

# Amines used for low temperature curing of PDMS-based gel-networks impact $\gamma$ -irradiation outcome

Ivana Cetina<sup>a,\*</sup>, Irina Pucić<sup>b,\*\*</sup>, Vlasta Mohaček Grošev<sup>b</sup>, Ana Šantić<sup>b</sup>

<sup>a</sup> Croatian Defense Academy "Dr. Franjo Tuđman", Ilica 256b, 10 000, Zagreb, Croatia

<sup>b</sup> Ruder Bošković Institute, Bijenička Cesta 54, 10 000, Zagreb, Croatia

## ARTICLE INFO

### Keywords:

Polysiloxane  
Aliphatic amines  
Ionizing radiation  
DSC  
Vibrational spectroscopy  
Dielectric spectroscopy

## ABSTRACT

Four structurally different amines: 1,3-diamino-2-propanol (DAP), diethylenetriamine (DETA), tris(2-aminoethyl)amine (TAEA) and triethylenetetramine (TETA) were reacted with diglycidyl ether terminated poly(dimethylsiloxane) (PDMS-DGE) at relatively low temperature of 50 °C. Stable transparent networks with gel-like properties but without a liquid component, "gel-networks" were obtained. Raman spectra revealed presence of residual epoxy-group absorptions in cured gel-networks but secondary amine absorption intensities in FTIR spectra were used for monitoring of the curing reaction extent. To assess their radiation stability gel-networks were gamma-irradiated to absorbed dose of 50 kGy. Even though contribution of amine segments to PDMS-based gel-networks is relatively small, their structure significantly influenced the properties of studied PDMS-based gel-networks. The most important property of an amine was the ability to either form hydrogen bonds, or produce denser network like a triamine. However there were also significant differences in properties of gel-networks prepared with mutually similar diamines DETA and TETA that can be considered a dimer and a trimer of ethylenediamine. In the studied gel-networks there is a complex interaction of extent of initial curing that depended on the amine used and the resulting (dis)order that strongly influenced the outcome of irradiation. An endothermic transition presumably caused by reversible gel-network collapse was observed in DSC thermograms of all the gel-networks. Its temperature depended on the amine type and shifted to higher values on irradiation. Changes in most properties like residual gel content on extraction or DC electrical conductivity and its frequency dependence were more pronounced in gel-networks prepared with diamines DETA and TETA than in those prepared with amines capable of significant secondary valent interactions (DAP and TAEA). Radiation curing and/or crosslinking seem to have occurred only in TETA-cured gel-network and it was mostly due to lower extent of initial reaction. Since swelling is a measure of gel quality and it was higher in irradiated gel-networks it may be concluded that irradiation to D = 50 kGy improved their properties.

## 1. Introduction

Polymer gels are generally defined as polymer-solvent system in which macromolecular three-dimensional network retains the solvent that is not chemically bound to the polymer (Rogovina et al., 2008; Yamauchi, 2001). However the term "gel" also describes other soft materials that keep their shape under the action of their own weight. Properties of the polymer gel may vary greatly depending on the polymer backbone and chosen solvent that can be present in large amounts. Polymer gels can be prepared by crosslinking monomers or oligomers with reactive terminal groups in a solvent or by swelling of a gel-network, a previously crosslinked polymer. Although gel-networks do not contain a liquid component they exhibit most of gel properties

(Jones et al., 2009).

Poly(dimethylsiloxane), PDMS is often used as a polymeric backbone for various gels. It is the most common semi-inorganic polysiloxane polymer (Mark, 2004). It is a versatile, non-toxic, environmentally friendly polymer with many excellent chemical, physical, and electrical properties so it is widely used for commercial, industrial and military purposes. PDMS is highly tissue equivalent, thus 3D polymer gel dosimeter phantom for dose verification have been prepared for medical purposes (De Deene et al., 2015). Gels are easily obtained by curing of PDMS oligomers terminated with reactive groups with appropriate reactants (Petrie, 2006). The rate of curing process can be controlled by temperature and/or by use of additional accelerating agents (e.g. alcohols). In general curing can be divided into

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [ivanacetina@gmail.com](mailto:ivanacetina@gmail.com) (I. Cetina), [pucic@irb.hr](mailto:pucic@irb.hr) (I. Pucić), [mohacek@irb.hr](mailto:mohacek@irb.hr) (V.M. Grošev), [Ana.Santic@irb.hr](mailto:Ana.Santic@irb.hr) (A. Šantić).



room temperature and elevated-temperature curing. Room temperature curing often requires very reactive curing agents like aliphatic amines. Less shrinkage and internal stress resulting from thermal expansion differences, moderate strength, better heat and chemical resistance and good toughness are advantages of room temperature curing. The downside is potentially lower crosslink density (Petrie, 2006).

The aim of this research was to prepare low-temperature cured PDMS gel-networks with selected aliphatic amine curing agents and to determine if and how the amine type affects some of the properties of obtained gel-networks. Because polysiloxanes are transparent and have excellent properties they have a number of military applications like top-side coatings of metal surfaces on military airplanes and ships, especially the ones exposed to salt water corrosion. One of the important aspects that has to be assessed for the military used materials is their response to ionizing radiation produced after bursts of nuclear weapons and radiological dispersal devices (RDD) or after longtime exposure to certain radioactive sources. Wide range of radiation induced processes occurs on exposition to ionizing radiation that can either degrade (main chain scission) or crosslink polysiloxanes. Crosslinking mainly happens as a result of radicals formed by Si-C and C-H bond scission (Hill et al., 2001). Both processes occur simultaneously and their outcome depends on the side groups on polysiloxane chain and the irradiation conditions (Palsule et al., 2008). In case of PDMS-DGE the irradiation will not only affect -Si-C- bonds but also the isopropanol segment formed on opening of the epoxy ring during curing process (Djouani et al., 2014). These reactions can then influence various characteristics of an irradiated gel or gel-network such as mechanical and thermophysical properties what is particularly important since PDMS is an elastomer. Thus we irradiated the PDMS-based gel-networks that were cured at low temperature and compared their properties to those of non-irradiated ones.

