INFLUENCE OF NANOFILLERS AND MASTERBATCH ON PROPERTIES OF SILOXANE MATERIALS

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Nanocomposites based on siloxane and silicon(IV)oxide nanoparticles (with a hydrophilic and hydrophobic surface) were synthesized to design the desired final properties of the composite material. Masterbatch, a mixture of siloxane containing vinyl functional groups and reinforcing fillers, was added to improve the mechanical properties and topology of siloxane networks. Silicon(IV)oxide was added in amounts of 1, 5, 10, and 20 wt% and masterbatch in amounts of 5 and 10 wt% to examine the effect of the amounts of fillers and masterbatch in the synthesized samples. Fourier transform infrared spectroscopy was used to analyze the chemical structure of the obtained materials. Transmission electron microscopy (TEM) was used to examine the dispersion of filler particles in siloxane nanocomposites. To examine the thermal stability and phase transition temperature of siloxane materials, thermogravimetric analyzes (TGA) and differential scanning calorimetry (DSC) were performed. The addition of masterbatch did not lead to a significant difference in melting temperature, but stoichiometry was disturbed, which decreased the thermal stability compared to samples without masterbatch. The addition of masterbatch to nanocomposites with hydrophilic fillers increases both elongations at break and tensile strength. According to the results, the combination of masterbatch and nanofillers affects the properties of siloxane materials, which could enable obtaining materials with the desired properties.

Introduction

Technological progress and the increasing demands of modern society are paving the way for the development of novel hybrid materials, which show improved properties compared to the materials from which they are obtained. Composite materials are obtained by inserting usually inorganic filler into a "matrix" material that is usually organic (polymer). The structural elements that are inserted into the matrix are generally in sizes ranging from millimetres to nanoscale. Reducing the dimensions of the inorganic phase leads to homogeneous dispersion which allows further manipulation with the properties of the final material [1]. Today, several polymeric materials are used as a polymer matrix for obtaining nanocomposite materials with different properties, but siloxane materials are increasingly imposed as suitable from the aspect of obtaining nanocomposites with outstanding physical and mechanical properties [2,3]. Poly(organosiloxanes), of general formula -(SiR2–O)n–, are the first commercial and today the most important representatives of polymers with a completely inorganic main chain structure. The combination of "organic" groups and "inorganic" main chains in siloxanes gives them unique properties and allows their application in many areas [4-7]. However, due to some characteristic properties such as low reactivity, low compatibility with water and low solubility in polar and non-polar solvents, poor mechanical properties, silicone materials are not suitable for certain applications. There are more and more studies and researches on how to improve their properties and reduce their shortcomings. By changing the chain length, adding different organic groups to the polysiloxane molecule, and adding different fillers, their properties can be changed [8].

Fillers are an essential component in most siloxane elastomers. Some of the fillers most commonly used to improve their properties are montmorillonite [9], metal oxide nanoparticles [10, 11], graphene [12], carbon nanotubes [13] and fumed silica [14, 15]. For in situ synthesised PDMS/sepiolite nanocomposites, different polymer/filler interaction relationships were investigat-

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ed and the results showed that good filler dispersion in the polymer matrix significantly contributes to the improvement of thermal and mechanical properties of composite materials [16]. Moni et al. investigated the thermal properties of polysiloxane-derived ceramics depending on the type of carbon nanofillers used. The nanofillers used had a positive effect on thermal stability by shifting the decomposition temperature towards higher values [17]. Crosslinking and incorporation of silicates as fillers into the polysiloxane matrix usually minimized the disadvantages of siloxanes (poor mechanical properties and high costs) [18]. The behaviour of silicon(IV)oxide in certain environments is also influenced by the chemistry of the surface of the given particles, i.e. characteristic functional groups that are incorporated on the surface in the post-production process. The essential difference between hydrophobic and hydrophilic silicon(IV)oxide is actually in the difference between siloxane and silanol functional groups (Figure 1). As silanol functional groups are hydrophilic, they are, in fact, the cause of the hydrophilic character of the silicon(IV)oxide containing them, while silicon(IV) oxides with siloxane groups have a hydrophobic character. Silicate is a useful additive for improving various properties of many polymers (thermal stability, mechanical strength, insulating properties etc.). Previous research has shown that the addition of nano-silica sol to polyimide composite films can improve their thermal behaviour, permeability and mechanical properties [19]. The effect of the amount of nano-silica sol on the optical properties, thermal stability and mechanical properties of PDMS nanocomposites were investigated. The obtained results showed that increasing the amount of nano-silica sol leads to a slight decrease in the transparency of PDMS nanocomposites, but significantly improves the mechanical properties and resistance to degradation at high temperatures [20]. In our previous work, by Manjenčić et al. [21] the effect of nanosilicon(IV)oxide with differently functionalized surfaces on the mechanical and thermal properties of siloxane elastomers was investigated. It was found that the thermal stability of the obtained siloxane nanocomposites was significantly improved by the addition of nanoparticles of silicon(IV) oxide. Also, it was observed that there was an increase in the elasticity of the synthesized materials with the addition of nanoparticles of silicon(IV)oxide, as well as an increase in tensile strength and hardness. This has shown that the properties of siloxane elastomers can be adjusted with silicon(IV)oxide fillers.

