14th Tihany Symposium on Radiation Chemistry, Siófok, Hungary, 25-30 May 2019.

γ-irradiated PDMS gel networks cured with selected amines

Ivana Cetina[1], Irina Pucić[2], Vlasta Mohaček Grošev[2], Ana Šantić[2]

[1] Croatian Defense Academy „Dr. Franjo Tuđman“, Zagreb, Croatia
[2] Ruđer Bošković Institute, Zagreb, Croatia

INTRODUCTION

Unlike gels, gel networks [1] do not contain a liquid component while having most of gel characteristics. Polysiloxanes produce stable gels with excellent properties so we chose PDMS-DGE and selected amines to prepare low-temperature cured gel networks. [2] On exposition to ionizing radiation polysiloxanes can either degrade or crosslink. [3] The aim of this work was to determine if and how the amine type affects some properties of non-irradiated gel networks and those irradiated to a relatively low dose of 50 kGy.

Table 1 Peak temperature and enthalpy of endothermic transformation (DSC), AC electrical conductivity, residual mass on Soxhlet extraction and results of swelling in hexane of non-irradiated PDMS-DGE gel networks and those irradiated to D= 50 kGy (average values of two measurements).

Sample		T_t (°C)	ΔH (Jg^{-1})	σ(real) (S/cm)	% remaining mass after 48 hours of Soxhlet extraction	Equilibrium swelling (%)	Equilibrium swelling time (hr)
DAP	non-irradiated	110.02	9.62	$2.62\cdot10^{-10}$	85.42	55.83	0.85
	50 kGy	107.96 121.80	35.46	$5.63\cdot10^{-10}$	87.03	59.38	0.65
DETA	non-irradiated	98.19	7.90	$2.83\cdot10^{-10}$	67.31	87.93	2.00
	50 kGy	123.97	38.55	$2.62\cdot10^{-8}$	68.50	94.48	1.35
TAEA	non-irradiated	112.72	28.56	$1.90\cdot10^{-10}$	91.74	65.46	1.70
	50 kGy	129.50	31.13	$3.35\cdot10^{-9}$	89.24	69.41	1.25
TETA	non-irradiated	91.33	8.25	$1.81\cdot10^{-8}$	66.45	73.90	1.70
	50 kGy	116.45	62.24	$2.77\cdot10^{-8}$	74.32	79.79	1.40