## 2. Materials and methods

### 2.1. Preparation and irradiation of PDMS-based gel-networks

Gel-networks were prepared by reaction of PDMS-DGE with selected aliphatic amines as curing reagents: diamines 1,3-diamino-2-propanol (DAP), diethylenetriamine (DETA), triethylenetetramine (TETA) and a triamine tris(2-aminoethyl)amine (TAEA). Their structural formulas are shown in Fig. 1. PDMS-DGE with molecular weight of about 800 was purchased from Sigma Aldrich, amines DAP and DETA from Alfa Aesar and TAEA and TETA from Acros Organics. All reagents were used as received. Each particular amine and PDMS-DGE were mixed in 1:1

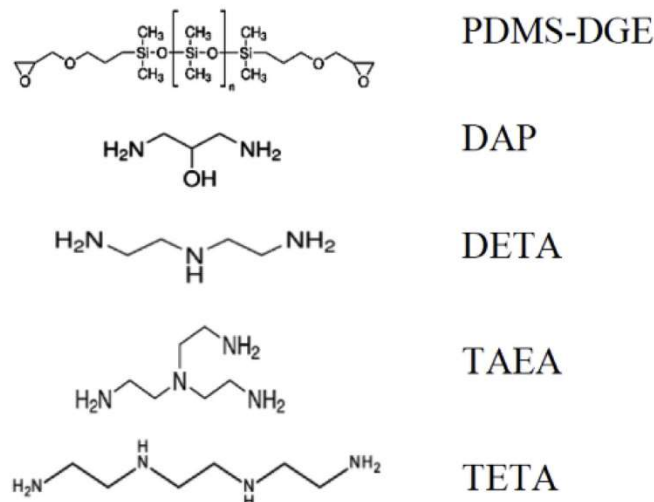


Fig. 1. Chemical structure of PDMS-DGE and selected aliphatic amine curing agents.

Table 1

List of abbreviations used for reactants and samples.

Abbreviation	Sample
PDMS-DGE	poly(dimethylsiloxane), diglycidyl ether terminated
DAP	1,3-diamino-2-propanol
DETA	diethylenetriamine
TAEA	tris(2-aminoethyl)amine
TETA	triethylenetetramine
DAP-GN non-irradiated	PDMS-DGE gel-network cured with DETA amine
DAP-GN 50 kGy	
DETA-GN non-irradiated	DAP amine
DETA-GN 50 kGy	
TAEA-GN non-irradiated	TAEA amine
TAEA-GN 50 kGy	
TETA-GN non-irradiated	TETA amine
TETA-GN 50 kGy	

stoichiometric ratio and the reaction was carried out for 144 h at 50 °C. All the abbreviations for reactants and samples are listed in Table 1.

A part of each obtained gel-network (size about 1 cm × 1 cm × 1 cm) was irradiated in the panoramic <sup>60</sup>Co γ-irradiator at a Laboratory for Radiation Chemistry and Dosimetry irradiation facility of Ruder Bošković Institute (RBI) in Zagreb, Croatia. The samples were exposed to dose of 50 kGy at a dose rate of 7.8 Gy/s, in ambient conditions. The dose rate was established by dose mapping of the γ-source using dosimetric system based on 10% chlorobenzene/ethanol (ISO/ASTM 51538:2017 Practice for use of the ethanol-chlorobenzene dosimetry system). Prior to any characterization, irradiated samples were kept in ambient conditions for at least five days to ensure that any immediate post-irradiation processes have terminated.

### 2.2. Characterization of non-irradiated and irradiated PDMS-based gel-networks

The ATR-FTIR spectra of amines, PDMS-DGE and prepared gel-networks were recorded using Bruker TENSOR II FTIR spectrophotometer equipped with A225/Q Platinum diamond ATR unit. Spectral range was 400–4000 cm<sup>-1</sup> and 16 scans were recorded with resolution of 4 cm<sup>-1</sup>. For each gel-network sample spectra were taken on at least four locations. OPUS software was used for spectra collection and SpectraGryph v1.2.12 software for further processing (Menges, 2019). All gel-networks spectra were normalized to 2960 cm<sup>-1</sup> PDMS-DGE absorption.

For acquisition of Raman spectra a T64000 HORIBA JobinYvon Raman spectrometer operating in triple subtractive mode using a 90° macro chamber and equipped with a liquid nitrogen cooled CCD detector with 256 × 1024 pixels array was used. Liquid samples were injected in glass capillaries, while solid ones were positioned on a holder in front of the focusing lens. The entrance slit was 300 μm. Diode laser of the DPSS type with 532 nm wavelength produced by Changchun New industries Optoelectronics Tech. served as an excitation source. The power at the sample was 4 mW. Time accumulation of spectra varied from 20 s to 30 s, with four repetitions to increase the signal to noise ratio. Spectral resolution was 0.6 cm<sup>-1</sup> per pixel. All spectra were obtained within spectral interval from 50 to 3800 cm<sup>-1</sup>. LabSpec NGS software was used for spectra collection and SpectraGryph v1.2.12 software for further analysis (Menges, 2019).

For Soxhlet extraction *n*-hexane was chosen as the most suitable solvent for PDMS according to Brockmeyer et al. (2015). ACS reagent grade *n*-hexane was purchased from Honeywell and was used without any further purification. The non-irradiated and irradiated samples were extracted in Soxhlet apparatus for total of 48 h. The temperature of the condensed *n*-hexane flushing the sample was measured using infrared thermometer (TFA 31.1134.06) and it was around 50 °C. After extraction, samples were dried in vacuum dryer for 24 h at 50 °C. Percentage of remaining mass was calculated using equation:



$$\% \text{ remaining mass} = \left(1 - \frac{m_0 - m_t}{m_0}\right) \cdot 100 \quad (1)$$

where  $m_0$  presents sample mass before extraction and  $m_t$  sample mass after extraction and drying.

Swelling was conducted in *n*-hexane (the same as was used for the Soxhlet extraction) at 23 °C using continuous method described by Liu et al. (2013). Samples were submerged in *n*-hexane and their mass was measured at selected intervals for at least 24 h. Before each weighing the samples were wiped with paper tissue to remove external *n*-hexane on sample surface. The degree of swelling was calculated using equation:

$$\% \text{ swelling} = \frac{m_t - m_0}{m_0} \cdot 100 \quad (2)$$

where  $m_0$  presents sample mass before swelling and  $m_t$  sample mass after swelling time  $t$ .

