Spectroscopic Study of Poly(dimethylsiloxane) ZnO Nanocomposites Exposed to Proton Irradiation

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Summary: In this study poly(dimethylsiloxane) (PDMS) nanocomposites with 1wt % of zinc oxide (ZnO) and 1wt % of silanized ZnO nanoparticles were prepared through cross-linking reaction. The prepared samples were irradiated under vacuum at room temperature with a 2 MeV proton beam with fluences in the 10^{13}–10^{15} cm^{-2} range. The influence of nanoparticles on the cross-linking processes and structural degradation of irradiated PDMS nanocomposites was investigated using Raman and Fourier transform infrared spectroscopy (ATR). The analysis of vibrational spectra has shown that prepared PDMS nanocomposites have higher resistance to proton irradiation in comparison to pristine PDMS. Under the highest proton irradiation fluence (10^{15} cm^{-2}) PDMS with 1% ZnO provided the best radiation protection.

Keywords: cross-linking; nanocomposites; poly(dimethylsiloxane); proton irradiation

Introduction

Poly(dimethylsiloxane) (PDMS) is versatile silicone polymer due to the unique chemical structure that combines an inorganic backbone and organic methyl groups attached to Si atoms. The polymer can be used in many conventional technologies, such as adhesives, coatings and sealing but it also has great potential for applications in biomaterial science, in the aerospace as well as in electronics and semiconductor industry[1–3]. PDMS is linear polymer with repeating unit [-Si$(CH_3)_2$-O]. PDMS polymer chains containing two vinyl end groups react with a multifunctional cross-linker forming a three-dimensional network. The hydrosilylation reaction has been usually used to prepare cross-linked PDMS materials. The rheological,[4] thermoelastic[5] and mechanical[6] properties of PDMS can be improved by addition of nanofillers. When nanoparticles are present during cross-linking reaction they can interact with polymer components or influence the reaction indirectly by changing the properties of cross-linked network.[7] These interactions can have different effects on the cross-linking density of PDMS nanocomposites.[7,8]

ZnO nanoparticles as an important wide bandgap semiconductor have drawn attention due to their important properties such as chemical stability, biocompatibility, high radiation resistance, etc. The introduction of ZnO nanoparticles into polymer may improve the properties of polymer matrix.[9]

The study of irradiation induced changes in PDMS and its nanocomposites is of interest as PDMS has been often used in medical devices and spacecraft. The desire is to develop an understanding of the effects of irradiation on PDMS nanocomposites for application in high irradiation environment. Recently we reported that PDMS nanocomposites exhibit enhanced stability against high energy proton irradiation as compared to pure PDMS.[10,11] We have also investigated the influence of nanofiller's

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(carbon nanotubes, nanodiamond and zinc oxide) on the radiation resistance of PDMS nanocomposites exposed to proton irradiation.[11]

In this paper PDMS nanocomposites with 1wt% of ZnO nanoparticles (PDMS + 1% ZnO) and 1wt% of silanized ZnO nanoparticles (PDMS + 1% ZnO silanized) with a size specification of 5–30 nm were prepared through cross-linking reaction. The prepared samples were irradiated under vacuum at room temperature with a 2 MeV proton beam with fluences in the 10^{13}–10^{15} cm^{-2} range. The aim of this study is to investigate the infuence of silanized ZnO nanoparticles on the cross-linked structure of PDMS nanocomposite and its stability against high energy proton irradiation. Modification of the structures of the prepared nanocomposite materials were monitored as a function of proton fluence using Raman and ATR spectroscopy.