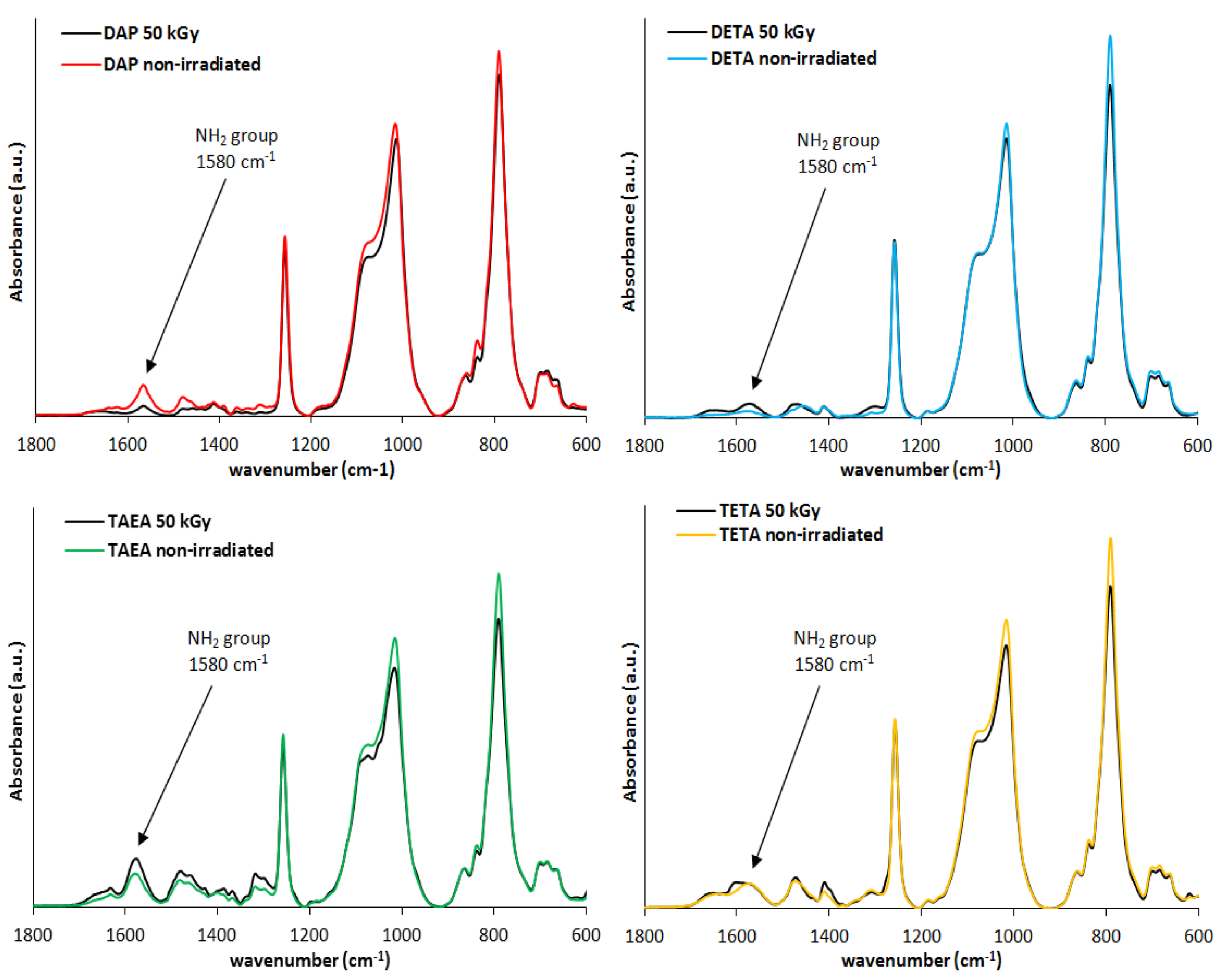


Figure 2 Partial ATR-FTIR spectra of non-irradiated PDMS-DGE gel networks prepared with selected amines and those irradiated to D= 50 kGy.