Dielectric spectra (DS) were recorded at room temperature (23 °C) on Novocontrol Technologies instrument with Alpha-AN High Performance Frequency Analyzer, standard BDS1200 cell and brass electrodes. Samples were placed in 3 mm high cylindrical Teflon holder with diameter of 5 mm and measured under AC voltage of 0.1 V, in frequency range from  $1 \cdot 10^6$  to  $5 \cdot 10^{-2}$  Hz. The data were collected using Novocontrol system analysis software WinDETA v5.65. DC conductivity was calculated as the average of conductivity value of low-frequency plateau.

DSC measurements were performed on PerkinElmer Pyris Diamond DSC in nitrogen atmosphere. The gel-network samples were cut to weight of about 5 mg, put in 50  $\mu$ l aluminum sample pan and crimped. For each sample two heating and cooling thermograms were recorded in the temperature range between -50 °C and 250 °C, at a rate of 20 °C/min. The data were collected and analyzed using Pyris software provided by PerkinElmer.

### 3. Results and discussion

All the selected amines reacted with PDMS-DGE at 50 °C and produced transparent and firm gel-networks. Fig. 2 shows two step addition reaction of primary amine with DGE (epoxy) group. At low temperature curing is slower so heat distribution is even and resulting gel-networks are more uniform.

Apparent firmness of gel-networks noticeably differed depending on the amine used for curing. The firmest was the one prepared using DAP, amine with the shortest chain of selected aliphatic amines. The contribution of amine residues to length of polymer chains that constitute studied gel-networks is similar and relatively insignificant. However, DAP amine can form hydrogen bonds to secondary amine groups and/or to -OH groups of another DAP residue. Such inter- and intramolecular hydrogen bonds may contribute to firmness of the

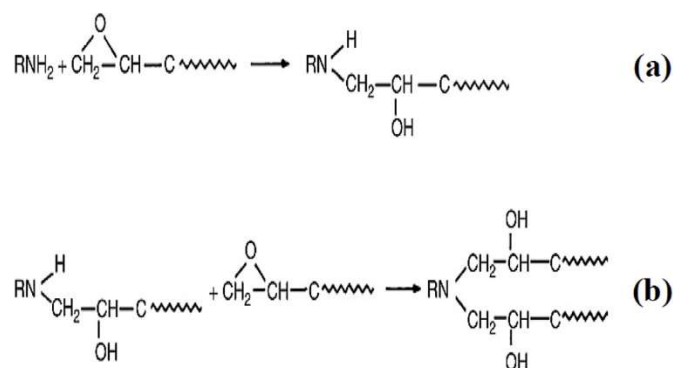


Fig. 2. Scheme of the reaction of the epoxy group with primary amine (Petrie, 2006).

obtained gel-network. A triamine, TAEA that has six amine hydrogens available to reaction with DGE groups produced similarly firm gel-network. The ones obtained by reaction with diamines DETA and TETA that can be considered a dimer and a trimer of ethylenediamine were somewhat less firm.

Because the low reaction temperature and the fact that PDMS molecules tend to coil, some of the end epoxy (DGE) groups must have remained inaccessible to reaction. To detect unreacted end epoxy groups and to compare reaction extents spectroscopic analysis was performed. Characteristic vibrational frequencies observed in ATR-FTIR and Raman spectra of studied gel-networks and the reactants used to prepare them are listed in Table 2. The most prominent infrared absorption of epoxy group (-C-O- stretching) at  $1250 \text{ cm}^{-1}$  in spectra of pure PDMS-DGE overlapped with much stronger methyl group absorption at  $1258 \text{ cm}^{-1}$  while  $370 \text{ cm}^{-1}$  (ring deformation) absorption was outside measurement range of the FTIR instrument. The only epoxy ring absorption visible in ATR-FTIR spectra of pure PDMS-DGE was a low intensity peak at  $910 \text{ cm}^{-1}$ . That peak was absent in all of the spectra of the gel-networks whether non-irradiated or irradiated. Still, due to the weakness of initial absorption that is no proof that all the DGE groups have reacted. In Raman spectra of PDMS-DGE (Fig. 3, middle) epoxy absorption was observed at  $1260 \text{ cm}^{-1}$ . It was also present in Raman spectra of all the studied gel-networks but its intensity was much lower. That confirms the presumption that some DGE groups remained unreacted.

Since infrared epoxy absorptions were weak and not appropriate for assessment of the radiation effects in irradiated gel-networks amine absorptions were used. In a first step of two-step preparation reaction (Fig. 2) primary amine reacts with an epoxy group and is converted into secondary amine. In the second step it may react with another epoxy group to be converted into tertiary amine. Although those absorptions between  $1600 \text{ cm}^{-1}$  and  $1550 \text{ cm}^{-1}$  are weak they provided useful information on reaction outcomes. N-H bending absorption of primary amine at  $1596 \text{ cm}^{-1}$  is seen only in FTIR spectra of pure amines (Fig. 4, inserts). No primary amine absorptions were seen in any of gel-network spectra apparently indicating that first reaction step of curing was completed. Secondary amine absorptions appeared at about  $1570 \text{ cm}^{-1}$ . Since no N-H bond exists in tertiary amine and C-N absorptions overlap with those of PDMS the changes related to second step of curing reaction could not be monitored. The amines used for curing contain different number of secondary amine groups (0 in DAP and TAEA, 1 in DETA, 2 in TETA) so their relative contribution to  $1570 \text{ cm}^{-1}$  absorption intensity had to be taken into account. Overall it can be concluded that the extent of curing in non-irradiated gel-networks increased in order DETA < TETA < DAP < TAEA.

On irradiation to  $D = 50 \text{ kGy}$  no new absorptions that would indicate chemical changes in the gel-network were detected neither in ATR-FTIR spectra nor in Raman spectra. On the other hand, the changes in secondary amine group absorptions intensities were observed in all spectra of irradiated gel-network samples. A relative increase of  $1570 \text{ cm}^{-1}$  FTIR absorption intensity in irradiated DETA-cured gel-network indicated that further reaction between residual primary amines and DGE took place. Since TETA amine itself contains two secondary amine groups changes due to radiation induced reaction can produce only minor effect on  $1570 \text{ cm}^{-1}$  absorption intensity so it is no surprise that none were observed. Still there is a relative intensity increase of  $1410 \text{ cm}^{-1}$  absorption intensity that can be attributed to radiation induced curing (Huszank, 2014). A decrease in secondary amine group intensity was observed only in the spectra of irradiated DAP-cured gel-network indicating further conversion to tertiary amine. In the spectra of irradiated TAEA-cured gel-network there was no clear trend probably because the chance of reaction of DGE and amine group in relatively dense network formed by initial curing is low.

