Influence of nanofillers on the properties of siloxane elastomers

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Abstract

In this study, the influence of nanosilicon(IV)-oxide (with hydrophobic and hydrophilic functionalized surfaces) on the properties of siloxane elastomers was studied. The elastomers were prepared from vinyl and hydrogen oligosiloxanes, while the nanocomposites were obtained by addition of nanofillers at different concentrations (1, 5, 10 and 20 wt%). The chemical structure of the obtained materials was analyzed by Fourier transform infrared spectroscopy. Transmission electron microscopy confirmed good dispersion of the hydrophobic filler within the polymer matrix, while the hydrophilic filler formed a net on the siloxane sample. Type of the filler modification did not affect hardness of the siloxane hybrid materials, while the samples with the highest content of hydrophobic nanosilica have shown the highest value of tensile strength. Influence of the nanosilica type on thermal degradation of elastomeric materials was investigated by using thermogravimetric analysis, while the influence of the fillers on the phase transition temperature was analyzed by differential scanning calorimetry. Lower compatibility of the hydrophobic matrix and hydrophilic filler caused a decrease in the crystalline melting temperature with the lowest value determined for the sample with the highest filler loading. Increase in the nanofiller content resulted in the improved thermal stability of the obtained hybrid materials.

Keywords: nanocomposites; vinyl siloxane; thermal properties, polymer network, elastomers

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1. INTRODUCTION

Elastomers exhibit large reversible deformations with an exceptionally low modulus, which is not typical for solid materials due to the entropic origin of elasticity. Such unique mechanical properties of elastomers are a result of the three-dimensional network structure that includes long and flexible polymer chains bonded together [1,2]. These chains can be connected by physical (secondary interactions) or chemical bonds (chemical bonds established between polymer chains in the crosslinking reaction). Crosslinking of macromolecules is a topologically critical phenomenon in which a three-dimensional network arises by assembling the linear chains. Siloxane elastomers are a special type of elastomeric materials, due to their specific properties that distinguish them from the other elastomers. Siloxane materials are available in many physical forms, from highly volatile to high molecular weight liquids, and can be highly elastic thermoplasts and crosslinked elastomers. However, these materials mainly refer to the same dimethylsiloxane structure, which is known for its biocompatibility. Excellent biocompatibility is, in part, due to the low chemical reactivity, low surface energy and hydrophobicity of poly(dimethylsiloxane) (PDMS)[3]. PDMS is known as one of the most flexible polymers, due to structural characteristics of Si-O bonds; they have longer bond lengths, higher bond angle, and much lower torsion potential than C-C bonds. Poly(dimethylsiloxane)s also have a unique combination of

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properties, which include excellent thermal, electrical, oxidative and UV stability, very low surface energy and low glass transition temperatures, high gas permeability and low toxicity [4–6]. Vinyl-functionalized siloxanes, with a vinyl terminal group, could be obtained by equilibrium anionic polymerization by means of certain initiators in one step, by the sequential addition of hexamethyl cyclosiloxane and methylvinylcyclosiloxane. Also, the oligomers can be synthesized by a heterogeneously catalyzed siloxane equilibration polymerization reaction [7]. These materials are used mainly in reactions with hydrogen containing compounds[8].

The addition reaction of silicon hydrides (Si-H) across multiple bonds (*e.g*. vinyl groups) with using a Pt catalyst, is called catalytic hydrosilation (hydrosilylation), and is one of the most known reaction in silicone chemistry [9]. Trofimov investigated synthesis of poly(hydrogensiloxanes) with alkyl vinyl and divinyl ethers of ethylene glycol, which opened a route for synthesis of sensitive polymer electrolytes [10]. These polymers can be of interest as hydrophilic materials for contact lenses. Urayama and coworkers studied different types of polysiloxane elastomers with a controlled network topology [11]. They showed that end-linked elastomers with controlled network topology can be used as a model system that can enables understanding of structural-mechanical properties of polymer networks on a molecular level. Properties of siloxane materials can be significantly improved by using various additives (micro or nanofillers) or by blending and copolymerizing with other polymers [12,13]. In this way, hybrid materials can be obtained, with predicted properties suited to the desired applications. Mechanical properties of siloxanes can be improved by adding reinforcing fillers such as carbon based materials [14,15], montmorillonite [16], fumed silica [17] and polyhedral oligomeric silsesquioxanes[18] into the polymer matrix by physical blending, solution mixing and chemical crosslinking.

Development of hybrid materials is certainly a challenge for scientists and becomes the subject of numerous industrial and academic studies. Research on siloxane based hybrid materials began with the work of the Wen and Wilkes group on modification of PDMS, $(\text{-Si(CH}_3)_2\text{O-})_n$ with silica gels, since it was assumed that the structural similarity of the main Si-O-Si chain and the SiO_2 gel will facilitate connection of the two phases. This resulted in comparative filling and "vulcanization", *i.e*. crosslinking of this elastomer, with considerable improvement of mechanical properties. After these initial studies, the research has spread practically to all types of polymers, from elastomers to thermoplastics and thermosets, with a whole range of inorganic modifiers [19–21]. Cho has developed with his associates a simple technique for production of polysiloxane-based hybrid composite films containing nano sheets of nitridine boron [22]. They have shown that the obtained composite materials have a flat and coordinated anisotropy and improved transmittance. Roy and coworkers synthesized *in situ* PDMS/sepiolite nanocomposites and tested different relationships of polymer/filler interactions [23]. They showed that good filler dispersion in the polymer matrix greatly contributes to the improvement of mechanical and thermal properties of composite materials. PDMS elastomer composites can be used for applications, such as protective masks, medical and industrial tubings, and light guides that require transparency [24].

In this work, influence of the siloxane matrix structure and addition of nanofillers on mechanical and thermal properties of siloxane elastomers was studied. For this purpose, polymer networks with α,ω-divinyl poly(dimethylsiloxane) and poly(methyl-hydrogensiloxane) precursors were synthesized. Hydrophobic and hydrophilic nanosilicon(IV)–oxide particles were used as fillers for nanocomposite preparation. The influence of possible interactions between the fillers and polymer matrices at the supramolecular level, on mechanical and thermal properties of siloxanes, was investigated.

2. EXPERIMENTAL PART

2.1. Materials

Precursors for the siloxane elastomer were α,ω-divinyl poly(dimethylsiloxane) (Sil V) (HANSA SFA 42500, vinyl content 0.19 mmol g^{-1}, Mn = 34500 g mol^{-1}) and poly(methyl-hydrogensiloxane) (Sil H) (HANSA SFA 11230, hydrogen 2.3 mmol g^{-1}, Mn = 19800 g mol^{-1}) provided from CHT GMBH BEZEMA, Germany). Platinum complex in poly(dimethyl-siloxane) containing vinyl groups (ALPA-KAT, CHT GMBH BEZEMA, add country) was used as a catalyst, while methyl siloxane resin (ALPA-RETARD, CHT GMBH BEZEMA, Germany) containing 20% active ingredient, was used to prevent early crosslinking. From Evonik Resource Efficiency GmbH, Germany was provided surface modified silica nanoparticles (hydrophilic and hydrophobic), according to the reaction at Figure 1. Hydrophobic silicon(IV)-oxide of a specific surface area of 130 m^2 g^{-1} and an average particle size of 16 nm (Aerosil® R 972) nad hydrophilic silicon(IV)-oxide of a specific surface area of 200 m^2 g^{-1} and an average particle size of 12 nm (Aerosil® 200) were used as a filler.