Experimental Part

The poly(dimethylsiloxane), Sylgard, was purchased from Dow-Corning as a two part material: base (Sylgard-184A) and a curing agent (Sylgard-184B). The base contains predominantly vinyl-terminated poly(dimethyl siloxane) oligomers, dimethylvinylated and trimethylvinilated silica and Pt based catalyst. The curing agent is predominantly a mixture of poly-(dimethylmethylhydrogensiloxane) and vinyl-endcapped PDMS precursor.[8] The cross-linked PDMS sample was prepared by mixing the base with the curing agent in a 10:1 ratio by weight. The ZnO nanoparticles and ZnO nanoparticles treated with silane coupling agent with a size specification of 10–30 nm were purchased from SkySpring Nanomaterials Inc (silane coupling agent is not specified by supplier). When forming PDMS-ZnO nanocomposites, an intermediate solvent was employed that served as a dispersion medium for the nanoparticles prior to mixing with the polymer matrix. The nanoparticles were dispersed in the solvent and sonicated to break up large agglomerates, then the suspension was combined with un-cured PDMS and solvent subsequently removed by vacuum. The curing time was 48 h at room temperature. Curing of the PDMS-nanoparticle mixture resulted in films with good nanoparticle dispersion. The prepared nanocomposites contained 1 wt% nanoparticles. The thickness of prepared samples was approximately 3 mm.

Samples of nanocomposites were irradiated in vacuum with a 2 MeV proton beam that was delivered by the 1.0 MV Tandetron accelerator at the "Rudjer Bošković" Institute, Zagreb, Croatia. A homogeneous circular beam 5 mm in diameter was used. Low fluence irradiations with proton beam currents between 30 and 100 nA were carried out. All samples were irradiated in the range of fluences from 10^{13} protons/cm^2 to 10^{15} protons/cm^2 in four areas with different conditions. The fluence corresponding to region 1 (D1) and 2 (D2) is $5.7 \cdot 10^{13}$ protons/cm^2, for region 1 a beam current of 30 nA was used while for region 2 a beam current of 50 nA was used; the total charge for regions 1 and 2 was the same, 5.6 μC. The fluence and total charge delivered to D1 and D2 was kept the same while the beam current was different to explore the influence of the beam current.

The fluence for region 3 (D3) was $5.7 \cdot 10^{14}$ protons/cm^2 delivered using a 80 nA beam current for a total charge of 56 μC and for region 4 (D4) was 10^{15} protons/cm^2 delivered using a 100 nA beam current for a total charge of 100 μC. The fluences delivered to region D3 and D4 are the same as the fluences used in our previous experiments on different nanocomposites so the results for different nanocomposites could be easily compared. All irradiations were done at room temperature.

Raman spectra were recorded on Horiba Jobin Yvon T64000 instrument equipped with the Olympus open microscope stage and CCD Symphony detector. Spectrometer was operating in triple subtractive mode during the acquisition of spectra of PDMS and PDMS nanocomposites in the

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frequency region from 50–3100 cm^{-1}. The 514.5 nm line of a Coherent INNOVA-400 argon ion laser was used for excitation. Laser power used to measure the Raman spectrum of pure PDMS and PDMS nanocomposites was 20 mW at the sample place. Raman spectra of nanocomposites were recorded 2.0 μm below the surface. A comparison of Raman spectra of unirradiated (D0) and irradiated (D1, D2) samples are presented in Figures 1, 2 and 3. Due to the very high fluorescent background. it was not possible to record Raman spectra of samples irradiated with fluences D3 and D4. In our previuos study we have reported that proton irradiated PDMS samples showed blue photoluminiscence (PL).[10] The PL intensity increased with irradiation fluence. Under irradiation Si-O-Si chains are broken and can result in formation of defected silica domains with photoluminiscent properties.[10] A study on the effects of proton irradiation on the photoluminiscent properties of PDMS-ZnO nanocomposites is in progress.

