Thermal Properties of Networks Prepared from α,ω-Diepoxy Terminated Poly(ethylene glycol)s and Aliphatic Polyamines

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The thermal properties of a novel family of xerogels prepared from diepoxy-terminated poly(ethylene glycol)s of approximate molecular weights 600, 1000, 2000 and 4000 Da and various aliphatic polyamines (ethylenediamine, 1,4-diaminobutane, hexamethylenediamine, 1,8-octanediamine, 1,10-decanediamine, 1,12-dodecanediamine, diethylenetriamine, triethylenetetramine, tris(2-aminoethyl)amine) were studied by DSC and TGA measurements in order to establish the influence of several structural parameters that may affect the physical state of the network-forming polymer at a certain temperature. All xerogels synthesized displayed crystallinity which was affected by the MW of the PEG precursors, number of carbon atoms within the diamine chain, amine functionality and structure and amine/epoxy groups mole ratio. Both melting temperature and amount of crystalline phase were lower for networks with either shorter PEG chains, longer diamine chain, higher amine functionality and stoichiometric amine/epoxy groups ratio, while the thermal stability was higher for either longer PEGs, diamines with higher carbon atom numbers, higher amine functionality and stoichiometric amine/epoxy groups ratio.

Keywords: networks; poly(ethylene glycol); aliphatic polyamines; melting temperature; glass transition temperature; thermal stability

Hydrogels are networks of hydrophilic homo- and copolymers, able to absorb and retain large amounts of water [1,2]. The field has been intensely researched during the last decades, as hydrogels have found important applications in medicine and pharmacy [3-6], agriculture [7], and many other areas. The agricultural applications of hydrogels include soil conditioners and controlled release of agrochemicals, while the main biomedical ones are in the area of biosensors, controlled drug delivery and tissue regeneration and repair.

The controlled release applications of hydrogels, including both prolonged and targeted delivery of the active principle, are amongst the most important. For the slow-release systems with either diffusion or swelling control, the rate of diffusion and the mechanism of transport of either the drug or agrochemical are very important parameters [8,9], which are strongly influenced, besides other factors, by some of the physical properties of the dry hydrogel (xerogel). Amongst them, the physical state (rubbery, glassy or semicrystalline) of the network-forming polymer at the hydrogel application temperature has a strong influence upon the release profile of the active principle. Therefore, knowing in advance the characteristic temperatures of the xerogel, like glass transition and melting temperatures, and their dependency on the structural features of the network may speed up the design of a valuable slow-release hydrogel system.

In previous works, we have described the synthesis and swelling behavior [10] as well as the compression properties [11] 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 both environmental and synthesis conditions, the swelling characteristics and compression properties depended on the molecular weight of PEG precursors, number of carbon atoms within the diamine chain, amine functionality and amine/epoxy groups mole ratio. The present work aims at investigating the influence of the same factors upon the thermal properties of the resulting DEPEG – polyamine networks.

Experimental part
Materials

α,ω-Dihydroxy PEG with an approximate molecular weight of 600 mol/g (DHPEG$_{600}$), DHPEG$_{1000}$, DHPEG$_{2000}$ and DHPEG$_{4000}$ (DHPEG$_X$, Fluka) were used as received. Their hydroxyl numbers, determined by the acetylation 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 assuming the presence of two hydroxy groups within each PEG macromolecule. Diepoxy-terminated PEGs (DEPEG$_X$) were synthesized from the corresponding DHPEG$_X$ and epichlorohydrin, in benzene, in the presence of NaOH, as previously described [10]. Their functionality (f) is shown in table 1. Ethylenediamine (EDA, Scharlau, 99%), 1,4-diaminobutane (DAB, ACROS, 99%), hexa-methylenediamine (HMDA, Merck, 99%), 1,8-octane-diamine (ODA, ACROS, 99%), 1,10-decanediamine (DDA, Fluka, 98%), 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 employed without further purification. Amine solutions of known concentrations were prepared in volumetric flasks by employing bidistilled water or 75/25 v/v ethanol - water mixture.