In all irradiated gel-networks siloxane absorptions at  $864 \text{ cm}^{-1}$  and  $1015 \text{ cm}^{-1}$  became relatively weaker relative to the corresponding methylene absorption. Since the intensities in ATR-FTIR, among else,

**Table 2**

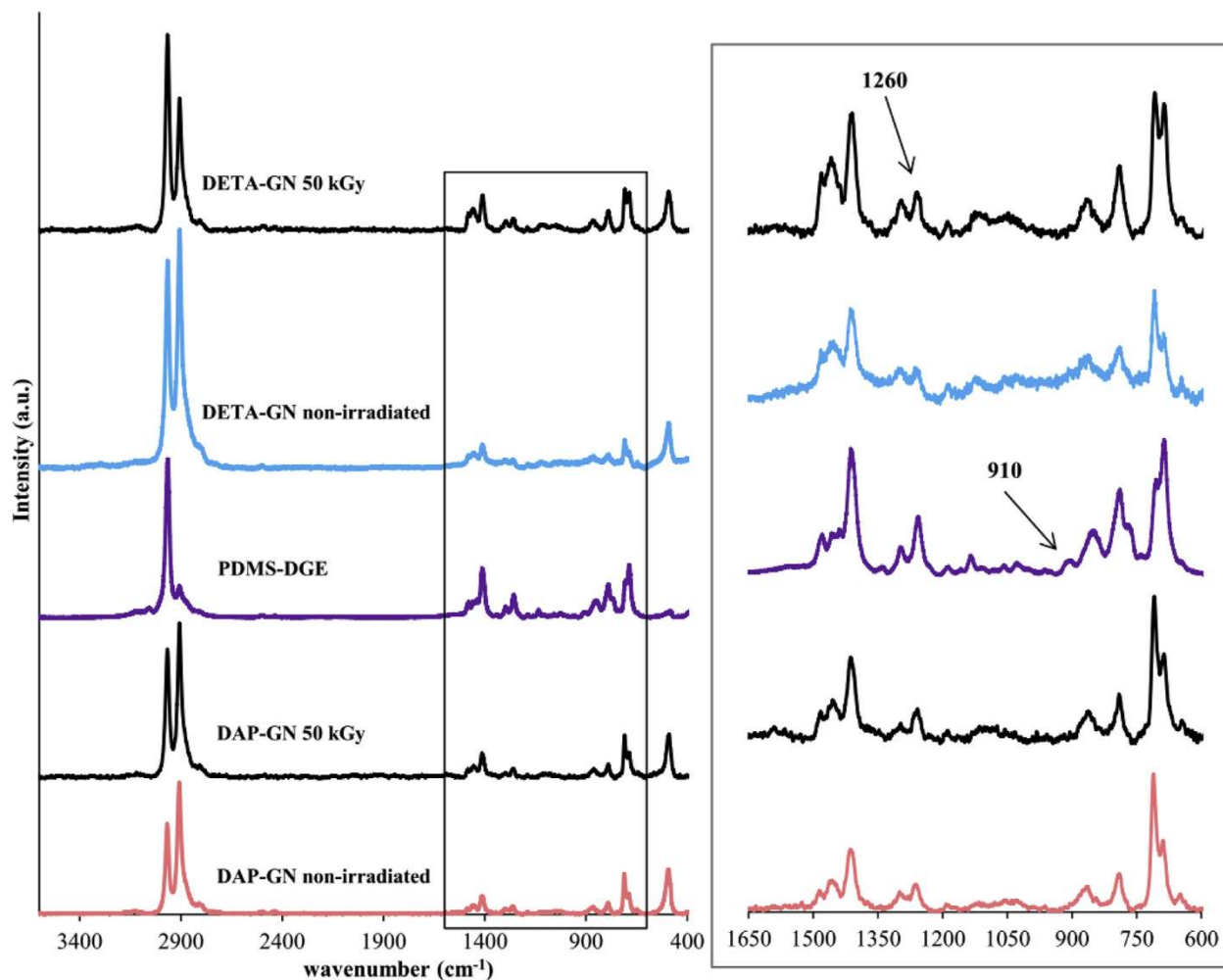
Infrared and Raman absorptions observed in spectra of PDMS-based gel-networks and their assignments (Cai et al., 2010; Socrates, 2001).

ATR-FTIR		Raman		Vibrational mode	
Wavenumber (cm <sup>-1</sup> )	Relative band strength	Wavenumber (cm <sup>-1</sup> )	Relative band strength	PDMS-DGE	amine
505	w	495	m	$\pi(\text{CH}_2)$ in glycidoxy, $\tau(\text{CH}_2)$ in propyl chain, $\delta(\text{C-H})$ in glycidoxy	$\delta(\text{CH}_2\text{-NH-CH}_2)$
687	m	686, sh	w	$\pi(\text{CH}_3)$	-
696	m	709	m		
791	vs	793	vw	$\rho(\text{CH}_3)$	$\rho(\text{CH}_2)$ , $\pi(\text{NH}_2)$
868	m	864	m	$\nu(\text{Si-(CH}_3)_2)$	-
-	-	910	vw	$\nu(\text{C-O-C})$ in epoxy	-
1015	s	1017	vw	$\nu(\text{O-Si-O})$	-
1075, sh	-	1053	-		
-	-	1125	w	$\pi(\text{CH}_2)$ in epoxy, $\delta(\text{C-H})$	-
1250	s	1260	vw	$\nu(\text{Si-CH}_3)$ , $\nu(\text{-C-O-})$ in epoxy	-
1306	w	1300	vw	$\delta(\text{CH}_3)$	$\tau(\text{NH}_2)$
1410	w	1411	w	$\delta(\text{CH}_3)$ , $\delta(\text{CH}_2)$ in epoxy, $\delta(\text{C-H})$ in epoxy, $\pi(\text{CH}_2)$ in glycidoxy	-
1570	w	-	-	-	$\delta(\text{NH})$
1596	w	-	-	-	$\delta(\text{NH}_2)$
3437	w	-	-	-	$\nu(\text{N-H})$
3200-3600	w	3200-3600	vw	$\nu(\text{O-H})$	-

Note: sh-shoulder, vw-very weak, w-weak, m-medium, s-strong, vs-very strong.