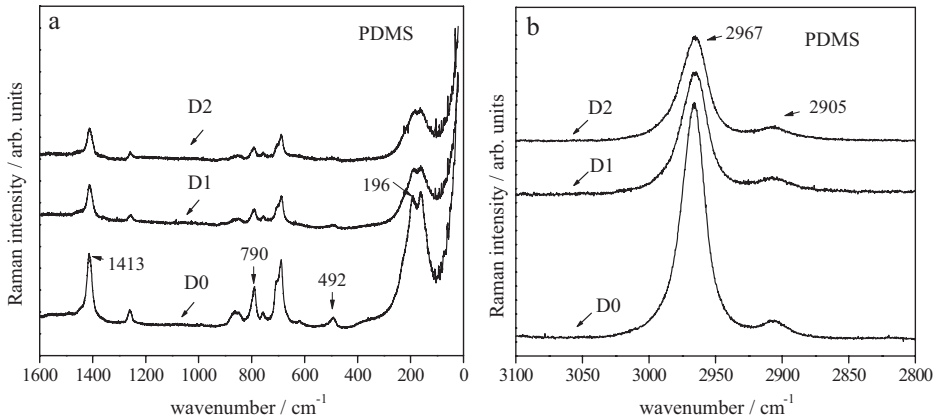

Figure 1.
Raman spectra of unirradiated (D0) and irradiated (D1, D2) cross-linked PDMS in the wavenumber ranges 1600–50 cm^{-1} (a) and 3100–2800 cm^{-1} (b)[11].

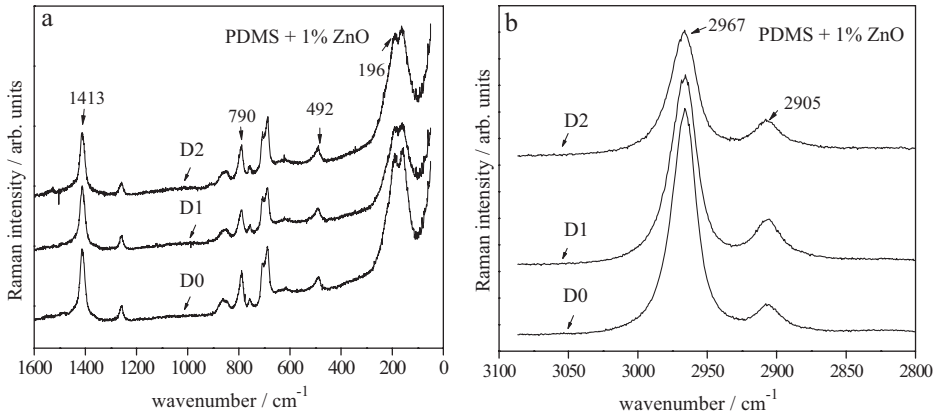

Figure 2.
Raman spectra of PDMS¬ + 1% ZnO nanocomposite before (D0) and after (D1, D2) irradiation in the wavenumber ranges 1600–50 cm^{-1} (a) and 3100–2800 cm^{-1} (b).

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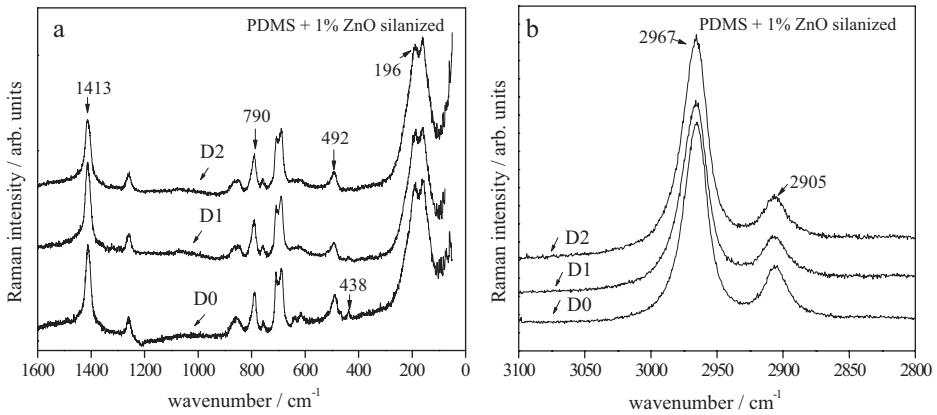

Figure 3.
Raman spectra of PDMS−+1% ZnO silanized before (D0) and after (D1, D2) irradiation in the wavenumber ranges 1600–50 cm^{-1} (a) and 3100–2800 cm^{-1} (b).