Xerogel preparation

A 30 wt.-% DEPEG$_X$ solution was prepared by dissolving 0.5 g oligomer into the appropriate amount of bidistilled water, followed by the addition of the calculated volume of the polyamine solution. In the case of DDA and DDDA, whose solubility in water is very low, a 75/25 v/v ethanol - water mixture was used as the solvent instead. The reaction mixture was very well stirred and transferred by means of a syringe into a 10 mm diameter glass tube, which was

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 acetic anhydride/pyridine method

[b]determined by the HCl addition method

sealed by a rubber septum and kept in an oil bath at 60°C for 140 h. At the end of the reaction time, the tube was removed from the bath, 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 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 obtained. Just before testing, the xerogels were additionally dried at room temperature in a vacuum oven over anhydrous CaCl$_2$ for 48 hours.

Characterization
The functionality $(\bar{f})$ of the synthesized DEPEG$_X$ was titrimetrically determined by the addition of HCl to the epoxy ring, in dioxane, at room temperature [12].

The melting (T_m) and crystallization (T_c) temperatures were determined by differential scanning calorimetry (DSC) measurements carried out on a NETZSCH DSC 204 F1 Phoenix instrument operating under nitrogen flow at 5°C/min heating rate. Samples weighing about 10 mg were cycled between -70°C and 70°C in nitrogen atmosphere, and T_m and T_c were determined from the peak maxima obtained during the second heating/cooling cycle, whereas the enthalpies of fusion (ΔH_m) and crystallization (ΔH_c), expressed as J/g xerogel, were calculated from the peak areas. The degree of crystallinity (DC) was calculated with equation (1):

$$DC = \Delta H_{m,E}/\Delta H_m^0 \qquad (1)$$

where $\Delta H_{m,E}$ (J/g PEG chains) is the melting enthalpy of the PEG chains only, calculated from ΔH_m by taking into account the PEG chain content of the xerogels, while ΔH_m^0 is the enthalpy of fusion of perfectly crystalline poly(ethylene oxide), which can be calculated with equation (2) [13]:

$$\Delta H_m^0 (J/g) = 178.6 + 0.629 T_m - 2.93 \times 10^{-3} T_m^2 \qquad (2)$$

In equation (2) T_m is expressed in °C.
The thermogravimetric analysis (TGA) of the xerogels was carried out on a Thermal Analysis Q500 instrument by heating samples of about 4 mg from room temperature to 600°C at 10 °C/min heating rate under nitrogen flow.

Results and discussion
Xerogels with different structures and crosslinking degrees were synthesized by the end-linking reaction between diepoxy-terminated PEGs of various molecular weights and aliphatic polyamines with different numbers of carbon atoms, structure and functionality, in water, according to the procedure already reported by us and others [10,11,14,15]. In all experiments a stoichiometric ratio of amine hydrogen atoms (H$_{amine}$)/epoxy endgroups (EG) was used, unless otherwise is stated.

The thermal properties of the prepared PEG – based networks were investigated by DSC and TGA and the dependence of both thermal transitions and thermal stability on their structure was determined.

Influence of PEG molecular weight onto the thermal behavior of the networks
The DSC measurements revealed the presence of the crystalline phase for all the PEG – based networks investigated, irrespective of the molecular weight of the PEG chain, as reported also previously [10,16-18]. The melting temperature of the crystalline areas of xerogels decreased with the molecular weight of PEG, being below or around room temperature for the PEG$_{600}$- and PEG$_{1000}$-based xerogels, respectively, whereas for higher molecular weight PEG chains it was well above room temperature. The tendency kept for the melting enthalpy, as well, i.e. ΔH_m was smaller in the case of networks with shorter PEG chains, indicative for a lower degree of crystallization. Table 2 displays the dependence of T_m and $\Delta H_{m,E}$ on the M_n of the PEG oligomer for both networks synthesized from DEPEG$_X$ and EDA, and the corresponding DHPEG$_X$. We considered that DHPEG would be a better model for the xerogel PEG chains than DEPEG because of the presence of hydroxy groups at the end of the PEG chains within the network.