 $\nu$  – stretching,  $\delta$  – bending,  $\rho$  – rocking,  $\pi$  – wagging,  $\tau$  – twisting.

In case of multiple possible vibrational modes, the main is written first.

**Fig. 3.** Partial Raman spectra of non-irradiated DAP- and DETA-cured PDMS-DGE gel-networks and those irradiated to D = 50 kGy.



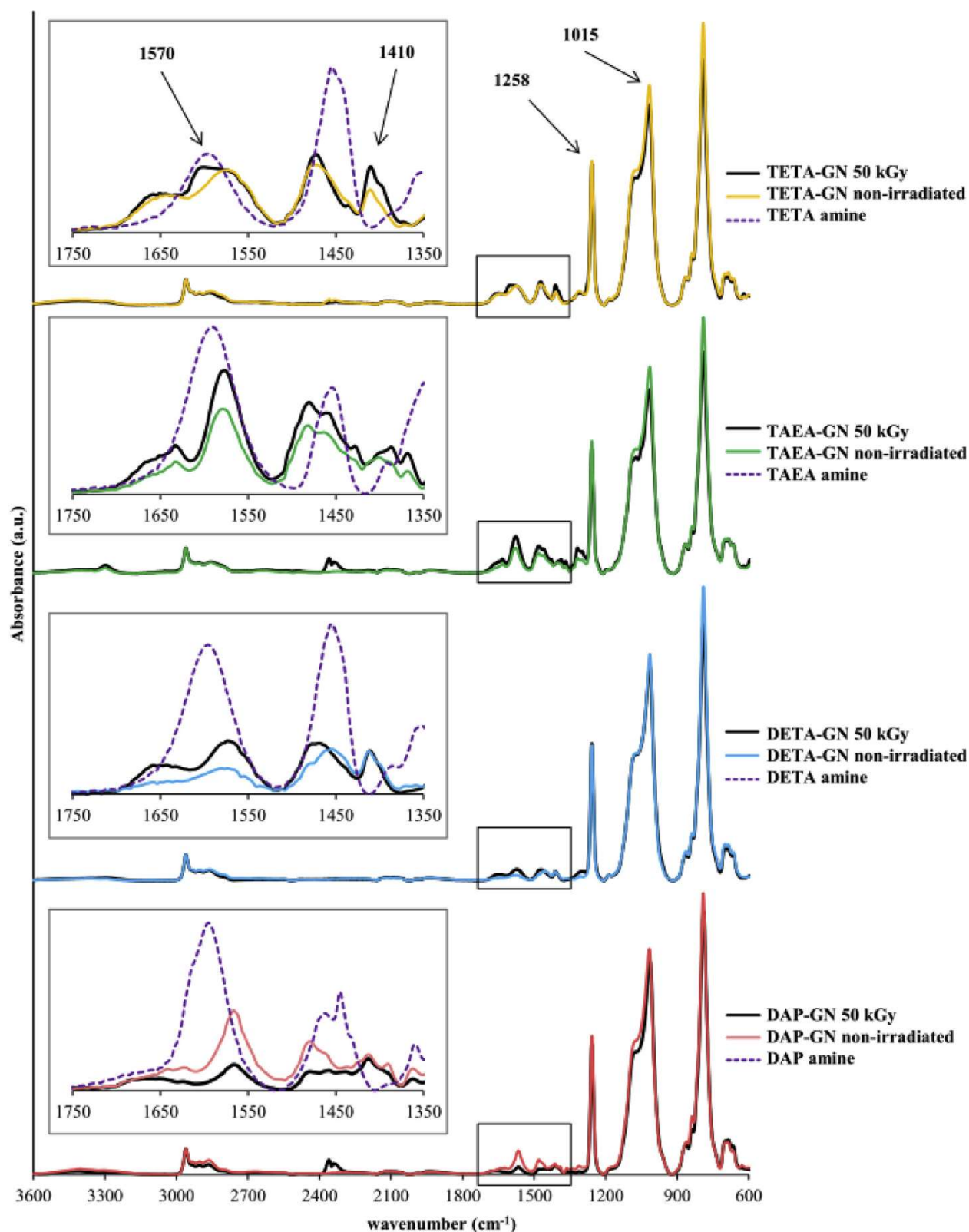


Fig. 4. ATR-FTIR spectra of non-irradiated and irradiated DAP-, DETA-, TAEA- and TETA-cured gel-networks. The spectra of corresponding pure amines are added to inserts (dashed line) for clarity.

depend on the contact between ATR crystal and the sample, that decrease may indicate that the gel-network became somewhat firmer on irradiation (Buffeteau et al., 1996). The change of polysiloxane absorption intensity was the least in DAP-cured gel-network because it was firm even before irradiation.

Non-irradiated gel-networks were relatively stable and their residual masses after Soxhlet extraction were above 66% (Fig. 5, Table 3). The effect of the amine type used was again observed. The residual mass increased in order TETA- DETA < DAP < TAEA. The order is similar to that of the secondary amine FTIR absorption intensity