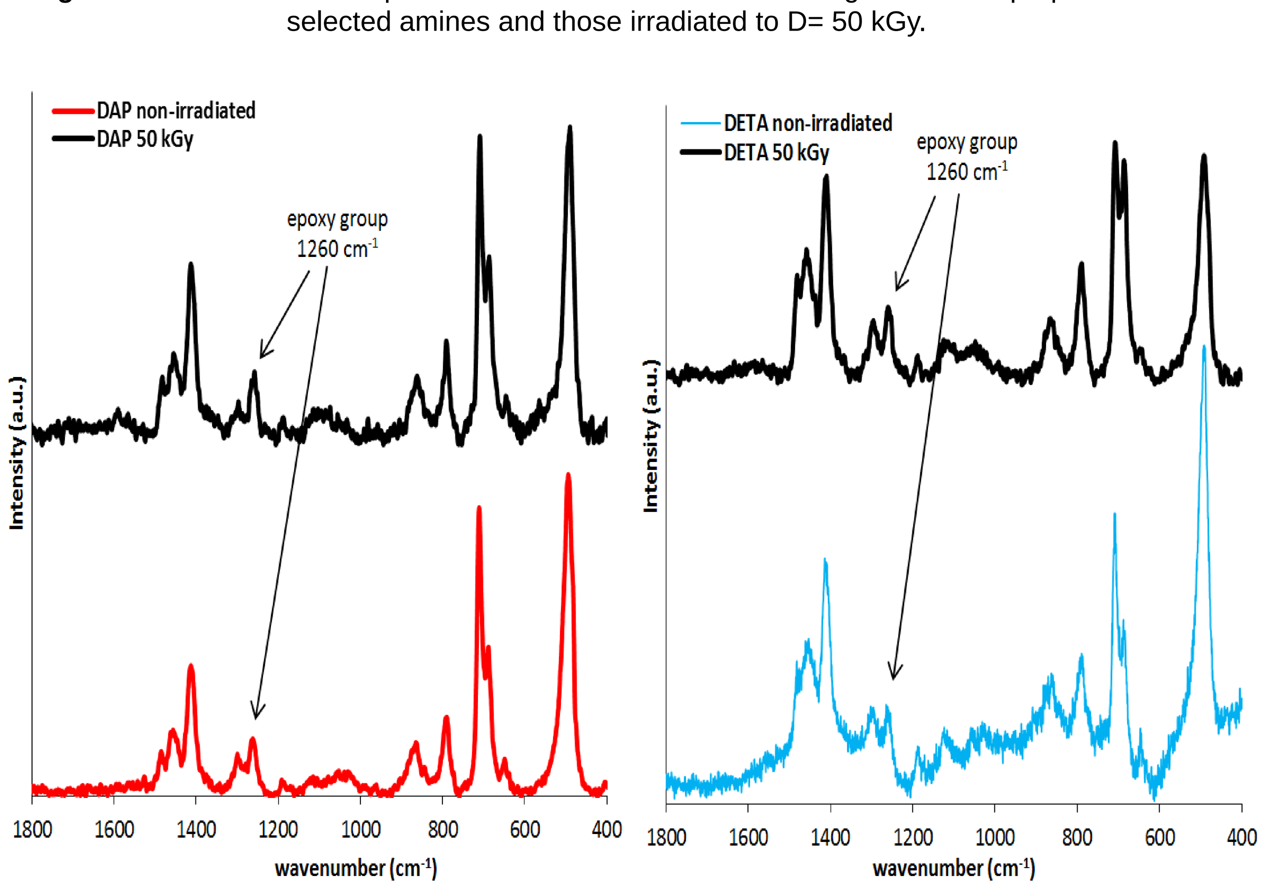
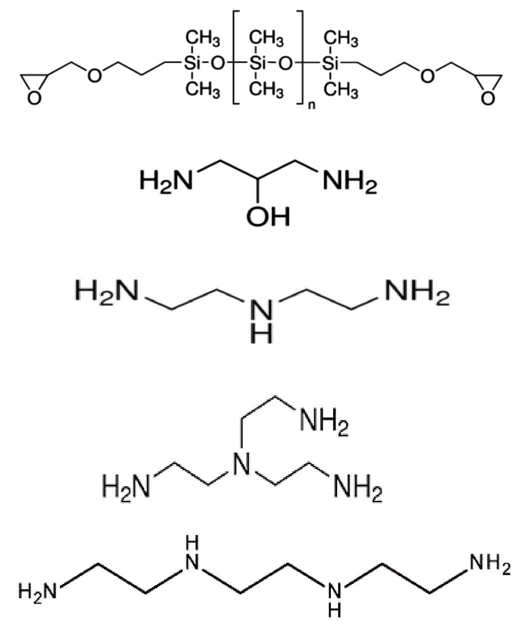


Figure 3 Partial Raman spectra of non-irradiated DAP- and DETA-cured PDMS-DGE gel networks and those irradiated to D= 50 kGy.



PDMS-DGE

DAP

DETA

TAEA

TETA

Figure 1 Formulas of PDMS-DGE and aliphatic amines used.

RESULTS AND DISCUSSION

According to ATR-FTIR spectra (normalized to 2960 cm^{-1} peak) the extent of reaction of PDMS-DGE and amines that produced gel networks varied. It was greater in DETA- and TETA-cured ones than in those obtained by reaction with DAP and TAEA (figure 2).

Raman spectra revealed that non-irradiated gel networks contained at least some unreacted epoxy groups (figure 3) so we expected that radiation crosslinking will prevail. Indeed, with the exception of TAEA-cured one, the residual mass after Soxhlet extraction was slightly higher in irradiated gel networks (table 1, inserts in figure 4). Almost 10 % increase in residual mass on irradiation of TETA-cured gel network indicates that its initial curing was less complete than of DETA-cured one although the diamines have very similar structure.

While apparent firmness of irradiated gel networks was preserved the increase in rates and extents of swelling in hexane (table 1, figure 4) in irradiated gel network samples compared to non-irradiated ones indicates that at least some radiation degradation occurred. The DAP-cured gel network was the least affected by irradiation most likely because hydroxyl group of DAP amine stabilized the gel network by hydrogen bonding strong enough to cause a slight shift of Si-O stretching peak compared to other gel networks.