The results showed that both melting points and melting enthalpies of the crosslinked xerogels were lower than those of the corresponding DHPEGs, confirming previous reports [10,16,18]. These differences can be ascribed to the lower mobility of the network chains, leading to smaller and less perfect crystals, and thus to lower values of T_m and $\Delta H_{m,E}$ [16,19]. The calculation of the degree of crystallinity (DC) with equation (1) by employing the ΔH_m^0 value calculated with equation (2) (table 2) showed a strong decrease of the DCs of the network PEG chains in comparison with the corresponding free oligomers of similar chain lengths.

The DSC curves of all the network samples displayed single melting peaks irrespective of the PEG molecular weight, while a cold crystallization phenomenon was noticed only for the PEG$_{600}$ gel under the DSC analysis conditions employed (fig. 1). All the other samples, both

Table 2

INFLUENCE OF THE MOLECULAR WEIGHT OF THE PEG CHAINS UPON THE THERMAL
PROPERTIES OF BOTH DEPEG$_X$ – EDA XEROGELS AND FREE OLIGOMERS

$M_{n,PEG}$	Xerogels[a]								DHPEG$_X$				
	T_m °C	$\Delta H_m{}^b$ J/g	$\Delta H_{m,E}{}^b$ J/g	DC	T_c °C	ΔH_c J/g	T_{onset} °C	T_{max} °C	T_m °C	$\Delta H_{m,E}{}^b$ J/g	DC	T_c °C	$\Delta H_c{}^b$ J/g
605	12.2	37	46	0.25	-22[c]	36	359.4	389.7	19.7	108	0.57	2.2	105
982	28.0	61	70	0.36	7.8	56	' -	-	37.7	143	0.72	19.0	140
2060	44.8	83	89	0.44	24.2	79	-	-	54.5	156	0.76	29.6	152
4010	56.0	103	107	0.52	31.3	100	374.4	398.1	61.9[d]	160	0.78	37.4	155

T_m, T_c = temperatures of melting and crystallization; ΔH_m, ΔH_c = enthalpies of melting and

crystallization; DC = degree of crystallinity; T_{onset} = temperature at which degradation begins;

T_{max} = temperature at which the degradation rate is the highest.

[a] H_{amine}/EG = 1/1 mole ratio.

[b] ΔH_m (J/g xerogel) ; $\Delta H_{m,E}$ (J/g PEG chains) ; ΔH_c (J/g xerogel).

[c] cold crystallization temperature, recorded during the second heating cycle.

[d] bimodal peak. The value corresponds to the highest peak.

gels and free oligomers, displayed crystallization during the cooling cycle only (program-cooled crystallization [20]). This different crystallization behavior may be rationalized through the modification of the movement rate of PEG chains immobilized at both ends within the network, similarly to the case of PEGs end-capped with bulky silsesquioxane moieties [21, 22]. The shorter the chain is, the more its mobility is affected by inclusion in a network. Thus, for PEG$_{600}$ gels, because of the very short segments (about 13 ethylene oxide units), crystallization on cooling was very much slown down, leading to the formation of a completely amorphous glassy state at the DSC cooling rate employed. On heating above the glass transition temperature (T_g), the chain mobility increased and at a certain temperature the crystalline phase formed [20]. In the case of networks with longer chains, the mobility of the PEG segments located farther from the junction points is sufficiently high to allow crystallization during the cooling cycle to occur.

One should also mention that in the case of DHPEG$_{4000}$ the melting peak obtained during the second heating cycle was bimodal (double peak), which was observed previously as well and explained through the presence of folded-chain lamellae with different fold numbers [23].