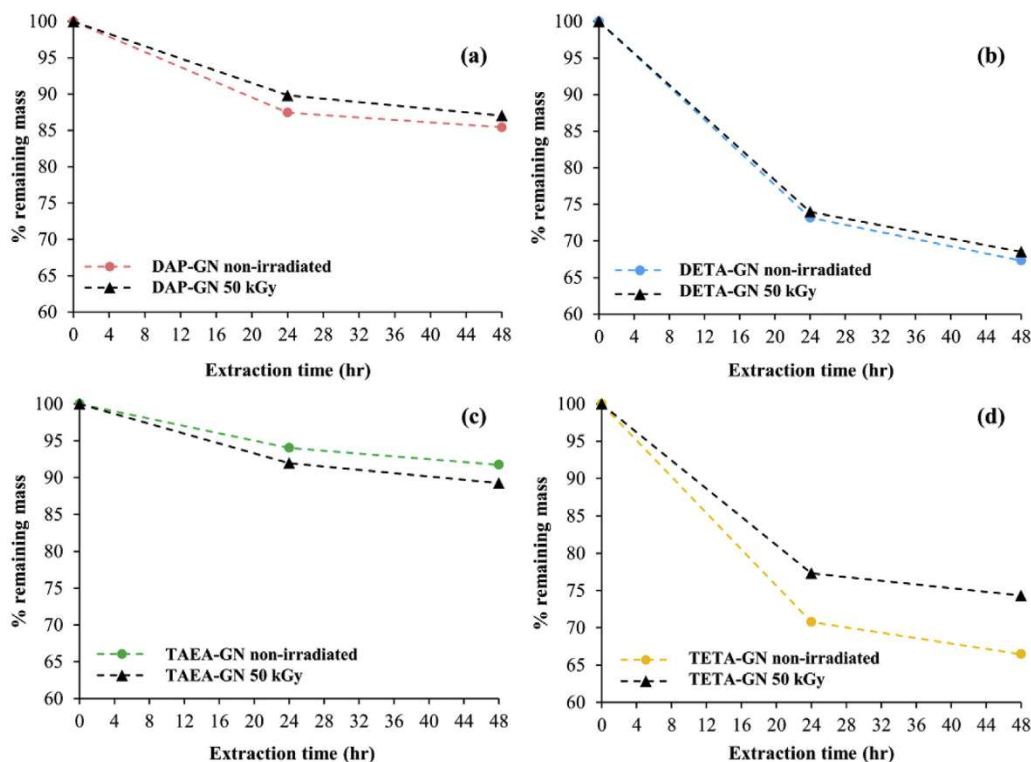


Fig. 5. Residual mass after 24 and 48 h of Soxhlet extraction in *n*-hexane for non-irradiated and irradiated gel-networks: (a) DAP-cured, (b) DETA-cured, (c) TAEA-cured, (d) TETA-cured.

Table 3

Residual mass on Soxhlet extraction, results of swelling in *n*-hexane, DC electrical conductivity, peak temperature and enthalpy of endothermic transformation (DSC) of non-irradiated PDMS-DGE gel-networks and those irradiated to  $D = 50$  kGy (average values of two measurements).

Sample		% remaining mass after 48 h of Soxhlet extraction	Equilibrium swelling (%)	$\sigma_{DC}$ (Scm <sup>-1</sup> )	$T_i$ (°C)	$\Delta H$ (Jg <sup>-1</sup> )
DAP	non-irradiated	85.4	55.8	$8.3 \cdot 10^{-11}$	110.0	9.6
	D = 50 kGy	87.0	59.4	$4.1 \cdot 10^{-10}$	108.0	35.5
DETA	non-irradiated	67.3	87.9	$2.7 \cdot 10^{-10}$	98.2	7.9
	D = 50 kGy	68.5	94.5	$2.1 \cdot 10^{-8}$	124.0	38.6
TAEA	non-irradiated	91.7	65.5	$1.1 \cdot 10^{-10}$	112.7	28.6
	D = 50 kGy	89.2	69.4	$3.2 \cdot 10^{-9}$	129.5	31.1
TETA	non-irradiated	66.5	73.9	$1.6 \cdot 10^{-8}$	91.3	8.3
	D = 50 kGy	74.3	79.8	$2.7 \cdot 10^{-8}$	116.5	62.2

Note: Irradiated DAP-cured gel-network has two peak temperatures in thermogram.

increase confirming that  $1570 \text{ cm}^{-1}$  FTIR absorption intensity is correlated to the extent of curing. It should be noted that the residual mass of TAEA- and DAP-cured gel-networks was similar and significantly higher than that of DETA- and TETA-cured ones. The change of residual mass on extraction of most of the irradiated gel-networks was so slight that it can be considered to be within the limits of the experimental error. That is consistent with results of Rogero et al. (2005) obtained on irradiation of PDMS to doses above 25 kGy. They proposed that the rigidity of previously formed network impedes the further reaction. A significant residual mass increase occurred only on extraction of irradiated TETA-cured gel-network most likely because of low extent of initial curing.

Considering the amine used for curing, gel-network swelling was the lowest for DAP-cured one and increased in order  $\text{DAP} < \text{TAEA} < \text{DETA} < \text{TETA}$  and the order was unaffected by irradiation to  $D = 50$  kGy. All samples reached equilibrium swelling after 12 h. In gel-networks prepared with diamines swelling increased about 10% compared to non-irradiated ones. Since the capacity of gel-networks to absorb *n*-hexane increased irradiation obviously improved their properties (Palsule et al., 2008). Irradiation effect was the least in

case of triamine (Table 3). The apparent firmness of the gel-networks is inversely correlated to the extent of swelling in *n*-hexane.

Electrical conductivity of polymers like PDMS is predominately due to charge carriers mobility so it is highly sensitive to changes in polymer microstructure. Thus dielectric spectroscopy (DS) was chosen to obtain additional insight into the effects of amines used for curing of studied PDMS-based gel-networks. In polymers the frequency dependence of real part of conductivity commonly consists of a low-frequency plateau (DC conductivity) and a characteristic slope (Jonscher, 1977; Papathanassiou et al., 2007). The low-frequency plateau results from the long-range transport of charge carriers and corresponds to DC conductivity whereas conductivity dispersion at higher frequencies is attributed to their localized short-range motions. Considering the effect of an amine, the DC conductivity of non-irradiated gel-networks increased in order  $\text{DAP} \sim \text{TAEA} < \text{DETA} < \text{TETA}$  (Fig. 6, left and Table 3), almost inversely as did the remaining mass on Soxhlet extraction. The DC conductivity of TETA-cured gel-network was the highest and the frequency range of its conductivity plateau was the widest. That is consistent with lower extent of initial curing and in accordance with extraction results. The conductivity of other non-