To our knowledge, no report illustrates the effect of masterbatch on the properties of siloxane materials. We assumed that combining the benefits of nanosilicon(IV) oxide and masterbatch can be a promising and attractive way for the preparation of high-performance polymer nanocomposites. In order to improve, primarily the mechanical properties, but also the topology of the siloxane networks themselves, a masterbatch (a highly filled mixture of siloxanes containing vinyl functional groups and reinforcing fillers) was added. A masterbatch containing 3.8 wt% SiO_2 was used in this work.

In this work, siloxane elastomer and its nanocomposites were prepared using a masterbatch as a reactive component for the first time. The effects of the addition of masterbatch in combination with different types and amounts of silicon(IV)oxide on the mechanical properties and thermal behaviour of the siloxane nanocomposites are discussed in detail.
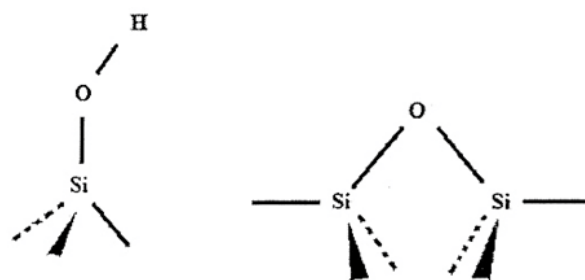

Figure 1. Silanol (left) and siloxane (right) groups

Materials and methods ——————————————————————

Materials

As precursors for siloxane elastomer synthesis α,ω-divinyl-poly(dimethylsiloxane) ViPDMS, (SFA 42500) and poly(methyl hydrogen siloxane), HPDMS, (SFA 11230) are used. MQ silicone resin (ALPA-RETARD A) as a crosslinking retarder and platinum complex in poly(dimethylsiloxane), (ALPA-KAT 1) as a catalyst, were used. As a reactive component, a preformulated concentrate masterbatch (vinyl content of 0.06 mmol g⁻¹) was used. All siloxane materials were supplied from CHT GMBH BEZEMA. Hydrophobic silicon(IV)oxide (Aerosil R 972) and hydrophilic silicon(IV)oxide (Aerosil A 200) are provided from Degussa.

Synthesis

Siloxane elastomers obtained from ViPDMS and HPDMS were prepared and tested. Also, nanocomposites with different content of hydrophobic and hydrophilic silicon(IV)oxide as fillers with the addition of masterbatch were synthesized. In order to examine the influence of nanofiller and masterbatch on the properties of silicone elastomer, a series of nanocomposites with 5 and 10 wt% of masterbatch and 1, 5, 10, and 20 wt% of functionalized silicon(IV)oxide nanoparticles (both hydrophobic and hydrophilic) were synthesized.

Silicone elastomers were synthesized with hydrogen functionalized and vinyl silicones in a 50:50 wt:wt ratio. The syntheses were performed with the addition of 0.2 wt% catalysts and 0.4 wt% crosslinking retarders. The mixing of the reaction components proceeded in the following order: first vinyl siloxane was added, then a crosslinking inhibitor was added to the reaction balloon and homogenized by mechanical stirring for a period of two minutes. After that, the crosslinking catalyst was added and homogenized for additional two minutes, after which hydrogen siloxane was added and the re-

action mixture was homogenized for 10 more minutes. The masterbatch in amounts of 5 or 10 wt% was added together with hydrogen siloxane. After homogenization of all components, the samples were curred at 80 °C into moulds. For nanocomposite preparation, nanoparticles were added together with all components and mixed for 20 minutes. Before being poured into the mould, the mixture with nanoparticles was treated in an ultrasonic bath for 5 minutes and then poured into the mould and crosslinked, according to the mechanism shown in