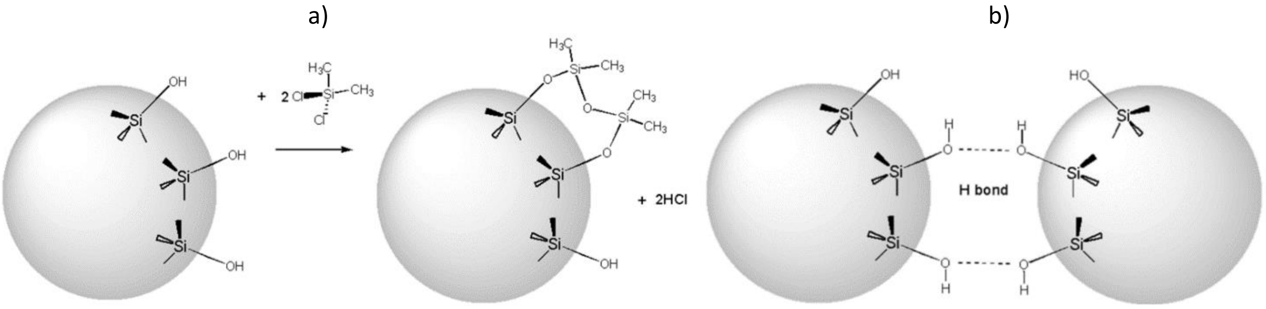

Figure 1. Nanoparticles of silicon(IV)-oxide: a) hydrophobic, b) hydrophilic (Evonik Resource Efficiency GmbH, Germany)

2.2. Preparation of siloxane elastomers

Siloxane elastomers were prepared by a conventional method, with the hydrogen- and vinyl-siloxane ratios 60:40; 50:50; 40:60 (wt:wt), Table 1. All syntheses were performed by addition of the catalyst (0.2 wt%) and the inhibitor (0.1 wt%), calculated on the total weight of monomers. First, all components were mixed in a round bottom flask at room temperature on a magnetic stirrer for 1 h at 100 rpm. Then the samples were poured into molds and cured at 80 °C for 1 h in a vacuum oven. After crosslinking, a final polymer network was obtained with the presumed structure shown in Figure 2.

Table 1. Formulations of prepared siloxane elastomers based on different contents of vinyl siloxane and the nanocomposites with hydrophobic or hydrophilic SiO$_2$

Sample name	Hydrogen/vinyl-siloxaneratio		Content of SiO$_2$, wt%	
	By weight	By mol	Hydrophobic	Hydrophilic
Sil H/Vi 50/50	1/1	12/1	/	/
Sil H/Vi 60/40	1.5/1	18/1	/	/
Sil H/Vi 40/60	1/1.5	8/1	/	/
Sil H/Vi 50/50-1-h-phob	1/1	12/1	1	/
Sil H/Vi 50/50-5-h-phob	1/1	12/1	5	/
Sil H/Vi 50/50-10-h-phob	1/1	12/1	10	/
Sil H/Vi 50/50-20-h-phob	1/1	12/1	20	/
Sil H/Vi 50/50-1-h-phil	1/1	12/1	/	1
Sil H/Vi 50/50-5-h-phil	1/1	12/1	/	5
Sil H/Vi 50/50-10-h-phil	1/1	12/1	/	10
Sil H/Vi 50/50-20-h-phil	1/1	12/1	/	20

Based on preliminary results of thermal and physico-mechanical analyses of pure siloxane elastomers, the ratio of vinyl- and hydrogen-functionalized siloxane precursors of 50:50 wt:wt was chosen for the synthesis of hybrid elastomers. In order to investigate the influence of the nanofillers on properties of siloxane elastomeric materials, two series of nanocomposites were synthesized based on different contents (1, 5, 10 and 20 wt%) of functionalized silicon(IV)-oxide nanoparticles (with hydrophobic and hydrophilic surfaces), Table 1. Nanocomposites were synthesized by adding nanoparticles immediately to the reaction mixture and mixing thoroughly all the components for 1 h. The reaction mixture was then treated in an ultrasonic bath for 15 min and poured into the mold, two samples were prepared for all formulation

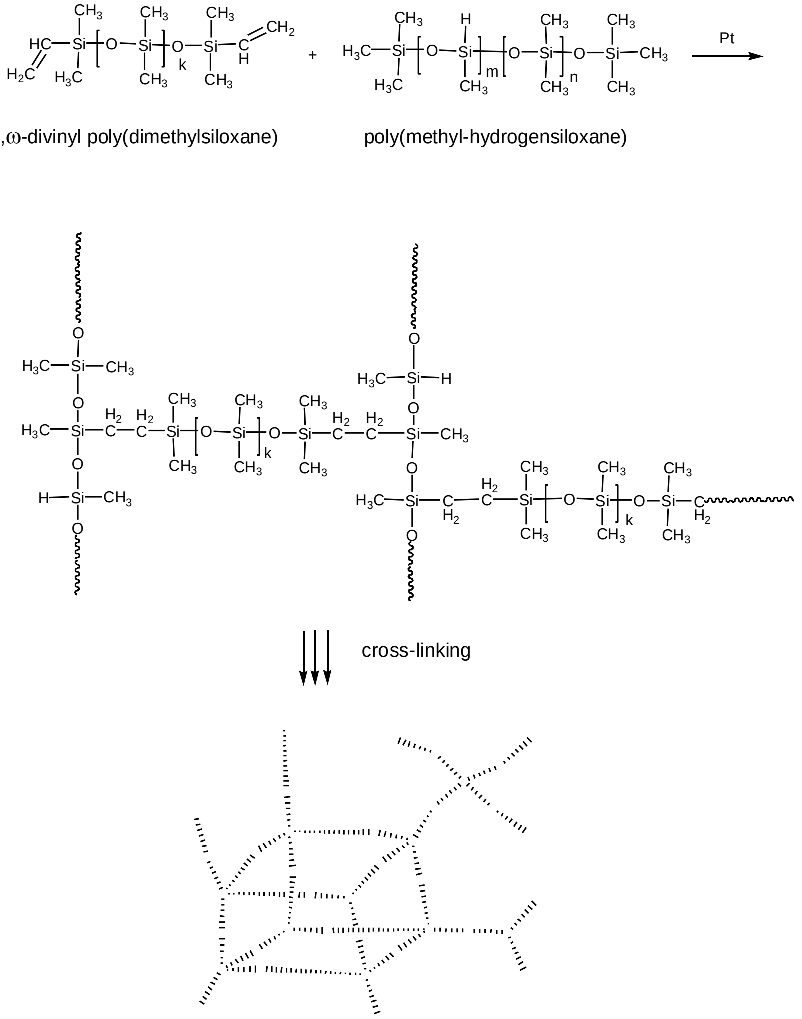

Figure 2. Structure of the obtained polymer network

2.3. Characterization of siloxane materials

Chemical structure of prepared materials was analyzed by Fourier-transform infrared spectroscopy (FTIR) by using FTIR spectrophotometer Thermo-Nicolet Nexus 670 (ThermoFischer Scientific, USA). Attenuated total reflection (ATR) with one reflection on the crystals of germanium was used for the recording. 100 scans were recorded per sample at a resolution of 4 cm^{-1}. Deuterated triglycerin sulphate, DTGS, was used as a detector. The Thermo-Nicolet Omnic 6.0 software was used to process the spectra.