The Fourier transform spectra in the attenuated total reflection mode (FTIR-ATR) were recorded using an ABB Bomem MB 102 spectrometer. The spectra of pure PDMS as well as PDMS nanocomposites were recorded in 600–4000 cm^{-1} frequency region using

Specac's Golden Gate Single Reflection Diamond ATR System with ZnSe lens. The spectra were collected with a resolution of 2 cm^{-1} by coadding the results of 10 scans. A reference spectrum was collected before each measurement. FTIR-ATR spectra of unirradiated (D0) and irradiated (D1, D2, D3 and D4) of PDMS as well as of PDMS nanocomposites are shown in Figures 4, 5 and 6.

Results and Discussion

The cross-linked PDMS network has been prepared through two cross-linking reactions. The hydrosilylation reaction between

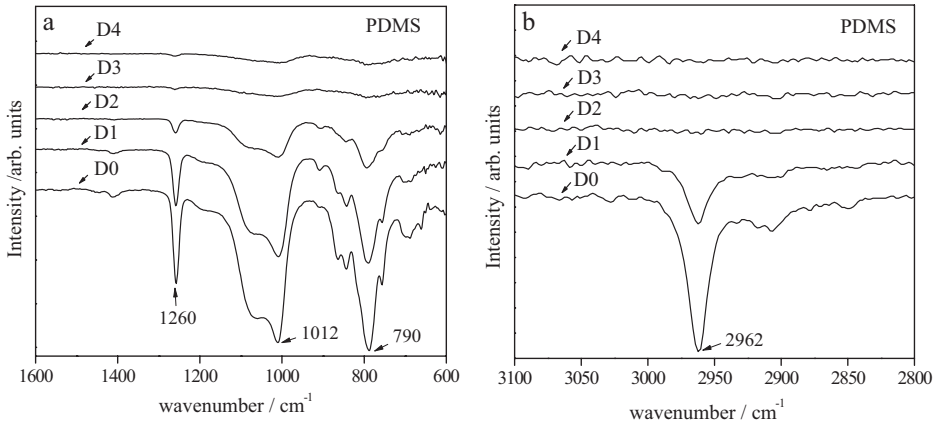

Figure 4.
Comparison of FTIR-ATR spectra for PDMS before (D0) and after irradiation (D1, D2, D3 and D4) in wavenumber region 1600–600 cm^{-1} (a) and 3100–2800 (b)[11].

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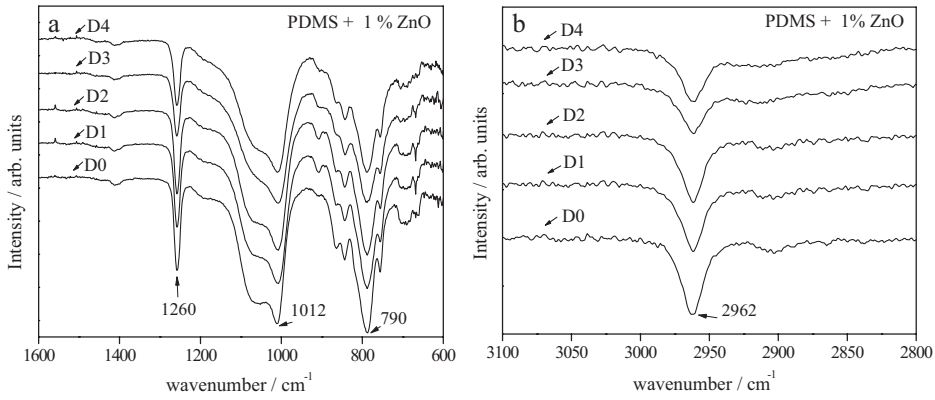

Figure 5.
FTIR-ATR spectra of PDMS + 1% ZnO nanocomposite before and after irradiation in wavenumber region 1600–600 cm^{-1} (a) and 3100–2800 (b).