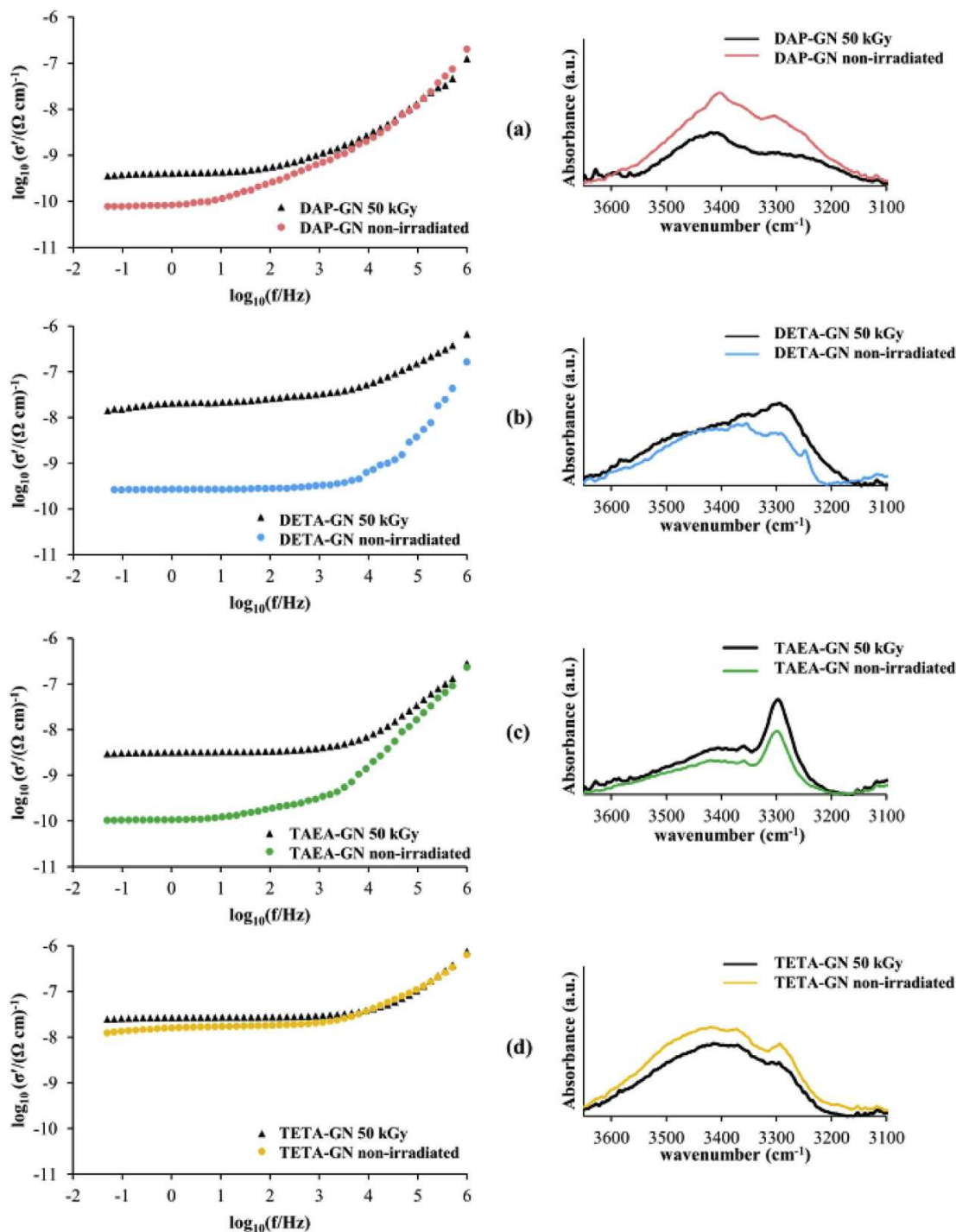


Fig. 6. Conductivity-frequency relationship (left) and partial ATR-FTIR spectra (right) of non-irradiated and irradiated gel-networks: (a) DAP-cured, (b) DETA-cured, (c) TAEA-cured, (d) TETA-cured.

irradiated gel networks were about two orders of magnitude lower and their dispersion more pronounced, particularly that of DAP- and TAEA-cured ones. In addition, non-irradiated TAEA-cured gel-network displays a slight step in frequency dependence of conductivity at intermediate frequencies that might be related to relaxation at the interfaces between regions of different conductivity. Such regions might arise due to a formation of more intertwined network when a triamine is used as a curing agent.

It is known that ionizing radiation induces charge carriers causing at least temporarily increase in conductivity. If crosslinking occurred a decrease in conductivity is expected because increased network density

reduces charge transport (Roggero et al., 2016). On the other hand, degradation should ease charge transport thus increasing the conductivity. At a particular temperature the resulting conductivity reflects the extent of each of those processes, as well as the properties of particular polymer. Since the DS measurements were performed at least 5 day after irradiation the contribution of radiation induced charge carriers should be negligible. However, the presence of some long-lived radiation-induced species cannot be excluded. Still the DS response of the irradiated gel-networks depended predominately on the amine used for curing. The conductivity of all gel-networks increased except that of TETA-cured one. Since the conductivity of non-irradiated TETA-cured