By immersion in a solvent, in which siloxane elastomers swell, it is possible to remove all soluble components, and calculate the gel fraction (cured fraction). Synthesized siloxane samples were placed in toluene at room temperature and mixed gently (at a magnetic stirrer) for 48 h in order to achieve the equilibrium swelling state (determined by weighing the samples till the constant mass). Then the swollen samples were dried to a constant weight and the gel fraction was calculated from the equation:

$$\text{Gel content, \%} = \frac{wt_2}{wt_1}100 \tag{1}$$

where, wt_1 is the initial weight of the siloxane elastomer sample (approximately 1g) and $wt_2$is the weight of the insoluble fraction of the sample (after draying).

The equilibrium swelling degree, Q_e, was calculated according to the conventional gravimetric method [25] by using the equation:

$$Q_e = \frac{w - w_0}{w_0} \tag{2}$$

where w_0 and $w$are the initial and the sample weight at the equilibrium, respectively.

By using the Flory-Rehner[26] equation the crosslink density (M_c, molecular weight between crosslink points) could be calculated according to the equation:

$$M_c = \frac{\rho_r V_S \left(V_r^{1/3} - 0.5\, V_r \right)}{-\left[\ln(1 - V_r) + V_r + \chi V_r^2 \right]} \tag{3}$$

whereχ is the Flory–Huggins polymer-solvent interaction parameter (0.45), $\rho_r$is the density of the sample, V_s is the molar volume of the solvent (toluene), and V_r is the volume fraction of siloxane in the swollen gel, calculated according to the literature[27].

Samples dedicated for transmission electron microscopy (TEM) were sectioned using a Leica UC7 ultramicrotome (producer, country. Triangular pieces with approximately 2 mm long sides were cut from the bulk material using razor blades. The pieces were glued to microtome sample carrier studs using a two-component epoxy glue. After glue hardening the carriers were mounted in the microtome and cooled down to -150 °C. The sample surface was flattened and a square area roughly 25 µm thick and with approx. 0.3 mm sides was trimmed by using a diamond knife (Diatomecryotrim 20, producer, country). Thin, 100 nm thick, sections were cut from the trimmed square while maintaining a temperature of -150 °C. The sections were placed on 300 mesh lacey carbon grids (Agar, producer, country) and subsequently imaged under bright field conditions using a JEOL JEM-2800 transmission electron microscope (producer, country).

Mechanical properties, such as tensile strength and elongation at break, were determined according to the ASTM 412-98a standard, using a universal testing machine Shimadzu EZ-LX model (Shimadzu Corp., Japan) with a cross-head speed of 10 cm min^{-1}. Hardness was determined according to the ASTM D2240 standard using a durometer model 306L type A (producer, country). The hardness values were expressed as Shore A.

Thermal properties of siloxane elastomers were analyzed by differential scanning calorimetry (DSC) by using a DSC Q20 device (TA Instruments). Hermetically sealed aluminum pans were used containing 3-5 mg of a sample. First, the samples were heated from 25 to 180 °C in a dynamic mode, then cooled to -90 °C, and finally heated up to 200 °C. In all phases a heating/cooling rate of 10 °C min^{-1} was used. Calibration of the device was performed by using indium.

Thermogravimetric analysis (TGA) was used to investigate effects of the composition and nanofiller addition on thermal stability of siloxane elastomers. The samples were analyzed by a TGA Leco device (Leco Corporation, USA), in the interval from 25 to 700 °C in a nitrogen atmosphere, with a flow rate of 50 cm^3 min^{-1} and a heating rate of 20 °C min^{-1}, used Leco software.

3. RESULTS AND DISCUSSION

Results of the FTIR analysis of the molecular structure of synthesized elastomers are shown in Figure 3 and Table 2. Two sharp bands at 2961 and 2905 cm^{-1} originated from the asymmetric and symmetric C-H stretching vibrations of Si-CH_3. Characteristic peaks of siloxane matrix that originated from the functional groups Si-CH_3, Si-O-Si, and Si-C are clearly observed. The absence of hydroxyl bond vibrations between 3200 cm^{-1} and 4000 cm^{-1} signifies that the surface OH groups of the fumed silica were successfully consumed by bonding with the silicon atom in the siloxane moiety in the PDMS. The absence of peaks at wavelengths greater than 3000 cm^{-1} shows the quantitative reaction of the C=C double bond in vinyl siloxanes, which confirms that the selected ratio of the reaction components, 50:50, is optimal. Sample Sil H/Vi 40/60 with an excess of vinyl siloxanes shows a small peak at 3080 cm^{-1} originated from an unreacted double bond. It can be also seen in Figure 3 that nanofillers did not chemically interact with the polymer matrix, but there were physical interactions, which resulted from the structural similarity of the filler and the matrix favoring also strong interactions among the SiO_2 hydrophilic fillers (*i.e*. SiO_2 particle agglomeration). A peak fom Si-O band shifted at 1100 cm^{-1} in composites containing hydrophilic silicon(IV)-oxide, which shows weaker physical interactions of the filler and the matrix. Based on the surface activity and the geometric factor of the filler, the filler-filler and the filler-polymer have shown the onlyphysically interaction as primary reinforcement mechanism.