Figure 1 reveals the presence of the glass transition temperature only for DEPEG$_{600}$ – EDA, unlike all the other samples including DHPEG$_{600}$. This can be rationalized through the amorphous character of the PEG$_{600}$ network at low temperature, because of the very slow crystallization of PEG$_{600}$ chains on cooling under the DSC measurement conditions employed. At similar low temperatures, all the other samples were semicrystalline, with a relatively high content of crystalline phase, and therefore a low amorphous phase content, which prevented us to detect the glass transitions.
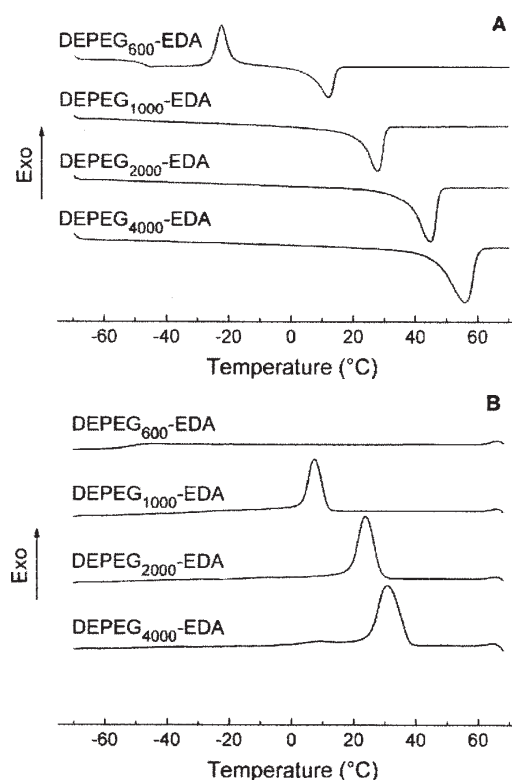

Fig. 1. DSC traces of the DEPEG$_X$ – EDA xerogels: A) second heating cycle; B) second cooling cycle

An increased DC is expected to bestow a higher thermal stability to the PEG-based networks. Indeed, as shown by TGA analyses (table 2, fig. 2), the thermal stability of PEG xerogels, characterized by T_{onset} and T_{max}, increased as the PEG chain length changed from 600 to 4000 Da, in
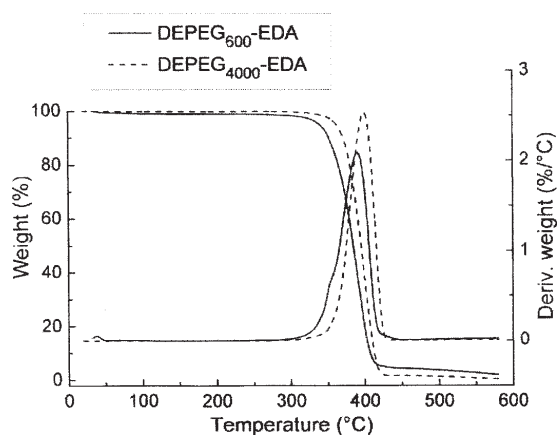
Fig. 2. TGA and DTG traces of DEPEG$_{600}$ – EDA and DEPEG$_{4000}$ – EDA xerogels

agreement with the increase of crystallinity (table 2). However, the thermal stability improvement was relatively small because the decomposition temperature was much higher than T$_m$ [24]. Figure 2 shows also that degradation occurred as a one step process in both cases, similarly to the free PEG oligomers.

Influence of amine chain length

To study the influence of the chain length, functionality and structure of the amine used as the crosslinking agent upon the thermal properties of the resulting xerogels, networks with PEG$_{600}$ chains were employed. Due to the shorter PEG chain length, the effect of the amine used upon the properties investigated should be higher, and therefore easier to record and analyze.

Table 3 shows the influence of the amine chain length upon the properties of DEPEG$_{600}$-diamine xerogels, while figures 3 and 4 display their DSC and TGA traces, respectively. The DSC curves indicated the presence of both cold crystallization and glass transition phenomena beside the melting endotherm peak in all cases (fig. 3). As

the number of carbon atoms in the amine chain increased, both T$_m$ and ΔH$_m$ decreased, indicative for a lower degree of crystallinity. Because of the different amine weight contents of the xerogels, ΔH$_{m,E}$ (J/g PEG chains), calculated from the experimentally determined ΔH$_m$ (J/g xerogel), allows for a more precise comparison between the melting enthalpies of these materials. ΔH$_{m,E}$ decreased with increasing amine chain length as well, in agreement with T$_m$ evolution. As far as the crystallization process is concerned, it can be seen that the negative cold crystallization temperatures increased as T$_m$ decreased, while ΔH$_c$ was practically equal to ΔH$_m$ in all cases, indicating that no slow rate crystallization had occurred below T$_c$. The results in table 3 also shows that T$_g$ slightly decreased while the thermal stability of the xerogels (T$_{onset}$ and T$_{max}$) slightly increased as the diamine carbon atoms number increased.