AC electrical conductivity and its frequency dependence of non-irradiated gel networks strongly depends on the amine type (table 1, figure 5). It is known that radiation induced charge carriers and degradation increase the conductivity while crosslinking reduces it. The frequency range of conductivity plateau increases if the disorder increases. On irradiation of gel networks both parameters increased but the effects again strongly depended on the amine type. Due to hydrogen bonding both the conductivity and the frequency range of its plateau are the lowest for DAP-cured gel network. High conductivity of non-irradiated TETA-cured gel network and its insignificant post-irradiation increase confirm at least some radiation crosslinking. An increase in conductivity of irradiated DETA-cured gel for almost 2 orders of magnitude along with the greatest increase in swelling strongly indicates degradation. Non-irradiated TAEA-cured gel network displays a step in frequency dependence of conductivity that might correspond to current relaxation at the interfaces between regions of different conductivity. Such regions might arise due to ability of a triamine to bond three PDMS molecules and produce an intertwined network.

An endothermic transformation in DSC thermograms was observed in all gel network samples. It probably originates from gel network collapse but its true nature is still under consideration. In non-irradiated gel networks prepared with diamines (DAP, DETA, TETA) enthalpies of that transformations (table 1) were similar and about an order of magnitude lower than that of gel network prepared with a triamine (TAEA). On irradiation all peak temperatures shifted to higher values. The enthalpies of gel networks prepared with diamines significantly increased while in TAEA cured gel network the increase was only slight.

MATERIALS AND METHODS

Gel networks were prepared by curing of diglycidyl ether terminated poly(dimethylsiloxane), PDMS-DGE with selected aliphatic amines (Figure 1): diamines 1,3-diamino-2-propanol (DAP), diethylenetriamine (DETA), triethylenetetramine (TETA) and a triamine tris(2-aminoethyl)amine (TAEA) at 50 ºC. Obtained gel networks were irradiated at a dose rate of 7.8 Gy/s in ^{60}Co γ-irradiation facility of Laboratory for Radiation Chemistry and Dosimetry, Ruđer Bošković Institute in Zagreb, Croatia to dose of 50 kGy, in ambient conditions. The non-irradiated and irradiated gel network samples were extracted with hexane in Soxhlet apparatus for 48 hours. Swelling in hexane at 23 ºC was measured at selected intervals for at least 12 hours. Samples about 5 mg weight were put in Al sample pans and DSC measurements were performed on Perkin Elmer Pyris Diamond DSC in nitrogen atmosphere at a rate of 20 ºC /min. Dielectric spectra of samples in teflon holder with geometry 3 mm height and 5 mm diameter were recorded at room temperature (23 ºC) on Novocontrol Technologies instrument with Alpha-A High Performance Frequency Analyzer, standard BDS1200 cell and brass electrodes. ATR-FTIR spectra were recorded using Bruker TENSOR II FTIR spectrophotometer equipped with A225/Q Platinum diamond ATR unit. 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 x 1024 pixels array was used.