Table 2. Characteristic bands in the FTIR spectrum of synthesized siloxane elastomers

Wavelength, cm^{-1}	Functional group
3000 – 2800	CH_3 and CH_2 group
1450	Asymmetric stretching CH_3
~1420	CH_2 bending
~1260	Si-CH_3
~1250	$(CH_3)_3$, Si
1130 – 1000	Si-O-Si
1000	Si-O
790	Si-C and CH_3 twisting

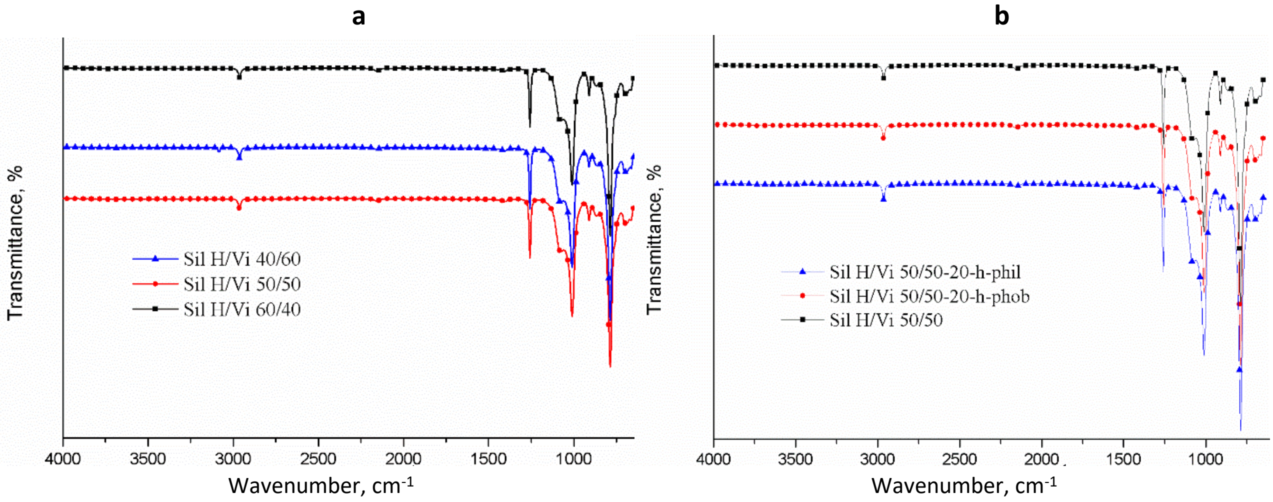

Figure 3. FTIR spectra of siloxane elastomers: a) hydrogen/vinyl siloxane elastomers; b) nanocomposites with 20 wt% hydrophilic and hydrophobic fillers

Gel contents, crosslink densities, and equilibrium swelling degrees of synthesized polysiloxane elastomers are presented in Table 3. It can be seen that the increase of the [hydrogen]/[vinyl] ratio above 12/1, resulted in the increase in the gel content, due to homogeneous crosslinking. At the ratio of [hydrogen]/[vinyl] = 12/1, the FTIR spectra has not shown unreacted C=C bound in Sil V, and a further increase of the [hydrogen]/[vinyl] ratio led to some excess of unreacted Sil H. This is confirmed by the values of molecular weight between crosslink points of synthesized polysiloxane samples (Table 3). M_c value for the sample with the [hydrogen]/[vinyl] ratio of 8/1 was 11200 g mol^{-1} and decreased to around 2700 g mol^{-1} for both samples with higher concentrations of Sil H. This result is expected due to the explained incomplete reaction of poly(methyl-hydrogensiloxane). In literature, it was also found that the optimal [hydrogen]/[vinyl] ratio deviates from the theoretical ratio of 1:1, up to 6:1, when a platinum catalyst is used [28,29]. Equilibrium swelling degrees of obtained siloxane samples were in the range from 0.051 to 0.104. The reason for the obtained small values could be the high crosslink density. The crosslink density determined by the equilibrium swelling method increases with the increase in the Sil H content, while $M_c$increases with the decrease in the amount of poly(methyl-hydrogensiloxane) [30].

Table 3. Gel content, molecular weight between crosslink points and equilibrium swelling degree of synthesized polysiloxane samples

Sample	Gel content, %	M_c / g mol^{-1}	Q_e
Sil H/Vi 60/40	91	2680	0.051
Sil H/Vi 50/50	93	2720	0.054
Sil H/Vi 40/60	79	11200	0.104

3. 1. TEM analysis of siloxane elastomers morphology

Morphology of the pure siloxanes and their nanocomposites was analyzed by TEM. Phase separation of the hydrogen and vinyl silicon can be clearly noticed in a pure siloxane elastomer (as a separate circle in Fig. 4a).

In the case of composite elastomers, TEM analysis has shown good dispersion of the filler, which was expected due to similar chemical structures of the filler and the matrix. By the addition of the filler at 1 wt%, it was possible to notice the effect of the filler functionalization type on its dispersion and distribution in the polymer matrix (Fig. 4b,c). Hydrophobic nanofillers were dispersed better in the hydrophobic matrix, whereas in the case of hydrophilic fillers, due to the lower compatibility of the filler and the matrix, small agglomerates were formed. In samples with higher contents of the hydrophobic filler (10 and 20 wt%) formation of larger agglomerates was not observed, *i.e*. good dispersion of the filler within the matrix was retained (Fig. 4d,f). However, the increase in the portion of the hydrophilic filler leads to the creation of a filler net in the sample, especially in the case of the sample with 20 wt% of the filler (Fig. 4g). The filler net was formed due to interactions at the surface of hydrophilic silicon(IV)-oxide such as hydrogen bonds between the OH groups (Fig. 1b).