There are two possible explanations for this dependency of the thermal properties of the PEG$_{600}$-xerogels on the diamine chain length, but none of them fully covers all the results obtained. The first one assigns the melting point decrease to the increasing degree of association of the amine hydrocarbon chains within the PEG network, as their number of carbon atoms increased. These associations through hydrophobic interactions acting like physical crosslinks have led to an enhancement of the crosslinking degree. Both T$_m$ and ΔH$_{m,E}$ decrease, on one hand, and thermal stability, expressed by T$_{onset}$ and T$_{max}$, increase, on the other hand, can be ascribed to this crosslinking degree increase. As far as the thermal stability is concerned, it seems that the effect of the crosslinking degree modification leading to higher T$_{onset}$ and T$_{max}$ was higher than the effect of the decreasing degree of crystallinity, which should have lowered T$_{onset}$ and T$_{max}$ [24]. However, this supposition does not explain why T$_g$ decreased with increasing amine chain length, as according to the general knowledge stating that less mobile chains should display a higher T$_g$, an increase of the crosslinking degree should have also led to an increase of T$_g$.

Table 3
INFLUENCE OF THE AMINE CHAIN LENGTH UPON THE THERMAL PROPERTIES OF DEPEG$_{600}$-DIAMINE XEROGELS[a]

Diamine		T$_m$	ΔH$_m$[b]	ΔH$_{m,E}$[b]	DC[c]	T$_g$	T$_c$[d]	ΔH$_c$[b]	T$_{onset}$	T$_{max}$
Name	Carbon atoms	°C	J/g	J/g		°C	°C	J/g	°C	°C
EDA	2	12.2	37	46	0.25	-46.8	-22.2	36	359.4	389.7
DAB	4	10.0	34.5	43.5	0.24	-47	-22.3	34	-	-
HMDA	6	8.4	29	37	0.20	-46.9	-19.5	29	366.8	393
ODA	8	6.0	27	35	0.19	-48.2	-20.2	28	-	-
DAD	10	2.6	17	22.5	0.12	-49.1	-15.5	16	-	-
DADD	12	1.5	15	20	0.11	-49.1	-16.6	15	370.4	396.5

[a] H$_{amine}$/EG = 1/1 mole ratio.

[b] ΔH$_m$ (J/g xerogel) ; ΔH$_{m,E}$ (J/g PEG chains) ; ΔH$_c$ (J/g xerogel).

[c] calculated with equations (1) and (2).

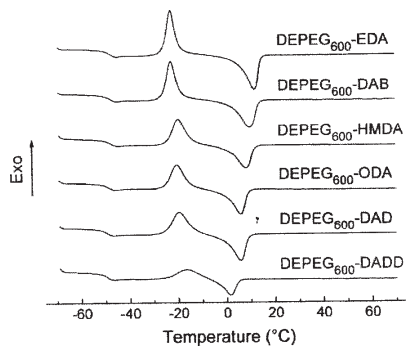[d] cold crystallization temperature, recorded during the second heating cycle.
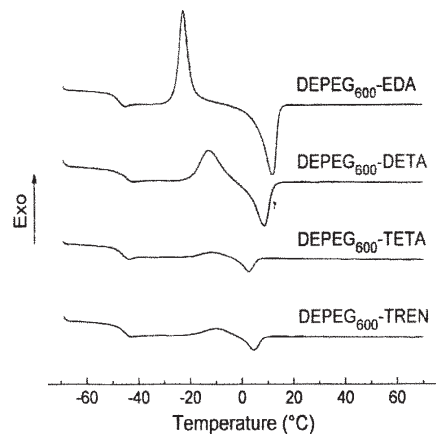
http://www.revmaterialeplastice.ro/