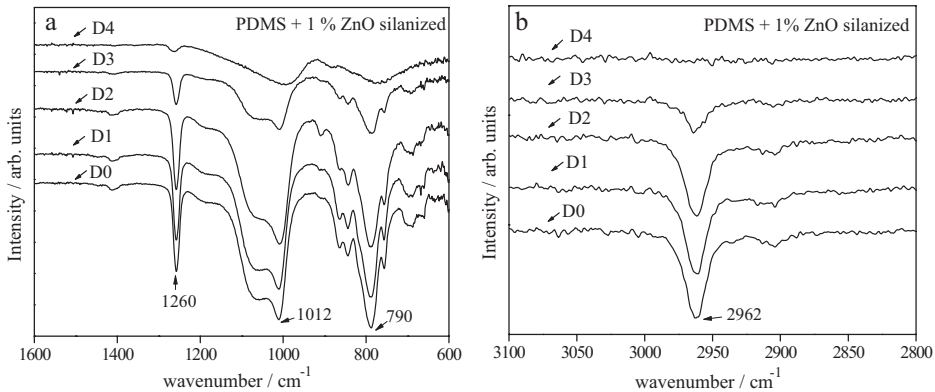

Figure 6.
FTIR-ATR spectra of PDMS + 1% ZnO silanized nanocomposite before and after irradiation in wavenumber region 1600–600 cm^{-1} (a) and 3100–2800 (b).

a vinyl group (-CH = CH_2) on vinyl-terminated poly(dimethylsiloxane) and a silyl (SiH) group of the poly-(dimethyl-methyl-hydrogensiloxane) (cross-linker**)** is the primary cross-linking reaction (cure reaction). The hydrosilylation reaction lead to the creation of a network with ethylene -CH_2-CH_2- bridges:[12,13]

$$\mathrm{R-Si-H + CH_2=HC-Si-R' \xrightarrow{catalyst} R-Si-CH_2-CH_2-Si-R'}$$

The SiH groups of cross-linker are further capable of forming ethylene bridges with dimethylvinylated and trimethylated silica. Simultaneously SiH groups can react with moisture and O_2 through secondary cross-linking reactions leading to the formation of Si-OH groups (post-cure reaction). The silanol groups (Si-OH) can react with each other or with SiH groups forming additional siloxane Si-O-Si bonds.[14]

To prepare cross-linked PDMS nanocomposites, nanoparticles were initially dispersed in base and after that the curing agent is added to the mixture. The cross-linking reactions lead to the tri-dimensional polymer network in which nanoparticles

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are entrapped. The presence of nanoparticles during cross-linking reaction influences the cross-linking process. Hydroxyl groups on ZnO nanoparticle surface can react with SiH groups of cross-linker forming additional Si-O-Si bonds.[8] Recently, it has been shown that OH groups on ZnO nanoparticles (40–100 nm) participate in a post curing reaction forming additional siloxane Si-O-Si bridges with polymer chains.[8] The formation of CH_2-CH_2 ethylene cross-links is reduced.[8] Here we explore how the incorporation of ZnO nanoparticles treated with silane coupling agent influence the cross-linking of PDMS polymer. It is important to understand changes caused by the introduction of silanized ZnO nanoparticles in the nonirradiated composites material, as later changes in vibrational spectra of irradiated sample may be connected with changes in polymer matrix before the irradiation.

Silane coupling agents, $(R)_{4-n}$-Si-X_n, are organofunctional monomers that possess dual reactivity. The R group is attached through hydrolytically stable carbon-silicon bond and may be inert or contain a reactive organic group such as vinyl, amino, epoxy, etc. On the other side, groups X at one end of the molecule (usually chloro, alkoxy or acetoxy) are capable to hydrolyse and form silanols, which are then able to react with suitable groups in its surrounding. The SiOH group has also a strong tendency to undergo self-condensation reaction forming siloxane structures with Si-O-Si linkages.

ZnO nanoparticles are prone to aggregate due to the large surface area and large surface energy. The modification of the surface of ZnO nanoparticles with silane coupling agent prevent the formation of agglomerated nanoparticles and ensure its better dispersion in polymer matrix.[15]

