine functionality and structure upon the various states of water in $DEPEG_{600}$-polyamine hydrogels

Polyamine	ESD	W_∞(%)	W_f(%)	W_{nf}(%)	X(%)	W_f /X	W_{nf}/X	W_f/W_{nf}
EDA	4.15	80.6	54.1	26.5	19.4	2.78	1.37	2.04
DETA	3.52	77.9	49.0	28.9	22.1	2.21	1.31	1.69
TETA	3.21	76.2	45.7	30.6	23.8	1.92	1.29	1.50
TREN	3.29	76.7	45.3	31.4	23.3	1.94	1.35	1.45

3.5. Influence of the amine/epoxy groups mole ratio

Hydrogels with different network structures, obtained at three different H_{amine}/epoxy group ratios (1:1, 1:0.7 and 1:1.3) were tested as well, in order to investigate the various states of water in these hydrogels. The H_{amine}/epoxy group ratio for excess $DEPEG_X$ (H_{amine}/epoxy groups = 1:1.3) was calculated so as to obtain, ideally, a hydrogel network with the same crosslinking degree as those resulted in the case of excess amine, (H_{amine}/epoxy groups = 1:0.7), as previously reported [13]. $DEPEG_{600}$ was employed as the end-functional oligomer, for the reasons explained above, and TETA was used as the crosslinking agent.

For the same PEG chain length, excess of any of the reacting functional groups led to higher ESD as compared to the hydrogel synthesized under stoichiometric conditions (table 6), as previously shown [13]. Thus, excess amine led to a lower degree of crosslinking due to the formation of larger meshes within the hydrogel network, while in the case of excess epoxy groups the ESD values were even higher than for amine excess, several effects contributing to ESD increase: i) formation of larger meshes within the hydrogel network; ii) formation of PEG grafts and iii) a smaller concentration of elastically effective network chains, formed in the case of excess epoxy groups than for excess amine, due to the lower conversion of DEPEG oligomers [13].

The intensity of the free water peak increased as compared to that of the freezing bound water for both non-stoichiometric hydrogels, particularly in the case of excess epoxy groups, in accord with the higher ESD, as revealed by figure 6.

The freezing water content, as well as that of the structured non-freezing water, best characterized by the W_f /X and W_{nf}/X ratios, increased in the presence of excess of any of the reacting functional groups, especially in the case of excess epoxy groups (table 6). In the case of freezing water, this may be explained through the increase of ESD. As far as the non-freezing bound water is concerned, it can be seen that for the excess epoxy groups hydrogel the W_{nf}/X ratio increased.

This may be rationalized through the higher amount of oligomer chains as compared with the equimolecular conditions, which are able to form additional hydrogen bonds with the water molecules. As shown in table 6, in the case of excess amino groups the non-freezing water/xerogel ratio increased slightly from the equimolecular conditions to excess amine. This behavior may be explained through an enhanced ability of the more hydrophilic NH groups within the excess amine hydrogels [13] to form additional hydrogen bonds with the water molecules in comparison to the less hydrophilic tertiary amine groups found in stoichiometric hydrogels.

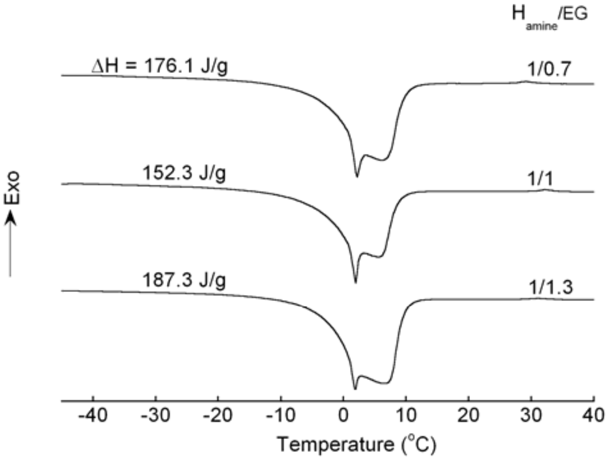

Fig. 6. DSC heating traces of $DEPEG_{600}$ - TETA hydrogels synthesized at various H_{amine}/epoxy groups ratios at equilibrium swelling

Table 6

Influence of H_{amine}/epoxy groups mole ratio upon the various states of water in $DEPEG_{600}$-TETA hydrogels

H_{amine}/epoxy groups	ESD	W_∞(%)	W_f(%)	W_{nf}(%)	X(%)	W_f /X	W_{nf}/X	W_f/W_{nf}
1/0.7	4.00	80.0	52.8	27.2	20.0	2.64	1.36	1.94
1/1	3.21	76.2	45.7	30.6	23.8	1.92	1.29	1.50
1/1.3	4.91	83.1	56.2	26.9	16.9	3.32	1.59	2.09

4. Conclusions

Hydrogels from diepoxy-terminated poly(ethylene glycol)s of different molecular weights and various aliphatic di- and polyamines were synthesized and characterized by DSC measurements from the point of view of the diverse forms of water contained. The factors investigated were the molecular weight of the PEG oligomer, the weight composition of the $DEPEG_{600}$-$DEPEG_{4000}$ mixtures, the diamine chain length, the amine functionality and structure and the amine/epoxy group mole ratio. The DSC measurements on the hydrogels swelled at equilibrium revealed qualitatively the presence of both free water and freezing bound water, while the non-freezing bound water could not be detected by these type of measurements, but it was calculated instead.

In almost all cases the largest part of the water in the hydrogel at the equilibrium swelling was represented by the slightly structured freezing water.

In the case of oligomers with various molecular weights, the freezing water amount showed a strong increase by rapport to the xerogel content of the hydrogel, in agreement with the increase of ESD, due to the formation of a polymer network with lower crosslinking degree. The non-freezing water amount increased slightly with the molecular weight of the oligomer, because of a higher amount of hydrogen bonds formed between the increasing PEG chain and the water molecules. A similar effect was noticed when the equivalent molecular weight of $DEPEG_{600}$-$DEPEG_{4000}$ mixtures increased.

The freezing water content strongly decreased with the amine chain length, due to the increase of the hydrophobic character of the hydrogel, which led to an apparent increase of the non-freezing water amount.

The freezing water amount decreased by rapport to the xerogel content as the amine functionality increased, due to the formation of smaller size meshes within the hydrogel network. Simultaneously, the non-freezing water /xerogel ratio changed very little, because of the similar hydrophilicity of the amines employed in this case, unlike the case where the chain length of the amine was varied.

The different structure of the amine, linear for TETA and branched in the case of TREN, did not have any influence upon both the freezing and non-freezing water content.

Also, it was observed that the freezing water/xerogel ratio increased for hydrogels prepared under non-stoichiometric conditions as a consequence of crosslinking degree reduction, while the non-freezing structured water increased for both excess oligomer and amine as compared to the equimolecular conditions.

To generalize, the results showed that the amount of slightly structured freezing water within the hydrogel depended on the structure and mesh size of the polymer network and displayed a strong dependence on ESD, while the amount of non-freezing water, strongly interacting with the polymer, depended mostly on the chemical structure of the polymer chains and crosslinking points of the polymer network.

The hydrogels described here may find aplications in the controlled delivery of drugs.

Acknowledgement

The financial support of the National University Research Council in Romania through the PN II - IDEAS grant no.389/2007 is gratefully acknowledged.

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