Fig. 3. DSC traces of the DEPEG$_{600}$ – diamine xerogels.
Second heating cycle

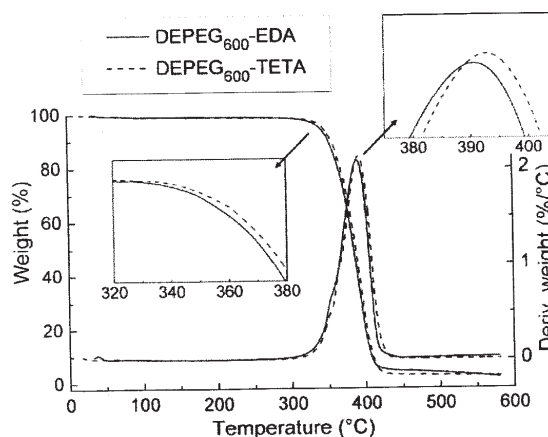Fig. 4. TGA and DTG traces of DEPEG$_{600}$ – diamine xerogels

Another possible explanation for the results obtained may be that the amines incorporated into the network acted as defects for crystallization and depressed both T_m and $\Delta H_{m,E}$ [19,24]. The higher the amount of amine, which increased with its chain length, the larger the depression of T_m and $\Delta H_{m,E}$ was. On the other hand, as the number of carbon atoms of the amine increased, the crosslinking points have become less crowded, allowing for a higher mobility of the PEG$_{600}$ chains, and thus leading to decreasing T_gs. This second supposition, however, does not provide a clear reason for the increase of the thermal stability of xerogels with the amine chain length.

Influence of amine functionality and structure
The formation of the networks occurred through the addition reaction between the epoxy groups and primary and secondary aliphatic amine groups, the functionality of

Fig. 5. DSC traces of the DEPEG$_{600}$ – polyamine xerogels. Second heating cycle

Fig. 6. TGA and DTG traces of DEPEG$_{600}$ – polyamine xerogels

the amine in this reaction being equal to its number of hydrogen atoms (H$_{amine}$). Therefore, the functionality of the amines employed to synthesize the xerogels was 4 in the case of diamines (EDA, DAB, HMDA, ODA, DAD, DADD), whereas for DETA, TETA and TREN it was 5, 6 and 6, respectively. TETA and TREN have the same functionality, but they differ as far as the type of the amine groups and the structure are concerned. Thus, TETA is a linear polyamine with 2 primary and 2 secondary amine groups, while TREN is a branched polyamine with 3 primary and one tertiary amine groups. As the H$_{amine}$/EG mole ratio was always 1/1, by increasing the functionality of the amine,

Polyamine		T_m	ΔH_m[b]	ΔH_m[b]	DC[c]	T_g	T_c[d]	ΔH_c[b]	T_{onset}	T_{max}
Name	H$_{amine}$	°C	J/g	J/g		°C	°C	J/g	°C	°C
EDA	4	12.2	37	46	0.25	-46.8	-22.2	36	359.4	389.7
DETA	5	8.7	22	1273	0.15	-44.6	-13.5	23	-	-
TETA	6	2.7	4.5	264	0.033	-45.4	-11.7	4	362.8	392.8
TREN	6	4.5	6	350	0.042	-45.3	-10.3	5.5	-	-

Table 4
INFLUENCE OF THE POLYAMINE
FUNCTIONALITY AND
STRUCTURE UPON THE
THERMAL PROPERTIES OF
DEPEG$_{600}$ XEROGELS[a]

[a] H$_{amine}$/EG = 1/1 mole ratio.

[b] ΔH_m (J/g xerogel) ; $\Delta H_{m,E}$ (J/g PEG chains) ; ΔH_c (J/g xerogel).

[c] calculated with equations (1) and (2).

[d] cold crystallization temperature, recorded during the second heating cycle.

Table 5

INFLUENCE Of H_{amine}/EG MOLE RATIO UPON THE THERMAL PROPERTIES OF DEPEG$_{600}$-EDA XEROGELS

H_{amine}/EG mole/mole	T_m °C	ΔH_m[a] J/g	$\Delta H_{m,E}$[a] J/g	DC[b]	T_g °C	T_c[c] °C	ΔH_c[a] J/g	T_{onset} °C	T_{max} °C
1.3/1	15.5	38	47.5	0.25	-45.8	-20.4	39	353.2	385.7
1/1	12.2	37	46	0.25	-46.8	-22.2	36	359.4	389.7
0.77/1	17.3	42	51	0.27	-48.8	-27.0	40	355.7	384.0

[a] ΔH_m (J/g xerogel) ; $\Delta H_{m,E}$ (J/g PEG chains) ; ΔH_c (J/g xerogel).