Raman and FTIR-ATR spectra of unirradiated samples (D0) were analyzed in order to investigate the influence of addition of ZnO nanoparticles and silanized ZnO nanoparticles on the cross-linked structure and on vibrational dynamics of PDMS polymer. The assignment of vibrational spectra of cross-linked PDMS supported by the normal coordinate analysis has been recently reported.[8] Comparative analysis of vibrational spectra of nonirradiated samples presented in Figures1–6 has shown that positions of vibrational bands characteristic for cross-linked PDMS polymer remain at the same positions in all samples. The vibrational band at 438 cm^{-1} due to the bending modes of O-O atoms in ZnO appears in Raman spectrum of PDMS +1% ZnO silanized. The addition of ZnO nanoparticles has impact on the intensities of vibrational bands due to the interaction of OH groups on the ZnO nanoparticle surface with SiH groups of cross-linker during post-cure reaction.[8] To see the influence of nanoparticles and proton irradiation on vibrational spectra we performed an analysis of intensities of vibrational bands in all recorded spectra. The intensities of Raman bands have been determined by integrating the area under the respective band after the baseline corrections. Lorentz functions were fitted to the measured vibrational bands, intensities and half-widths were allowed to vary in the fitting process. The maximum error connected with the fit was less than 5%. It was not possible to analyze the absorbance spectra by a fitting procedure because of the very high intensities of absorbance bands. Therefore the intensities of IR bands were estimated from the highs of IR bands. The calculated relative intensities of vibrational bands are presented in Tables 1, 2 and 3. As can be seen from results, the relative intensities of CH stretching vibrations connected with CH_3 and CH_2 vibrations (Raman bands observed at 2967 and 2905 cm^{-1}) in nonirradiated samples are changed in nanocomposites due to the changes in CH_2-CH_2 cross-linking density.[8] The pure Si-O-Si stretching vibrations are observed at 492 cm^{-1} in Raman spectra and at 1012 cm^{-1} in FTIR spectra. The analysis of Raman spectra showed the increased intensity of Si-O-Si stretching band at 492 cm^{-1} in PDMS +1% ZnO silanized sample in comparison with PDMS +1% ZnO. The normalised relative intensities of Raman bands observed at

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Table 1.
Relative intensities of Raman bands in spectra of nonirradiated PDMS and PDMS nanocomposites[a].

	$\left(\frac{I_{2967}}{I_{2905}}\right)_n$	$\left(\frac{I_{1413}}{I_{492}}\right)_n$	$\left(\frac{I_{790}}{I_{492}}\right)_n$	$\left(\frac{I_{196}}{I_{492}}\right)_n$
PDMS	1.00	1.00	1.00	1.00
PDMS + 1% ZnO	0.49	0.75	0.57	0.69
PDMS + 1% ZnO silanized	0.23	0.45	0.32	0.23

[a] Relative intensities are normalized to the value in PDMS

Table 2.
Relative intensities of Raman bands in spectra of nonirradiated and irradiated PDMS and PDMS nanocomposites.

		$\left(\frac{I_{2967}}{I_{492}}\right)$	$\left(\frac{I_{1413}}{I_{492}}\right)$	$\left(\frac{I_{790}}{I_{492}}\right)$
PDMS	D_0	32.31	5.36	2.81
	D_1	51.07	5.92	2.86
	D_2	72.98	7. 86	2.85
PDMS + 1% ZnO	D_0	28.97	4.01	1.60
	D_1	26.08	3.89	1.30
	D_2	16.99	4.10	1.75
PDMS + 1% ZnO silanized	D_0	27.93	2.57	0.91
	D_1	24.14	3.97	1.34
	D_2	18.00	2.97	1.23

Table 3.
Relative intensities of IR bands in spectra of nonirradiated and irradiated PDMS and PDMS nanocomposites.

		$\left(\frac{I_{2962}}{I_{1012}}\right)$	$\left(\frac{I_{1260}}{I_{1012}}\right)$	$\left(\frac{I_{790}}{I_{1012}}\right)$
PDMS	D_0	0.159	0.625	0.531
	D_1	0.080	0.548	0.443
	D_2	0.000	0.374	0.440
	D_3	0.000	0.324	0.027
	D_4	0.000	0.030	0.027
PDMS + 1% ZnO	D_0	0.167	0.651	0.537
	D_1	0.152	0.620	0.427
	D_2	0.151	0.628	0.419
	D_3	0.109	0.538	0.319
	D_4	0.110	0.549	0.363
PDMS + 1% ZnO silanized	D_0	0.172	0.662	0.573
	D_1	0.165	0.645	0.559
	D_2	0.148	0.622	0.576
	D_3	0.137	0.613	0.461
	D_4	0.000	0.347	0.000