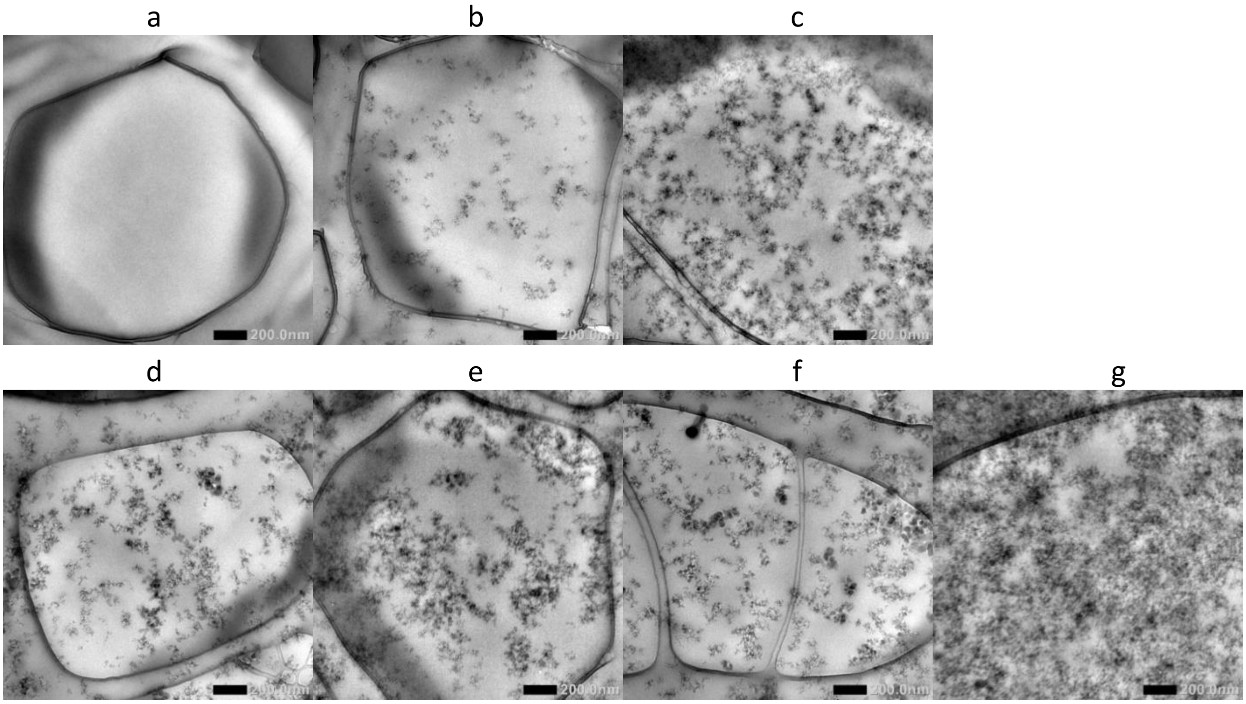

Figure 4. TEM images of pure siloxaneSil H/Vi 50/50(a) and their nanocomposites with 1 wt % of hydrophobic and hydrophilic fillerSil H/Vi 50/50-1hphob, Sil H/Vi 50/50-1hphil (b,c), 10 wt % of fillerSil H/Vi 50/50-10hphob, Sil H/Vi 50/50-10hphil (d,e) and 20 wt % of filler Sil H/Vi 50/50-20hphob, Sil H/Vi 50/50-20hphil(f,g) (scale bar = 200 nm)

3. 2. Mechanical properties of siloxane elastomers

Physical properties of elastomeric materials directly depend on the concentration of elastically active chains and the number and type of crosslink points, which in a certain way depend on the composition of the applied networking system. In the present work, the best mechanical properties of the elastomer were obtained with the ratio of vinyl and hydrogen siloxane precursors of 50:50 wt% (Table 4). By reducing the quantity of Sil Hleads to reduction in both the tensile strength and elongation at break, with the reduction in the tensile strength is more significant. This behavior can be explained by insufficient crosslinking in this material because due to the excess of vinyl siloxane in the system and consequently the presence of unreacted vinyl groups, as it was confirmed by FTIR (Fig. 3a). The increase in the content of Sil Halso leads to deterioration of mechanical properties, whereby reduction of the tensile strength is more significant in comparison to the reduction of elongation at break. In the case of Sil H excess, all vinyl groups reacted in the crosslinking reaction, the crosslinking was incomplete, *i.e*. dangling chains of unbounded poly(methyl-hydrogen-siloxane) were formed. These dangling chains additionally increased the elasticity, but led to the reduction in the material strength. The siloxane elastomer composition had an impact on the hardness of materials, and the sample Sil H/Vi 50/50 was the hardest, while the sample Sil H/Vi 40/60 exhibited the smallest hardness value due to the incomplete crosslinking reaction.

Behavior of elastomer nanocomposites depends primarily on specific molecular interactions at the boundaries of the filler and the polymer matrix. The complex constitution of nanomaterials is due to (a) the exotic nature of the pure elastomer, (b) sophisticated functionality of the active fillers, and (c) the processes of mixing the reactive components and crosslinking. Results of the mechanical testing showed the dependence of the mechanical properties on the filler content, with a trend of tensile strength increasing with the increase in the filler amount, Table 4. This behavior can be explained by the increase in the intermolecular interactions and more efficient networking at higher filler contents. Siloxanes are compounds that have a semi-organic molecular structure, in which the inorganic base consists of a main silica-like Si-O chain. For this reason, interactions of filler/siloxane matrix are stronger than in other combinations of silica fillers and other polymers, due to the same chemical structures. Also, surface functionalization has a strong influence on filler/polymer interactions, and decreasing the filler surface hydrophobicity decreases the compatibility of SiO_2 nanofiller and the hydrophobic siloxane matrix (*i.e*. in the case of the hydrophilic SiO_2 filler).

Table 4. Mechanical properties of prepared siloxane elastomers and their nanocomposites

Sample	Tensile strength, MPa	Elongation at break, %	Shore AHardness
Sil H/Vi 50/50	1.5	26	50
Sil H/Vi 60/40	0.6	20	48
Sil H/Vi 40/60	0.1	11.8	45
Sil H/Vi 50/50-1-h-phob	1.56	32	50
Sil H/Vi 50/50-5-h-phob	7.36	46	70
Sil H/Vi 50/50-10-h-phob	8.25	58	72
Sil H/Vi 50/50-20-h-phob	9.05	53	73
Sil H/Vi 50/50-1-h-phil	0.56	16.76	50
Sil H/Vi 50/50-5-h-phil	2.98	50.12	68
Sil H/Vi 50/50-10-h-phil	5.30	81.5	69
Sil H/Vi 50/50-20-h-phil	6.83	85.4	72

From the mechanical properties presented in Table 4 it can be concluded that the addition of nanosilicon(IV)-oxide leads to the increase in tensile strengths of the samples, whereby the increase is more significant at higher filler loadings that is samples with 10 and 20 wt% of the filler. The elongation at break also increases with the addition of the filler, so that the fillers, along with increasing the strength, increased the elasticity of the siloxane materials. This can be expected due to the same chemical composition of the filler and the matrix, so it that the silicon(IV)-oxide nanoparticles are very good fillers for adjusting the properties of the siloxane elastomers. Also a greater increase in the tensile strength of the nanocomposites with hydrophobic silicon(IV)-oxide can be noticed. For samples with hydrophilic fillers, a larger increase in the elongation at break was noticed, which can be explained by the lower degree of interactions of the hydrophobic siloxane matrix with a hydrophilic filler, compared to those with the hydrophobic one, resulting in a more elastic structure of siloxane nanocomposites. Stronger interactions of the hydrophobic filler (Fig. 1a) with the siloxane matrix, on the contrary, results in stronger materials with higher values of tensile strength. Addition of the filler increases hardness of composites, as it was expected, while it was not affected by the type of filler modification.

3. 3. Thermal properties of siloxane materials

Molecular structure had a slight effect on the crystalline melting temperature (T_m) of pure elastomers (Table 5 and Fig. 5). With the increase in the Sil H content in elastomers, the melting temperature decreased from -54 to -57 °C (Fig. 5a). This finding can be explained by the increased chain mobility of Sil Has its content increased, especially in the sample Sil H/Vi 60/40, due to the unbounded poly(methyl-hydrogensiloxane) chains.

The increase in the nanofiller loading significantly affected thermal properties of siloxane elastomers. In pure silicon elastomers (Sil H/Vi 50/50) melting temperatures were about -56 °C, but with addition of the nanofiller, T_m values changed.