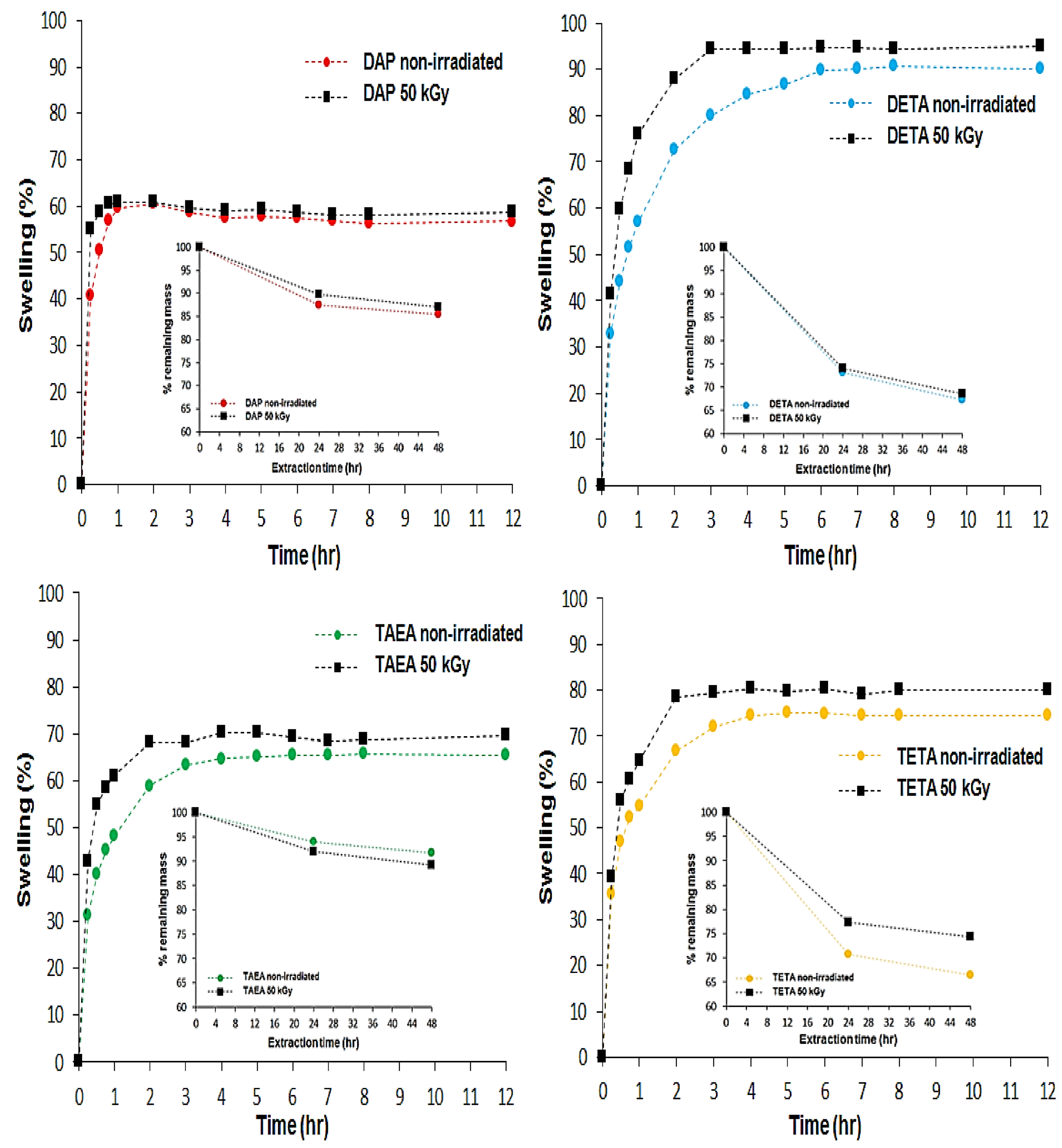


Figure 4 The percent of mass increase during initial 6 hours of swelling in hexane at 23 ºC. Inserts: the residual mass after 24 and 48 hours of Soxhlet extraction in hexane of non-irradiated PDMS-DGE gel networks prepared with selected amines and those irradited to D= 50 kGy.