Figure 2. The cross-linking was accelerated by heating all samples for 10 min at 80 °C. However, it has been observed that with increasing silicon(IV)oxide content, the crosslinking time is extended. The time for final crosslinking was longer for samples obtained by the addition of hydrophilic filler, compared to the samples with hydrophobic silicon(IV)oxide. It has also been observed that the addition of a masterbatch prolongs the crosslinking time. The material composition of the siloxane-based elastomer, as well as its nanocomposites, is given in Table 1.
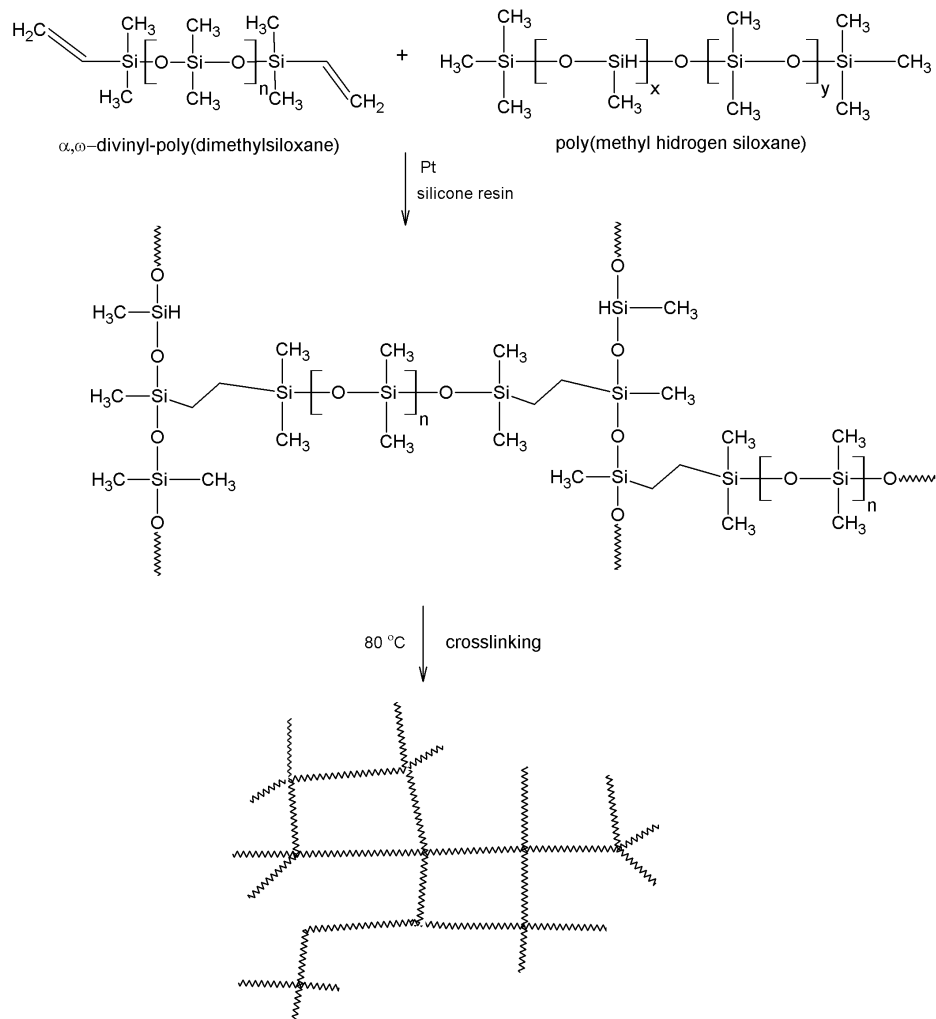

Figure 2. Schematic representation of proposed crosslinking of siloxane elastomers

Table 1. The raw material composition of siloxane elastomer and its nanocomposites with the addition of masterbatch

Sample label	Component				
	HPDMS, wt%	ViPDMS, wt%	SiO_2 - hydrophobic, wt%	SiO_2 - hydrophilic, wt%	Masterbatch, wt%
Siloxane-El	50	50	/	/	/
Siloxane-1-phobSil-5Mb	50	50	1	/	5
Siloxane-5-phobSil-5Mb	50	50	5	/	5
Siloxane-10- phobSil-5Mb	50	50	10	/	5
Siloxane-20- phobSil-5Mb	50	50	20	/	5
Siloxane-1-philSil-5Mb	50	50	/	1	5
Siloxane-5-philSil-5Mb	50	50	/	5	5
Siloxane-10-philSil-5Mb	50	50	/	10	5
Siloxane-20-philSil-5Mb	50	50	/	20	5
Siloxane-1-phobSil-10Mb	50	50	1	/	10
Siloxane-5-phobSil-10Mb	50	50	5	/	10
Siloxane-10-phobSil-10Mb	50	50	10	/	10
Siloxane-20-phobSil-10Mb	50	50	20	/	10
Siloxane-1-philSil-10Mb	50	50	/	1	10
Siloxane-5-philSil-10Mb	50	50	/	5	10
Siloxane-10-philSil-10Mb	50	50	/	10	10
Siloxane-20-philSil-10Mb	50	50	/	20	10

Characterization

Thermo-Nicolet Nexus 670 (Thermo Fischer Scientific, USA) FTIR spectrophotometer in ATR mode was used for evaluation of the chemical structure of obtained siloxane samples. The recording of samples was performed at a resolution of 4 cm^{-1}, with 100 scans per sample, on the crystals of germanium.

The morphology of the samples as well as the dispersion of silicon(IV)oxide particles in siloxane nanocomposites were investigated on a JEOL JEM-2800 transmission electron microscope (TEM). For TEM analysis, samples were excised using a Leica UC7 ultramicrotome. Thin samples, were cut to be 100 nm thick at -150 °C.

Mechanical properties of synthesized samples were analysed using a universal testing machine Shimadzu EZ-LX (Japan) according to the procedure defined by ASTM 412-98a standard (with a cross-head speed of 10 cm min^{-1}). The hardness of obtained siloxane and siloxane-based nanocomposites were measured on durometer model 306L type A (USA) (in Shore A units) according to the ASTM D2240 standard.