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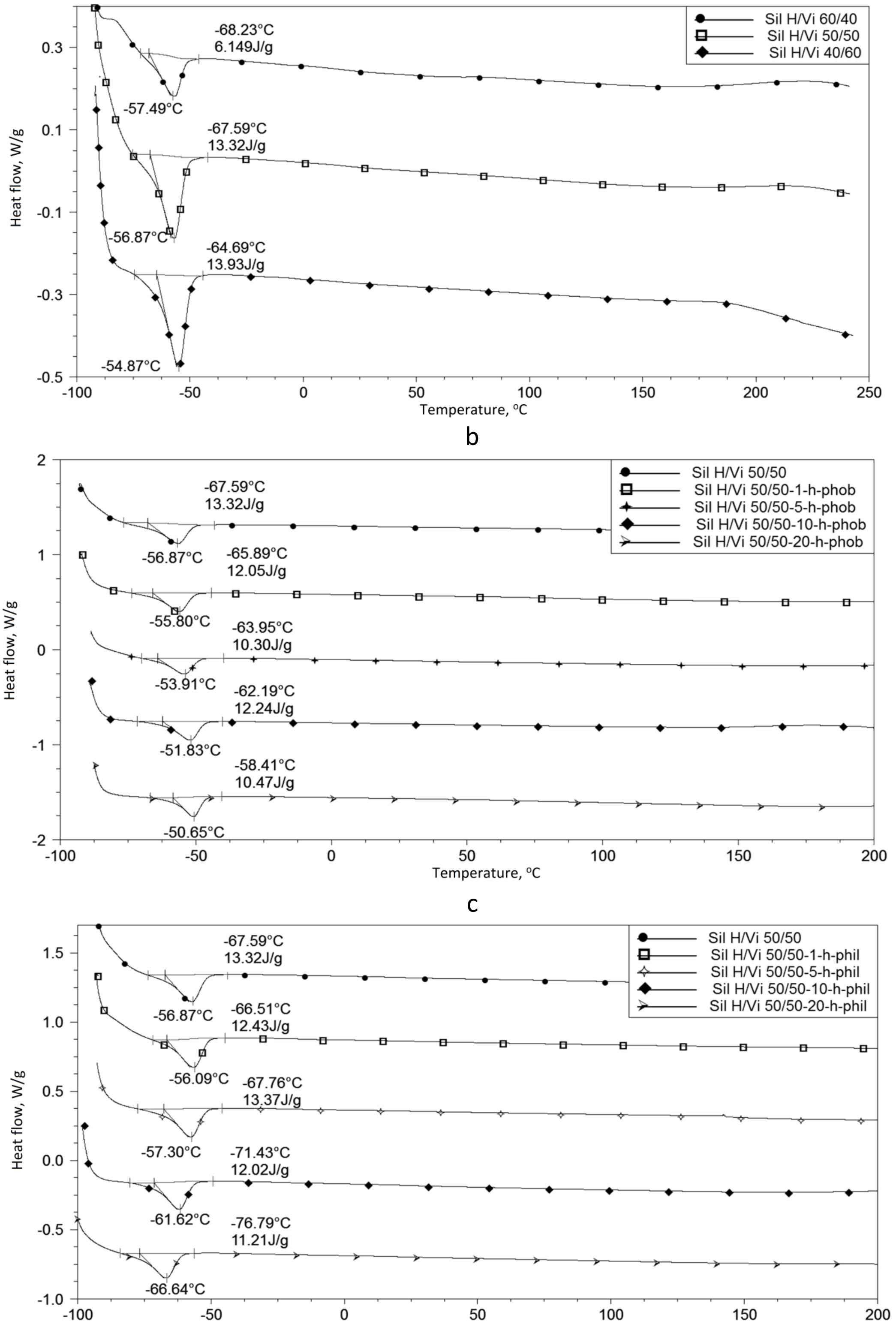

Figure 5. DSC thermograms of the silicon elastomers (a) and their nanocomposites with hydrophobic (b) and hydrophilic (c) fillers(exo up)

Namely, addition of the hydrophobic silica filler resulted in an increase of T_m values, probably due to strong filler/polymer interaction (Fig. 1a).Lower compatibility of the hydrophobic matrix and hydrophilic filler caused a decrease in T_m values, because the filler/polymer interactions were weaker. With addition of both nanofiller types a slight decrease in the melting enthalpy was observed for all samples, probably because the fillers caused disordering of polysiloxane chains.

3.4. Thermal stability of siloxane elastomers

Thermal stability can be quantified by the temperature of the onset of material decomposition (T_{ons}) at controlled heating. Temperatures reached at the predefined weight loss, usually 5, 10 or 50%, can be also compared. Many changes in physical and chemical properties can be observed during exposure of elastomeric materials to high temperatures. These changes can be divided into three types: a) subsequent crosslinking that results in higher network densities and increased material brittleness due to generation of additional crosslink points; b) chain breakage (degradation), and c) chemical changes in the polymer chain with formation of polar or other groups. Thermal energy required to degrade the polysiloxane chain is much higher than that required for most other polymer materials. This indicates high bond strength between silicon and oxygen in the main polymer chain.

Table 5.Thermal properties of siloxane elastomers and their nanocomposites

Sample	T_m (DSC) / °C	T_{ons}/ °C	$T_{5\%}$/°C
Sil H/Vi 50/50	-56.87	367	373
Sil H/Vi 60/40	-57.49	380	386
Sil H/Vi 40/60	-54.87	355	359
SilH/Vi 50/50-1-h-phob	-55.80	361	381
SilH/Vi 50/50-5-h-phob	-53.91	375	389
SilH/Vi 50/50-10-h-phob	-51.83	380	388
SilH/Vi 50/50-20-h-phob	-50.65	384	391
SilH/Vi 50/50-1-h-phil	-56.09	375	383
SilH/Vi 50/50-5-h-phil	-57.30	380	390
SilH/Vi 50/50-10-h-phil	-61.62	384	392
SilH/Vi 50/50-20-h-phil	-66.64	387	394

Thermal decomposition of siloxane can be caused by different chemical processes depending on the conditions in the environment, and may be related to hydrolysis of siloxane bonds, exchange of siloxane bonds, oxidation of hydrocarbon groups, which form crosslinks, oxidation of hydrocarbon side groups, depolymerization, condensation of silanol groups, as well as formation of silicates, which all can lead to deterioration of physico-mechanical properties [31].

Thermal stability of siloxane elastomeric samples with a content of Sil V less than 60 wt% was almost identical (Fig. 6). Thermal decomposition of pure elastomers starts with decomposition of siloxane groups at temperatures higher than 350 °C, whereby thermal stability of the SilH/Vi 40/60 elastomer was the lowest. This is expected due to the chemical structure of the vinyl siloxane macromolecule and due to the decrease in the Sil H content that affects the crosslinking density of the polymer network. With the increase in the Sil H content, thermal stability of elastomers increased along with the increase in the residue at 700 °C due to a slightly higher content of Si in Sil H siloxane.

The used silicon(IV)-oxide fillers significantly improved thermal stability of the siloxane elastomeric nanocomposites (Fig. 7). This finding is due to the increased interactions between silicon(IV)-oxide and silicon matrix, as well as due to the increased proportion of silicon(IV)-oxide particles. A sample containing 1 wt% of hydrophobic silicon(IV)-oxide did not show significant differences in thermal stability compared with a pure siloxane elastomer, whereas each subsequent increase in the amount of hydrophobic silicon(IV)-oxide caused greater thermal stability then that of the unloaded siloxane matrix (Fig. 7a). The highest thermal stability improvement was achieved with the highest filler loading (*i.e.* 20 wt%), so that T_{ons}increased for almost 20 °C. This result shows effectiveness of the silicon(IV)-oxide filler for the thermal stability improvement of elastomeric nanocomposites.