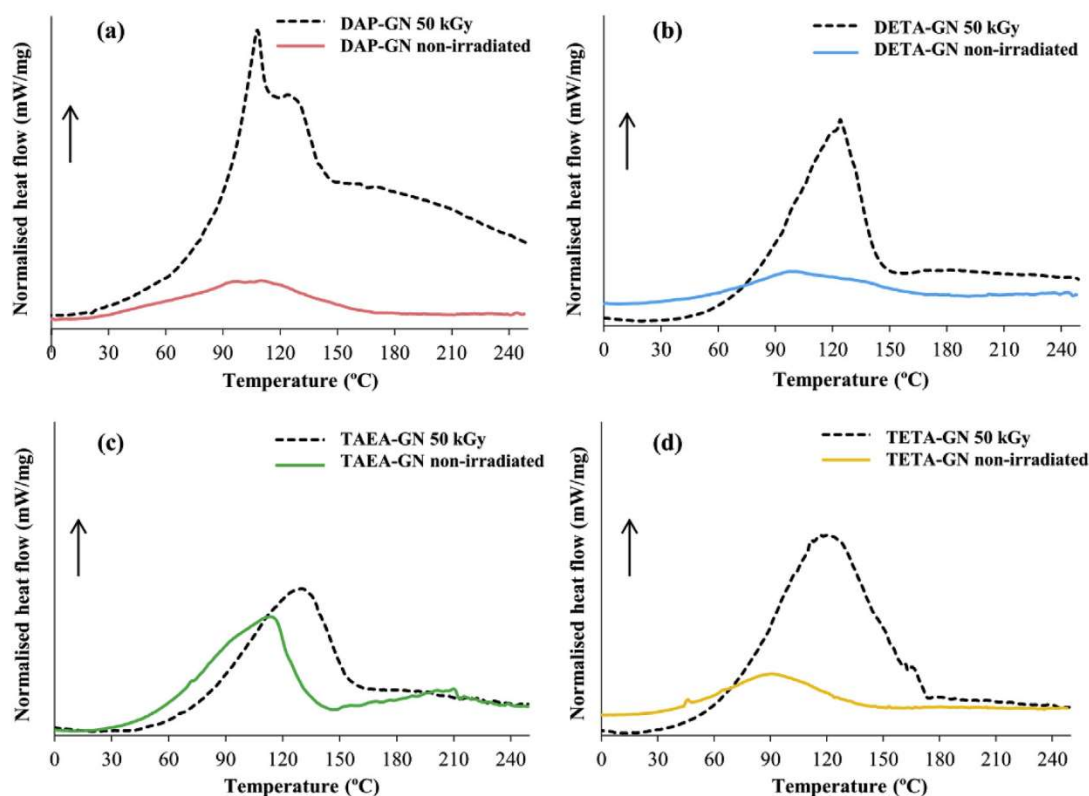


Fig. 7. DSC thermograms of non-irradiated and irradiated gel-networks: (a) DAP-cured, (b) DETA-cured, (c) TAEA-cured, (c) TETA-cured. Thermograms are normalized to sample mass.

gel-network was almost as high as that of irradiated one and extraction showed increase in residual mass it is obvious that reaction annulled radiation induced conductivity increase. While the conductivity of irradiated DETA- and TAEA-cured gel-networks increased significantly, that of DAP-cured increased only slightly. Since in DAP-cured gel-networks FTIR spectra revealed somewhat reduced free  $-OH$  intensities (Fig. 6, right), changes in hydrogen bonding and/or further curing are likely cause of observed differences. On the other hand, significant conductivity increase of DETA- and TAEA-cured networks is in accordance with increased intensity of  $-OH$  band observed in their FTIR spectra. Anyhow, on irradiation, the effect of the amine used for gel-network curing remained the same as for non-irradiated networks with the DC conductivity increasing in the direction: DAP < TAEA < DETA < TETA.

DSC thermograms of all gel-network samples (Fig. 7) revealed an endothermic transformation resembling a melting peak. It is not true melting because there is no corresponding exothermic transformation on cooling and it does not appear on immediate reheating. However, it reappears if the same experiment is repeated on the same sample after several days so it is not caused by residual reaction either. Since no water molecules are produced by an amine-DGE reaction and PDMS itself is not very hygroscopic, particularly if kept in closed vials, water evaporation can also be excluded as a cause for the observed transformation. Thus it presumably arises of a gel collapse process or volume phase transition (Shibayama and Tanaka, 1993). The highest gel collapse temperature is that of the TAEA-cured gel-network that is the firmest one. Among gel-networks prepared with diamines the highest collapse temperature is of the one prepared with DAP. Gel collapse temperatures decrease in the same order as the length of reactive diamine (DAP > DETA > TETA). This confirms that shorter chain diamines and branched triamine form denser network. On irradiation all peak temperatures shifted to higher values. In thermogram of irradiated DAP-cured gel-network an additional sharp peak appeared at somewhat

lower temperature probably due to increased hydrogen bonding. Enthalpies of endothermic transformations of all non-irradiated gel-networks prepared with diamines (DAP, DETA, TETA) were similar and about an order of magnitude lower than that of gel-network prepared with a triamine (TAEA). On irradiation enthalpies of gel-networks prepared with diamines significantly increased while in TAEA cured gel-network the increase was only slight.

#### 4. Conclusions

Low temperature curing of PDMS-DGE with selected amines produced stable transparent gel-networks. In spite of some overlapping with PDMS, strong absorption intensities in Raman spectra revealed presence of residual epoxy-group. However, the best way to gain insight into the curing reaction extent was to monitor secondary amine absorption intensities in FTIR spectra. Such approach is common in determination of epoxy resin curing extent but to our knowledge this is the first time it is used for following PDMS-DGE curing. Even though contribution of amine segments to PDMS-based gel-networks is relatively small their structure significantly influenced the properties of studied PDMS-based gel-networks.

The most important property of an amine that impacted gel-networks properties was the ability to form hydrogen bonds, in case of DAP, or produce denser network like TAEA, a triamine. However, there were also significant differences in properties of gel-networks prepared with mutually similar diamines DETA and TETA that can be considered a dimer and a trimer of ethylenediamine.

In the studied gel-networks there is a complex interaction of extent of initial curing that depended on the amine used and the resulting (dis) order that strongly influenced the outcome of irradiation to  $D = 50$  kGy. The temperature of an endothermic transition, presumably caused by reversible gel-network collapse, that was observed in DSC thermograms of all gel-networks depended on the amine type and



shifted to higher values on irradiation. Changes in most properties like residual gel content on extraction or electrical conductivity and its frequency dependence were more pronounced in gel-networks prepared with diamines DETA and TETA than in those prepared with amines capable of significant secondary valent interactions (DAP and TAEA). Radiation curing and/or crosslinking seem to have occurred only in TETA-cured gel-network and it was mostly due to lower extent of initial reaction. Since swelling is a measure of gel quality and it was higher in irradiated gel-networks it may be concluded that irradiation to  $D = 50$  kGy improved their properties.

#### CRedit authorship contribution statement

**Ivana Cetina:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Visualization, Project administration. **Irina Pucić:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision. **Vlasta Mohaček Grošev:** Formal analysis, Investigation, Resources, Writing - review & editing, Formal analysis, Investigation, Resources, Writing - review & editing. **Ana Šantić:** Formal analysis, Investigation, Resources, Writing - review & editing, Formal analysis, Investigation, Resources, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgement

The authors are grateful to dr. Friedrich Menges for letting us use his excellent Spectragryph™ spectroscopy software for free.

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