1413 (CH_3 bending), 790 (SiC stretching) and 196 cm^{-1} (CSiC deformation) in relation to the Si-O-Si stretching band at 492 cm^{-1} decreased mostly with addition of silanized ZnO (Table 1). It is evident that the number of Si-O-Si bonds in PDMS +1% ZnO silanized sample is enhanced with respect to PDMS +1% ZnO.

In silane coupling agent X groups are usually partially hydrolysed by water molecules forming silanol SiOH groups. During the modification of the surface of ZnO nanoparticles with silane, OH groups on ZnO surface react with silanol groups forming Si-O-Si bonds. Accordingly, hydroxyl group on ZnO surface is replaced

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with functional groups of silane. Unreacted OH groups on ZnO surface and unreacted silanol groups attached on ZnO surface can react with SiH groups of cross-linker during post-cure reaction forming additional Si-O-Si linkages. Thus, the Si-O-Si cross-linking density in PDMS +1% ZnO silanized sample is enhanced compared to PDMS +1% ZnO nanocomposite.

In order to explore the influence of addition of ZnO nanoparticles and silanized ZnO nanoparticles (with a size specification of 10–30 nm) on the proton irradiation stability of PDMS nanocomposites we analyzed Raman and FTIR spectra presented in Figures 1–6. We included in Figures 1 and 4 our previously published data which present the spectra of cross-linked PDMS exposed to proton irradiation under the same condition, due to the simplicity of comparison with PDMS nanocomposites.[10] The ratio of intensities of several vibrational bands for nonirradiated and irradiated samples is also presented in Tables 2 and 3. As can be seen in Tables 2 and 3, changes in relative intensities of vibrational bandsin irradiated samples are evident for all vibrational bands but they are not as significant as for irradiated pure PDMS polymer. The D1 and D2 irradiation conditions differ in the beam current, while the total charge delivered is unchanged. The difference in relative intensities for PDMS nanocomposites irradiated at conditions D1 and D2 are not as prominent as for pure PDMS.

The impact of higher fluences D3 and D4 on the nanocomposites is evident in FTIR spectra in Figures 4–6. In the spectra of PDMS CH stretching vibrations disappear already under D2 fluence, while in in the PDMS +1% ZnO silanized CH stretching vibrations is missing under D4 fluence. A comparison of the data in Tables 2 and 3 of nonirradiated and irradiated samples under D1–D4 conditions reveals that nanocomposites showed similar radiation resistance. At the fluence D4 all vibrational bands in FTIR spectra of PDMS + 1% ZnO nanocomposites are detected. Recently, we have reported that 40–100 nm ZnO nanoparticles provided the best protection for cross-linked PDMS polymer in comparison with PDMS nanocomposites containing carbon nanotubes or nanodiamond.[11] In this study comparable structural degradation of nanocomposites is obtained with smaller ZnO nanoparticles (10–30 nm). The role of ZnO particle size on the radiation resistance of PDMS-ZnO nanocomposites requires further explanation and will be the subject of a future research.

Conclusion

The analysis of vibrational spectra of cross-linked PDMS containing 1% of ZnO nanoparticles as well as 1% silanized ZnO nanoparticles has shown different impact on cross-linking of polymer. The intensity of Si-O-Si vibrational band in Raman spectra of PDMS +1% ZnO silanized is enhanced in comparison with its intensity in spectra of PDMS +1% ZnO. The reaction between silanol groups on surface of ZnO nanoparticles treated with silane with SiH groups of cross-linker increased the Si-O-Si cross-linking density.

PDMS +1% ZnO and PDMS +1% ZnO-silanized nanocomposites provide about the same level of radiation resistance at proton fluences in the 10^{13}–10^{14} cm^{-2} range. Under the highest proton irradiation fluence ($10^{15}\,cm^{-2}$) PDMS +1% ZnO provided the best radiation protection.

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