DSC Q20, TA Instruments, the analyser was used to investigate the thermal properties of obtained samples. For the analysis, 3-5 mg of sample sealed in aluminium pans were used. First, the samples were heated from 25 °C to 180 °C in a dynamic mode at a heating rate of 10 °C min-1, then cooled to -90 °C at a rate of 10 °C min^{-1}, and then heated to 200 °C at a heating rate of 10 °C min^{-1}. Using the DSC method, data on the temperature regions of melting of the synthesized samples were obtained.

To analyze the thermal stability of the siloxane materials, the thermogravimetric analyzer TGA Leco was used. Samples were analysed in the temperature range from 25 to 700 °C with a heating rate of 20 °C min-1 in the air atmosphere with a gas flow of 50 cm^3 min^{-1}.
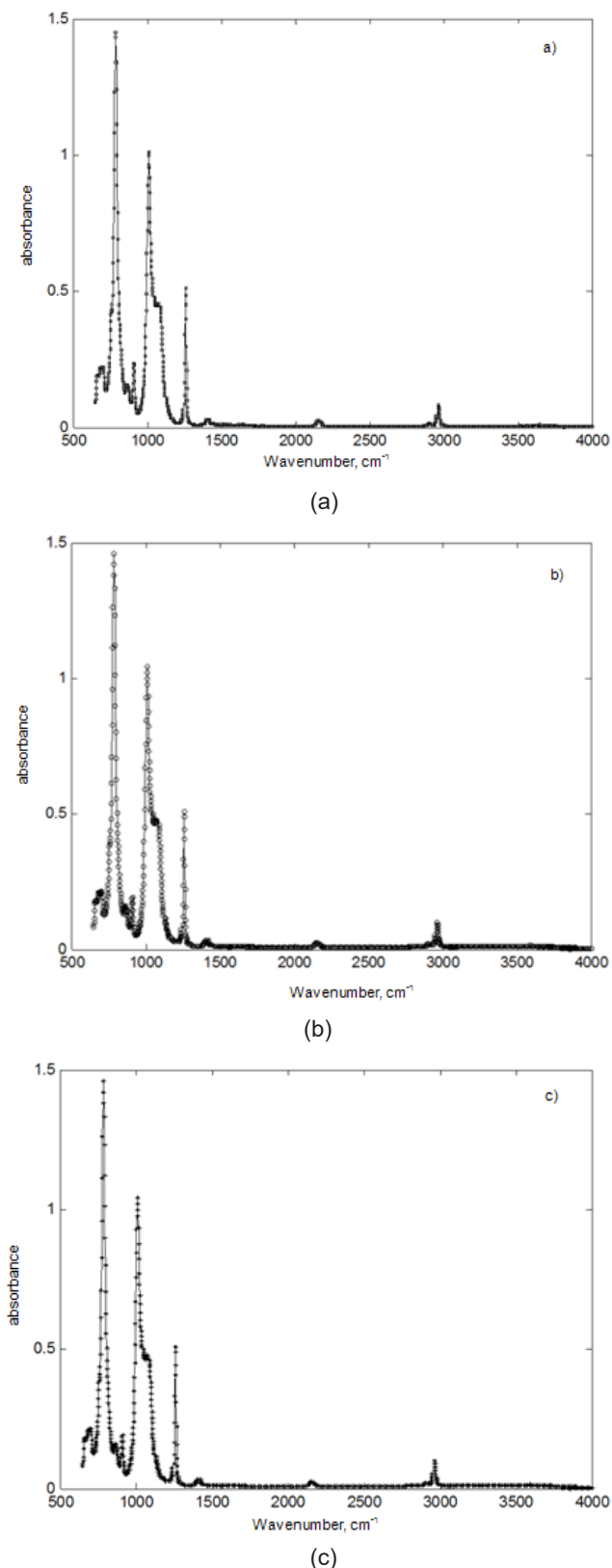
(a)

(b)

(c)

Figure 3. FTIR spectra of samples: a) Siloxane-El, b) Siloxane-5-philSil-10Mb and c) Siloxane-5-phobSil-10Mb

Table 2. Wavelengths of characteristic functional group in the FTIR spectrum of synthesized siloxane elastomer

Wavelength, cm^{-1}	Functional groups
790	Si-C and CH$_3$ twisting
1000	Si-O
1100	Si-O-Si
~1250	(CH$_3$)$_3$, Si
~1270	Si-CH$_3$
~1420	CH$_2$ bending
1450	Asymmetric stretching CH$_3$
3000–2800	CH$_3$ and CH$_2$ group

Results and discussion

The FTIR spectra of obtained samples Siloxane-El, Siloxane-5-philSil-10Mb and Siloxane-5-phobSil-10Mb are shown in Figure 3 and Table 2, on which the characteristic peaks of siloxane materials are clearly visible. The addition of masterbatches to Siloxane-El samples does not affect the movement of the peaks (not even the addition of 10 wt%), although they carry a certain content of vinyl, probably because the system can subsequently crosslink with residual H from poly(methyl-hydrogen siloxane), so the C=C bond peaks (occurring at wavelengths around 1600-1650 cm^{-1}) cannot be observed, as well as due to their low concentration and immersion in the crosslinked structure of the siloxane network.