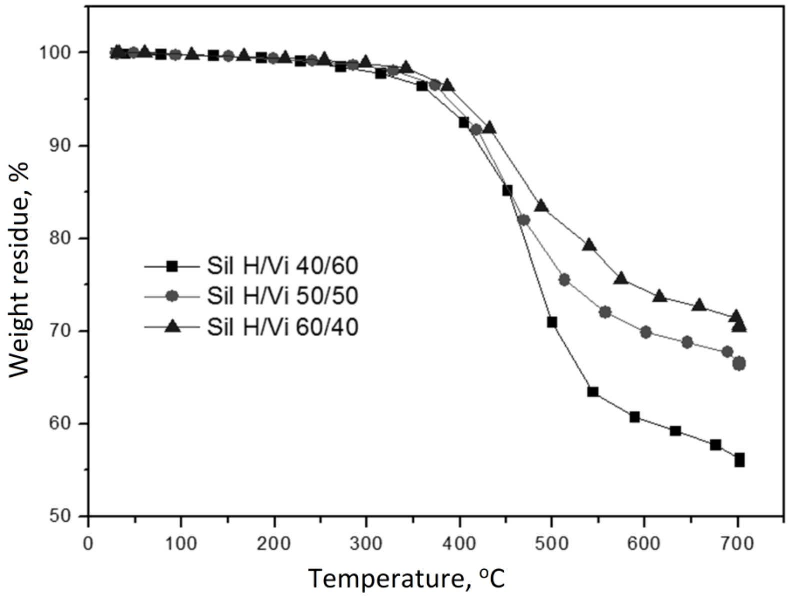

Figure 6. Thermogravimetric curves of siloxane elastomers based on different hydrogen/vinyl ratios

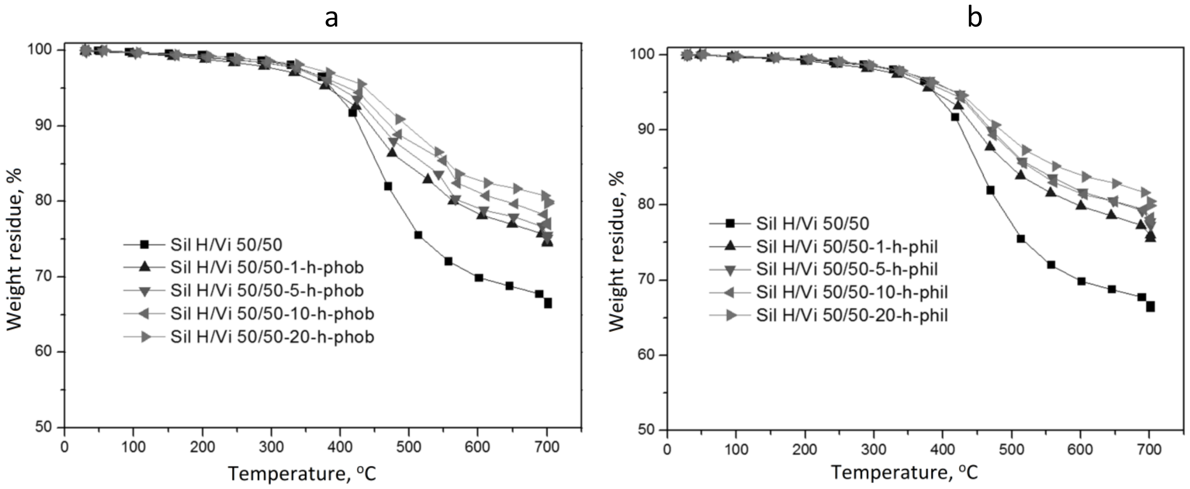

Figure 7. Thermogravimetric curves of siloxane elastomers and their nanocomposites with a hydrophobic (a) and hydrophilic filler(b)

The siloxane composite sample with 20 wt% of the filler (hydrophobic or hydrophilic) lost only 20 % of its weight at temperatures above 700 °C, which indicated that these materials can be used at very high temperatures. It can be observed that thermal stability of the elastomeric nanocomposites with hydrophilic silicon(IV)-oxide was better as compared to the ones with the hydrophobic filler. Differences in thermal stability were observed as a function of the calcination temperature, which could be related to physical interactions of siloxane chains with silanol groups (Si-OH) on the surface of silicon(IV)-oxide, according to the number of silanol groups. Interactions between the siloxane matrix and hydrophilic fillers should be weaker under these conditions and heat transfer easier, increasing the temperature of degradation (Fig. 7b). The network of the hydrophilic filler, confirmed by TEM analysis (Fig. 4e,g), also increased the degradation temperature of nanocomposite elastomers. However, in all cases, interactions of the filler with the matrix nevertheless increased the decomposition temperature of elastomeric nanocomposites [32]. Thermal stability of the nanocomposite elastomer with 20 wt% of hydrophilic silicon(IV)-oxide was the highest as compared to the other samples.

Differential thermogravimetric (DTG) curves of the synthesized silicon elastomers and their nanocomposites with hydrophobic and hydrophilic fillers are shown in Figure 8. It was found that all the synthesized samples had one degradative step during thermal degradation, which probably indicates the existence of a single degradation mechanism. DTG curves had similar shapes for samples with different hydrogen/vinyl ratios, and the maximum degradative peaks are shifted to higher temperatures with decreasing the Sil V content in elastomers. Also, increasing the silica nanoparticle amount in the siloxane matrix, caused shifting of these degradative peaks to 511 and 517 °C, for samples with hydrophobic and hydrophilic fillers, respectively, both higher than this of the pure elastomer (487 °C) (Fig. 8b,c). These characteristic temperatures at DTG maxima, which were shifted to higher values, are likely attributed to stronger interactions between the siloxane matrix and silicon(IV)-oxide nanofillers [32].