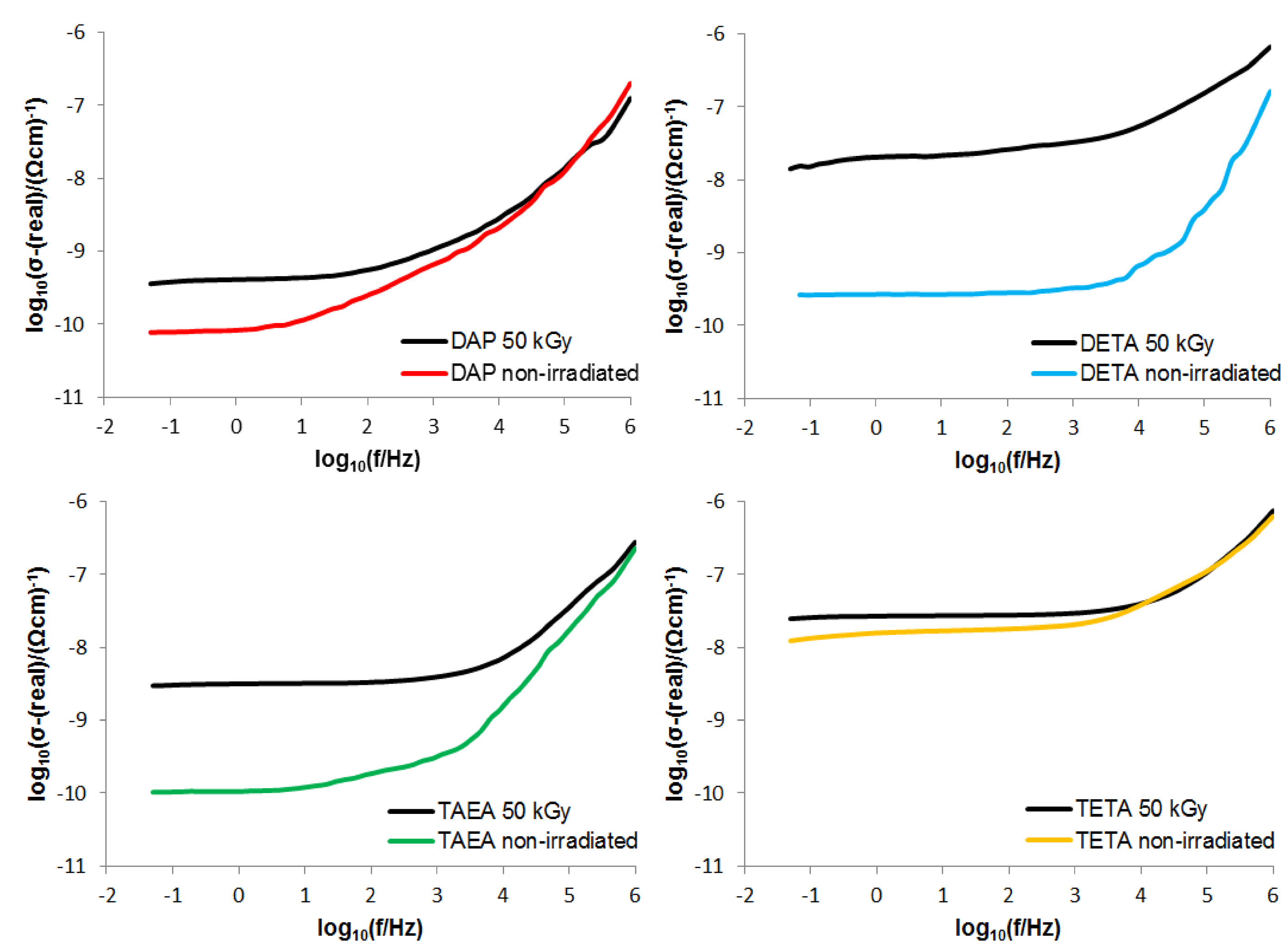


Figure 5 AC electrical conductivity of non-irradiated PDMS-DGE gel networks and those irradiated to D= 50 kGy.

CONCLUSIONS

- **Even though contribution of DAP, DETA, TAEA and TETA segments to PDMS gel networks is relatively small their structure significantly influenced both the network properties and the outcome of irradiation.**
- **Amine type particularly influenced thermal and electric properties of studied PDMS gel networks.**
- **Irradiation to D= 50 kGy caused some crosslinking only in a TETA-cured gel network.**
- **The gel networks prepared using the amine that can either form hydrogen bonds (DAP) or produce denser network (TAEA, a triamine) were less influenced by irradiation.**

References:

[1] E. M. Petrie, Epoxy Adhesive Formulations, McGraw-Hill, New York, 2006, pp. 85-110.

[2] R. G. Jones, J. Kahovec, R. Stepto, E. S. Wilks, M. Hess, T. Kitayama, W. V. Metanomski, IUPAC: Compendium of Polymer Terminology and Nomenclature, RSC Publishing, Cambridge, 2009, pp. 211-236.

[3] A. S. Palsule, S. J. Clarson, C. W. Widenhouse, Gamma Irradiation of Silicones, *J. Inorg. Organomet. Polym.*, 18 (2008) 207-221.