Based on the results of the mechanical properties of elastomeric nanocomposites presented in our previous work [21] it can be concluded that tensile strengths of the samples increased with the addition of silica nanofillers, with a more significant increase at higher filler loadings. With the addition of the filler, elongation at break also increases so the nanosilica fillers can be used to optimize the mechanical properties of siloxane nanocomposites.

Thus, the similarity in the chemical structure of the hydrophobic silica and the siloxane polymer matrix enables strong polymer/filler interactions, which improved the mechanical properties of obtained nanocomposites (increasing both tensile strength and elongation at break). In the Siloxane-El system with hydrophobic particles, as expected, the addition of a masterbatch does not lead to a significant increase in the tensile strength, because there are very few unreacted places in the PDMS chains, so the orderliness, i.e. regularity and additional crosslinking of the elastomer itself are lower, both in the case of the addition of 5 wt% and the addition of 10 wt% MB. This claim is supported by a slight decrease in the elasticity of the sample (due to additional crosslinking). Since the surface of hydrophilic particles is less compatible with the hydrophobic matrix and they form aggregates by establishing hydrogen bonds (which is shown by TEM analysis in Figure 7f) the polymer/filler interaction is significantly weaker, so the values of mechanical properties are lower [21]. But the addition of 5 wt% MB to nanocomposites with hydrophilic fillers multiplies the stress

Table 3. Mechanical properties of prepared siloxane elastomer and its nanocomposites with the addition of masterbatch

Sample label	Tensile strength, MPa	Elongation at break, %	Hardness
Siloxane-El	1,5	26	50
Siloxane-1-phobSil-5Mb	1,66	31,13	57
Siloxane-5-phobSil-5Mb	7,1	39	60
Siloxane-10- phobSil-5Mb	11,2	45,7	70
Siloxane-20- phobSil-5Mb	11,8	43,83	70
Siloxane-1-philSil-5Mb	0,62	17,6	60
Siloxane-5-philSil-5Mb	3,6	53,1	65
Siloxane-10-philSil-5Mb	6,86	84,16	68
Siloxane-20-philSil-5Mb	7,5	92	72
Siloxane-1-phobSil-10Mb	1,7	30,16	61
Siloxane-5-phobSil-10Mb	7,65	36,26	65
Siloxane-10-phobSil-10Mb	11,68	42,7	75
Siloxane-20-phobSil-10Mb	12,21	44.26	78
Siloxane-1-philSil-10Mb	0,64	18,15	62
Siloxane-5-philSil-10Mb	4	43,3	67
Siloxane-10-philSil-10Mb	8,31	87	75
Siloxane-20-philSil-10Mb	8,9	90,3	77

because, in addition to subsequent crosslinking with vinyl from the masterbatch, the mentioned filler/polymer interactions occur, increasing tensile strength and elongation at break, and the effect is more pronounced with the addition of 10 wt% masterbatches (Table 3).

The addition of filler increased the hardness of all synthesized samples, regardless of the type of surface modification. As expected, the highest hardness was shown by samples with 20% by weight of filler and the maximum values ranged up to 73 Shore A [21]. The addition of masterbatch had an additional increase in the hardness of the samples due to the addition of a new amount of filler, so the hardness values of the samples with the addition of masterbatch reached values up to 78 Shore A (Table 3).

Analysis of thermal properties of synthesized siloxane elastomer and its nanocomposites with the addition of hydrophilic and hydrophobic nano silicon(IV)oxide filler and masterbatch was performed using DSC devices, and the obtained thermograms are shown in Figure 4. The melting temperature (T_m) of pure siloxane elastomer was -56.87 °C. The addition of nanofillers leads to significant changes in this value in all synthesized samples, with hydrophobic or hydrophilic fillers. In particular, the addition of hydrophobic particles of silicon(IV)oxide and masterbatches increases the values of Tm, which are presumed to be caused by a strong nanofiller/polymer matrix interaction. In the case of adding hydrophilic SiO_2 and masterbatches, the melting temperature decreases, which we assume is due to poor compatibility of the hydrophobic matrix and hydrophilic nanofiller, which is why the nanofiller expresses the behaviour of plasticizers. Comparing the results from the work in which silox-

ane samples contain only hydrophilic nanofiller [21], it is noticed that the addition of masterbatches reduces the plasticizing effect of SiO_2 and the difference in melting temperature. The amount of masterbatch added in the samples did not significantly affect the T_m. Thus, in the case of the Sil H/Vi50/50-20-h-phob-5MB sample, the melting temperature was -50.87 °C, and -49.68 °C for the same sample with the addition of 10wt% masterbatch (Figure 4).