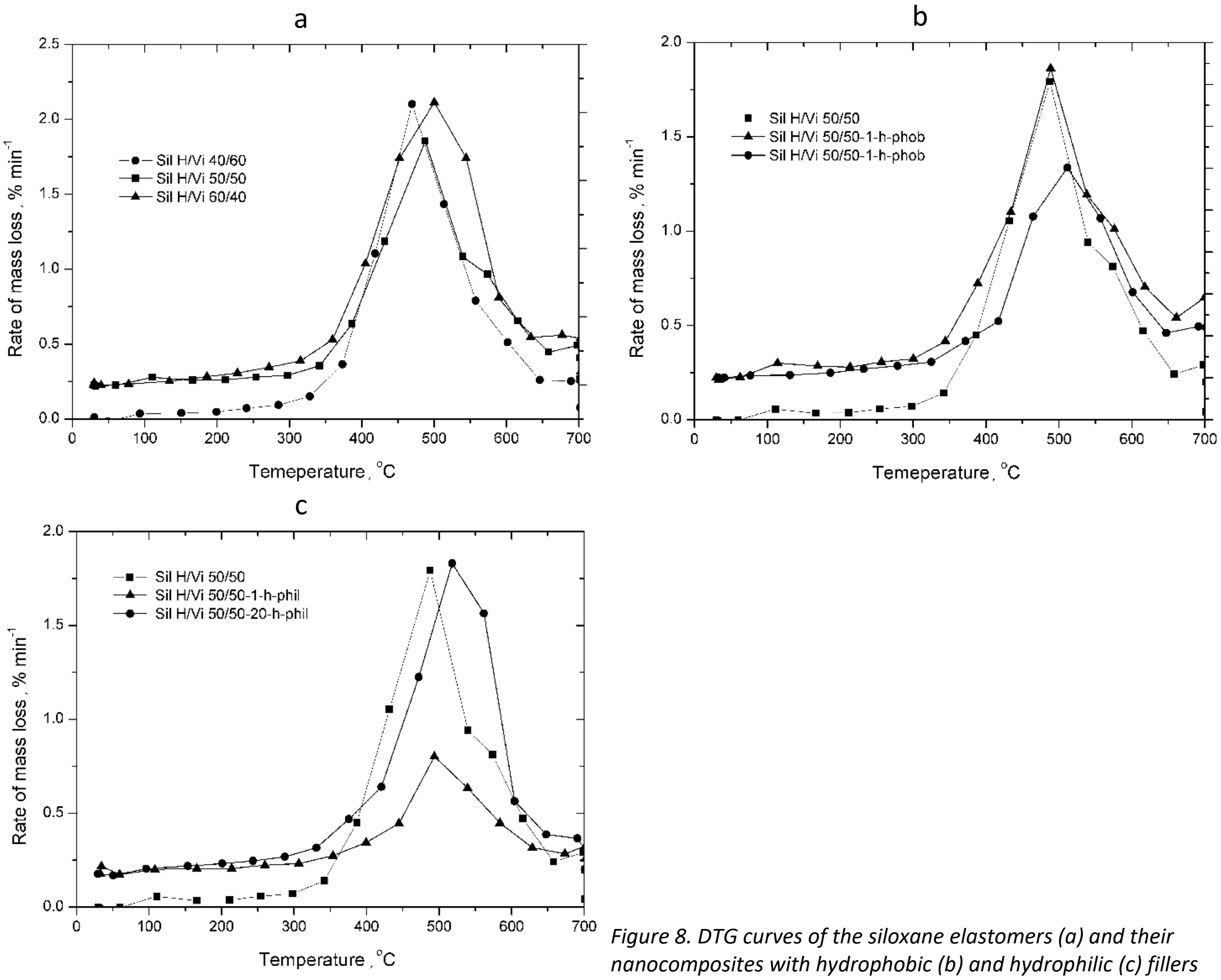

Figure 8. DTG curves of the siloxane elastomers (a) and their nanocomposites with hydrophobic (b) and hydrophilic (c) fillers

It can be noticed that thermal stability of the obtained elastomeric materials is substantially improved by addition of the nanofillers that are industrially acceptable for certain types of elastomers. The improvement of the thermal stability is due to strong interactions between silicon(IV)-oxide and polymer matrix, as well as due to the increased content of silanol and siloxane functional groups within silicon(IV)-oxide.

4. CONCLUSIONS

In this paper, the influence of nanoparticles on the properties of elastomeric materials based on different siloxane precursors was investigated. FTIR spectroscopy confirmed the presumed structure of the polysiloxane and the obtained siloxane elastomeric nanocomposites. It was found that the addition of silicon(IV)-oxide nanoparticles leads to an increase in hardness and tensile strength of the siloxane elastomers. This increase is more significant at larger filler contents, that is for samples with 10 and 20 wt% of the filler. The fillers, along with inducing the increase in the strength, increased elasticity of the siloxane materials. The improvement in mechanical properties is the result of an increase in the crosslinking network density. Thus, it has been shown that the silicon(IV)-oxide fillers are suitable for adjusting the properties of siloxane elastomers. DSC results indicate that addition of the hydrophobic silica filler increased T_m values, but the hydrophilic filler caused a decrease in these values, due to the lower compatibility of the filler and the polymer matrix in the latter case. It was observed that thermal stability of the obtained elastomeric materials was substantially improved by the addition of silicon(IV)-oxide nanoparticles, which are industrially acceptable. The highest increase in thermal stability was observed for the sample with 20 wt% of the hydrophilic filler, which can be attributed to the presence of siloxane functional groups within the silica and the formed filler network due to the lower compatibility of this filler and the hydrophobic siloxane matrix.

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SAŽETAK

Uticaj nano punila na svojstva silikonskih elastomernih materijala

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(Naučni rad)

Silikoni, tačnije polisiloksani, predstavljaju jednu od najzanimljivijih klasa polimernih materijala, usled svojih izvanrednih svojstava (kao što su elastičnost, hemijska otpornost, biokompatibilnost itd) koja se mogu unaprediti dodavanjem mikro i nanopunila. U ovom istraživanju proučavan je uticaj nanočestica silicijum(IV)-oksida (sa hidrofobno i hidrofilno funkcionalizovanom površinom) na svojstva silikonskih elastomera. Siloksanski elastomeri su sintetisani na bazi α,ω-divinilpoli(dimetil-siloksana) i poli(metil-hidrogensiloksana), dok su za dobijanje nanokompozita dodati različiti udeli nanopunila (1, 5, 10 i 20 mas.%). FTIR spektroskopija je korišćena za analizu hemijske strukture dobijenih materijala, a rezultati su potvrdili pretpostavljeni mehanizam reakcije umrežavanja siloksana. Primenom TEM analize potvrđena je dobra disperzija hidrofobnih punila u polimernoj matrici, dok je u slučaju hidrofilnog punila uočena mreža nanopunila u uzorku siloksanskog nanokompozita. Tip funkcionalizacije površine nanopunila nije pokazao značajniji uticaj na tvrdoću dobijenih materijala, dok je kod uzorka sa najvećim udelom hidrofobnog punila uočena najveća vrednost zatezne čvrstoće. Na osnovu DSC analize pokazano je da je smanjena kompatibilnost između hidrofobne matrice i hidrofilnog punila dovela do smanjenja vrednosti temeratura topljenja kod kompozitnih matrijala, i najmanja vrednost je uočena kod uzorka sa najvećim udelom hidrofilnog silicijum(IV)-oksida. Rezultati TGA analize su pokazali da porast sadržaja nanopunila prouzrokuje povećanje termičke stabilnosti dobijenih hibridnih materijala.

Ključne reči: Nanokompoziti; siloksanski elastomeri; vinil siloksani; termička svojstva, polimerne mreže, elastomerni materijali