[b] calculated with equations (1) and (2).

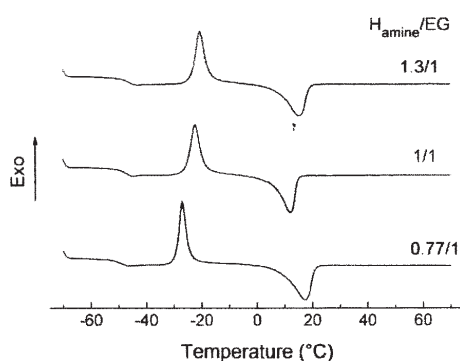[c] cold crystallization temperature, recorded during the second heating cycle.

Fig. 7. DSC traces of the DEPEG$_{600}$ – EDA xerogels synthesized at various H_{amine}/EG ratios. Second heating cycle
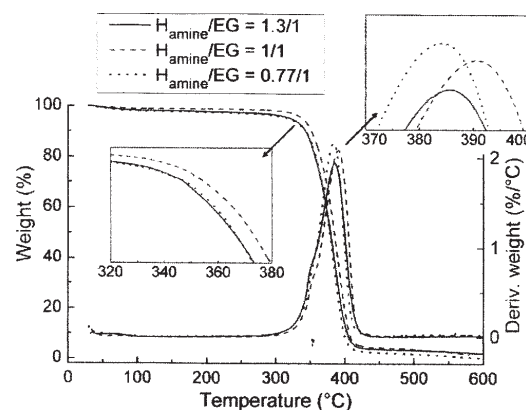

Fig. 8. TGA and DTG traces of DEPEG$_{600}$ – EDA xerogels synthesized at various H_{amine}/EG ratios

the functionality of the network junction points increased as well, and therefore, for a constant PEG chain length a network with a higher degree of crosslinking resulted.

In the case of PEG$_{600}$ networks, an increasing degree of crosslinking led, as expected, to lower melting temperatures and melting enthalpies, as well as to a small increase of the thermal stability, as shown by the variation of T_{onset} and T_{max} (table 4, figs. 5,6). The decrease of the degree of crystallinity may be ascribed to the increasing constrains imposed to the segmental motion of the PEG chains as the functionality of the junction points increased, leading to the formation of smaller and less perfect crystals.

The crystallinity of the network was affected by the structure of the crosslinking point as well. The more symmetrical TREN allowed for the formation of more flexible junction points leading to a xerogel displaying higher T_m and $\Delta H_{m,E}$ than the one crosslinked with the less symmetrical TETA, which led to more crowded and rigid crosslinking points.

All samples displayed the cold crystallization phenomenon, the difference between T_m and T_c decreasing as the amine functionality increased (fig. 5). A glass transition was also observed in the case of each sample, which increased from about -47°C for DEPEG$_{600}$-EDA xerogel to about -45°C for xerogels crosslinked with DETA, TETA and TREN (table 4), in agreement with the lower mobility of PEG$_{600}$ chains in the latter case.

As far as the thermal stability is concerned, as in the case of the amine chain length influence, it seems that the effect of the crosslinking degree modification leading to higher T_{onset} and T_{max} was greater than the effect of the decreasing degree of crystallinity, which should have

lowered T_{onset} and T_{max}. However, one should remark that the low crystallinity of all samples, in addition to the much higher T_{onset} than T_m as previously explained, may have strongly decreased the effect of crystallinity upon the thermal stability of the samples.

Influence of amine/epoxy groups mole ratio

The structure of the DEPEG$_x$-polyamine network is strongly affected by the H_{amine}/EG ratio. Both excess amine and excess epoxy groups lead to a network with a lower degree of crosslinking because of the formation of junction points with a smaller number of bridges attached. In addition, the network formed in the presence of excess epoxy groups contains PEG grafts connected to the crosslinking points [10].