Thermal properties can also be monitored through the change in melting enthalpy (Table 4). The melting enthalpy of the pure siloxane elastomer (Sil H/Vi 50/50) is 13.32 J g^{-1}. The addition of both types of nanoparticles and masterbatch affects a slight decrease in the value of melting enthalpy of the samples, while the decrease is much more prominent for nanocomposites with hydrophobic filler. The addition of masterbatches in nanocompositesiloxane networks does not lead to significant changes in T_m values and melting enthalpy compared to samples without masterbatch, because it does not show a significant plasticization effect. The situation is the same with the addition of a larger amount of masterbatch (10 wt%).
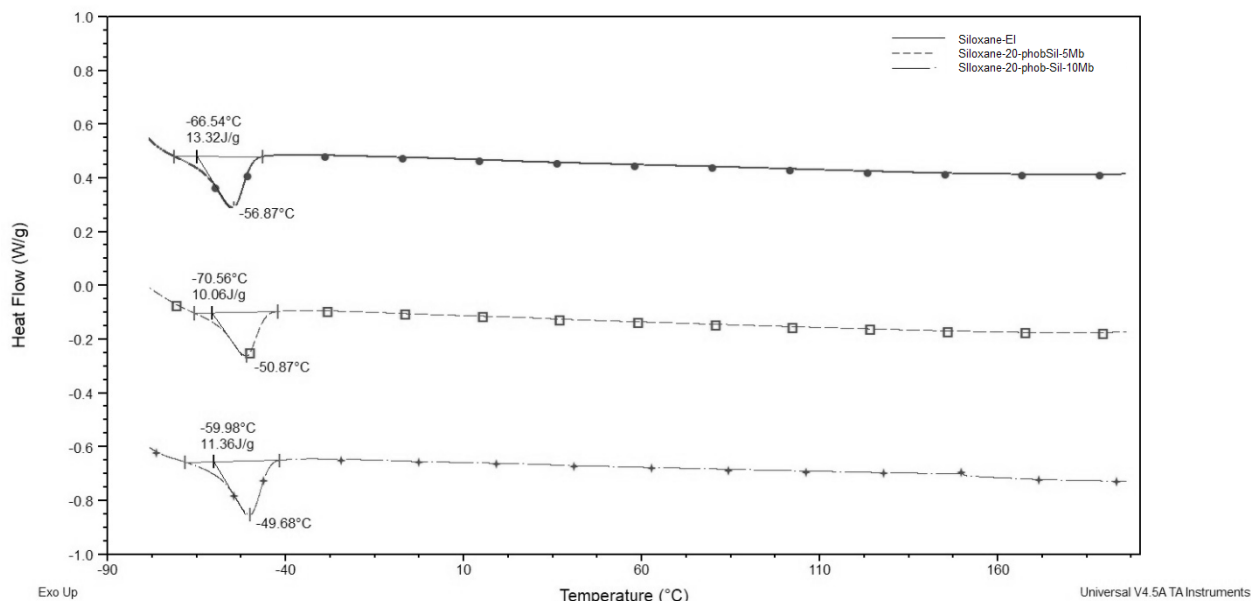
Figure 4. DSC thermograms of siloxane elastomer (Siloxane-El) and its nanocomposites with the addition of 5 wt% and 10 wt% of masterbatch

Table 4. Thermal properties of synthesized siloxane elastomer and its nanocomposites with the addition of masterbatch

Sample	T_m, °C	Enthalpy of melting, J g^{-1}
Siloxane-El	-56,87	13,32
Siloxane-1-phobSil-5Mb	-55.53	11.35
Siloxane-5-phobSil-5Mb	-51.08	10.12
Siloxane-10- phobSil-5Mb	-51.65	11.11
Siloxane-20- phobSil-5Mb	-50.87	10.06
Siloxane-1-philSil-5Mb	-55.21	10.98
Siloxane-5-philSil-5Mb	-52.47	11.09
Siloxane-10-philSil-5Mb	-51.69	12.45
Siloxane-20-philSil-5Mb	–49.68	11.36
Siloxane-1-phobSil-10Mb	-56.98	11.68
Siloxane-5-phobSil-10Mb	-58.61	11.96
Siloxane-10-phobSil-10Mb	-59.31	11.02
Siloxane-20-phobSil-10Mb	-59.71	11.35
Siloxane-1-philSil-10Mb	-56.26	12.98
Siloxane-5-philSil-10Mb	-57.06	11.58
Siloxane-10-philSil-10Mb	-56.75	11.61
Siloxane-20-philSil-10Mb	-60.67	12.55

Thermal decomposition of elastomers based on ViP-DMS and HPDMS begins at 350 °C and ends at 700 °C. The Si–O bond (450 kJ mol^{-1}) is stronger than the C–C bond (350 kJ mol^{-1}), which means that it is more difficult to break. Therefore, the thermal energy required to break the polysiloxane base, under neutral pH conditions, is much higher than with most other polymeric materials.

One way to compare the thermal stability of material under controlled heating is through the onset temperature of thermal decomposition (T_{ons}). Used silica filler significantly improves the thermal stability of siloxane nanocomposites based on hydrogen/vinyl precursors.

The increase in thermal stability can be explained by the increase in polymer/filler interaction, as well as due to the increased amount of filler nanoparticles. Improved thermal stability can also be explained as a function of calcination temperature, related to the physical interactions of polymer matrix with silanol groups (Si-OH) from the surface of modified silica nanoparticles [21]. However, the addition of vinyl masterbatch violates stoichiometry and leaves vinyl siloxanes in excess. This leads to a decrease in thermal stability, because unstable C=C bonds decompose at elevated temperatures, creating radicals that lead to the onset of the thermal degradation of siloxane elastomers. As the content of masterbatch increases (10%), the Tons decrease further (Figure 5 and Table 5). In the case of the use of hydrophilic fillers, the same conclusion can be drawn that the addition of masterbatches reduces thermal stability, as explained in systems with hydrophobic fillers.

The opposite behaviour than explained for T_{ons} was shown by samples with a higher percentage of hydrophobic filler and masterbatch (Siloxane-20-phobSil-5Mb and Siloxane-20-phobSil-10Mb). In these samples, with an increase in the content of masterbatch, there is an increase in thermal stability, so in the sample, Siloxane-20-phobSil-5Mb T_{ons} was 471 °C and in the sample Siloxane-20-phobSil-10Mb 476 °C. We assume that the addition of masterbatches facilitated the formation of a filler network in samples with this amount of filler, which can be seen in the TEM images (Figure 7).
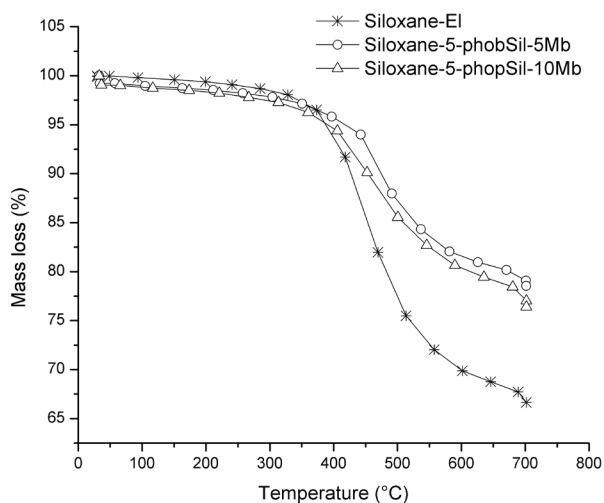
Figure 5. The thermogravimetric curve of siloxane elastomer and its nanocomposites with the addition of 5 and 10 wt% of masterbatch

Table 5. The onset temperature of the thermal decomposition (T_{ons}) and degradation temperatures (DTG_{max}) obtained from derivative thermogravimetric analysis

Sample	T_{ons}	DTG_{max}
Siloxane-El	367	487
Siloxane-1-phobSil-5Mb	335	484
Siloxane-5-phobSil-5Mb	344	489
Siloxane-10- phobSil-5Mb	353	491
Siloxane-20- phobSil-5Mb	357	493
Siloxane-1-philSil-5Mb	322	482
Siloxane-5-philSil-5Mb	335	486
Siloxane-10-philSil-5Mb	355	489
Siloxane-20-philSil-5Mb	372	491
Siloxane-1-phobSil-10Mb	328	472
Siloxane-5-phobSil-10Mb	330	476
Siloxane-10-phobSil-10Mb	337	479
Siloxane-20-phobSil-10Mb	341	481
Siloxane-1-philSil-10Mb	325	460
Siloxane-5-philSil-10Mb	329	465
Siloxane-10-philSil-10Mb	334	472
Siloxane-20-philSil-10Mb	340	475

From the DTG curves of the obtained siloxane elastomer and nanocomposites with different amounts of masterbatch, which are shown in Figure 6, it can be seen that in these samples thermal degradation occurs in one step. the DTG temperatures of the siloxane elastomer and nanocomposites with hydrophobic and hydrophilic fillers with 5 and 10 wt% of masterbatch are presented in Table 5. In samples with the addition of hydrophobic fillers and 5 wt% masterbatches, the maximum DTG peak shifts to higher temperatures compared to the Siloxane-El sample, but with an increase in masterbatch content to 10 wt%, the maximum DTG peak occurs at lower temperatures. In the case of samples with hydrophilic fillers and masterbatch, the degradation temperature decreases with the addition of 5 wt% masterbatch and further decreases with the increasing amount of masterbatch, which we assume is due to weaker interaction of hydrophilic SiO_2 from filler and hydrophobic SiO_2 from masterbatch.

In a pure siloxane elastomer, Siloxane-El, phase separation of the hydrogen and vinyl siloxane precursors can be noticed, according to the TEM results (Figure7a).