The DSC investigation of the PEG$_{600}$ xerogels synthesized at various H_{amine}/EG ratios confirmed their different network structure (table 5, fig. 7). Thus, both networks synthesized under non-stoichiometric conditions, i.e. H_{amine}/EG = 1.3/1 and 0.77/1, displayed higher T_ms than the xerogel prepared at equimolar H_{amine}/EG ratio, indicative for the presence of higher mobility PEG$_{600}$ chains. For the excess amine network, the chains connected to the less substituted junction points were more mobile and could crystallize easier because of the lower chain density around these points. In the case of excess DEPEG network, the mobility of the existing PEG grafts was much higher than that of the chains immobilized at both ends, allowing for a higher degree of crystallinity than both stoichiometric and excess amine networks.

In agreement with the increased average mobility of PEG chains within the excess DEPEG network, the T_g of this xerogel was lower than that of the stoichiometric one. The same behavior would have been expected in the case of excess amine network as well, by judging after the mobility of the PEG chains, while actually the opposite was observed, i.e. T_g was higher for excess amine network than that of the stoichiometric xerogel. This may be explained through the existence of unreacted NH groups within the excess amine network because of the initial EDA excess, which are able to form additional hydrogen bonds with the PEG chains, and thus increasing T_g [24].

As expected, the thermal stability (T_{onset} and T_{max}) of the DEPEG$_{600}$-EDA xerogels was lower for those synthesized with excess of one of the reactants because of the lower crosslinking degree networks resulted (table 5, fig. 8).

Conclusions

Xerogels from diepoxy-terminated PEGs of different molecular weights and various aliphatic di- and polyamines were prepared through end-linking reactions and their thermal properties were studied in order to determine the influence of several structural parameters that may affect the physical state (rubbery, glassy or semicrystalline) of the network-forming polymer at a certain temperature. The factors investigated were the molecular weight of the PEG precursors, the number of carbon atoms within the diamine chain, the amine functionality and structure and the amine/epoxy groups mole ratio, and their influence upon the thermal transitions and thermal stability of the xerogels synthesized was determined by DSC and TGA measurements.

The DSC analyses showed that all PEG-based xerogels investigated displayed crystallization, but their degree of crystallinity, as well as the melting temperature of the crystalline phase, were lower than for the corresponding free DHPEG$_x$ oligomers because of the reduced mobility of the PEG chains immobilized at both chain ends within the network, leading to the formation of smaller and less perfect crystals. Immobilization within the network affected more the mobility of the shorter chains than that of the longer ones, leading to lower rates of crystallization on cooling, especially in the case of DEPEG$_{600}$ xerogels.

Amongst the factors investigated, the length of the PEG chains had the strongest influence upon the melting temperature and the degree of crystallinity of the networks synthesized under similar conditions. The shorter the PEG chains, the lower both T_m and DC were. The melting temperature and the degree of crystallinity displayed also smaller values for the networks with a higher degree of crosslinking. This was obtained in the case of either xerogels crosslinked with higher functionality polyamines or networks synthesized under stoichiometric conditions, i.e. a H_{amine}/EG mole ratio equal to unity. The length of the hydrocarbon chain of the diamine employed as the crosslinking agent also affected the crystallinity of the xerogels. Longer chain amines depressed both T_m and DC of the network. The reason of this behavior is not clear yet.

Glass transition events were observed only for DEPEG$_{600}$ networks, as they are amorphous at reduced temperatures under the conditions of the DSC experiments, due to the low rate of crystallization. T_g was higher for the networks with a higher degree of crosslinking, as expected, and also for shorter diamine chains, as a consequence of a lower mobility of the PEG chains.

The thermal stability of the xerogels, as estimated from the T_{onset} and T_{max}, displayed a relatively small dependency on the structural characteristics of the network. It increased with the PEG chain length, as a consequence of the increasing DC, and also with the degree of crosslinking of the network. Longer chain diamines, i.e. a higher hydrocarbon chains amount, led also to higher T_{onset} and T_{max} of the xerogel.

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