In crosslinked elastomeric nanocomposites with hydrophobic fillers, the addition of masterbatch (which contains significantly larger SiO_2 particles) leads to the formation of agglomerates (Figure 7b). These agglomerates also occur due to the poorer compatibility of fillers from masterbatch and added fillers, which is confirmed by the given pictures. As the hydrophobic filler content increases, additional aggregates are formed (Figure 7c). The addition of 20% by weight of silicon(IV)oxide leads to the formation of more significant agglomerates, but they are separated by a network of added fillers and thus allow a desired dispersion of the silica nanofiller in the siloxane matrix (Figure 7d). In crosslinked elastomeric nanocomposites, the increase in the proportion of hydrophobic fillers, especially in the Siloxane-20-phobSil-10Mb sample, leads to a more pronounced structure of the filler network, which is positively shown in the increase of thermal stability of these composites, compared to samples with a lower percentage of nanofillers and masterbatch

The addition of masterbatches further complicates the homogenization of the hydrophilic fillers in the siloxane matrix, because the hydrophobic particles of the masterbatches cannot mix thermodynamically satisfactorily with the hydrophilic fillers, which is clearly seen in Figure 7e. With the increase of the filler content, smaller agglomerates are formed, but there are no larger agglomerates, which would deteriorate the properties of the obtained hybrid materials. In the system with the addition of 10 wt% of filler, it is noticed that there were larger contacts between individual particles and that the filler began to form its network. Since the interaction between the filler and the polymer is of lower intensity, filler networks begin to develop. It can be said that strong filler-filler interactions occur by establishing hydrogen bonds between silicon(IV)oxide particles where hydrophilic silanol or hydroxyl groups are present (Figures 7f and 7g).
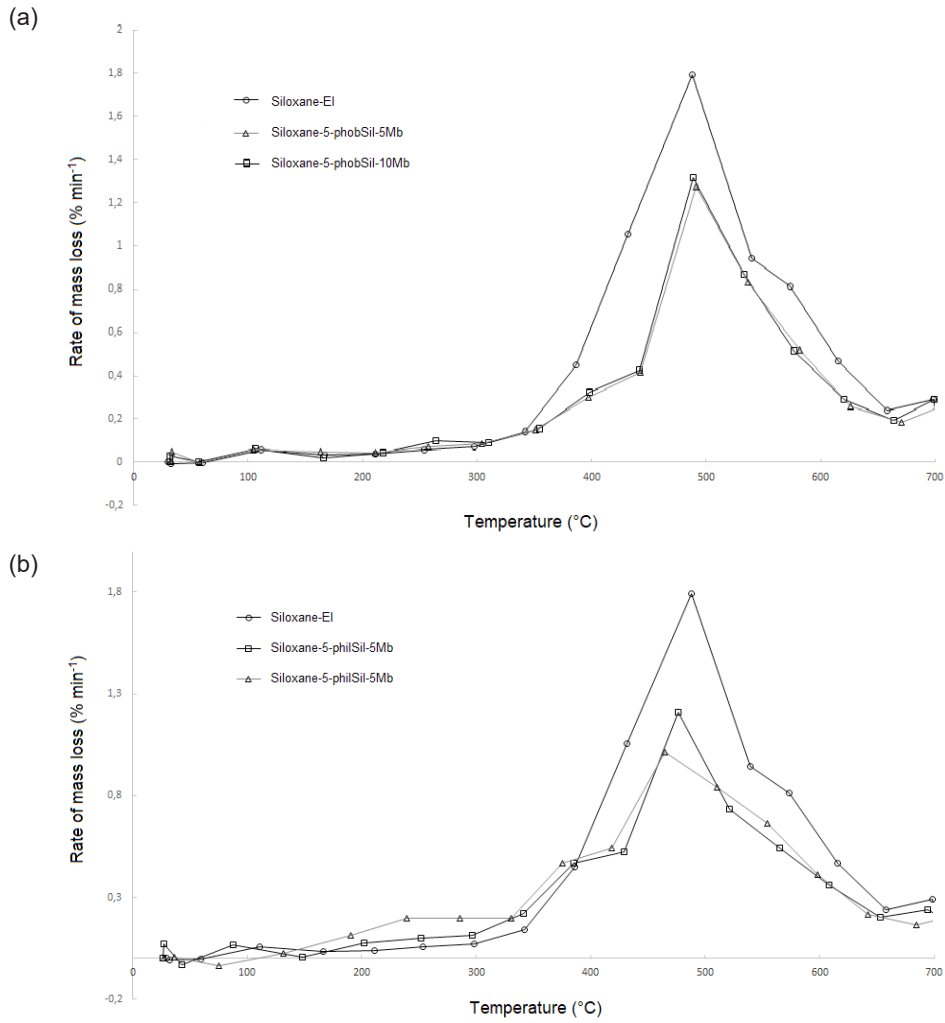
(a)

(b)

Figure 6. DTG curves of siloxane elastomer and its nanocomposites with 5 and 10 wt% of masterbatch with the addition of a) hydrophobic and b) hydrophilic fillers
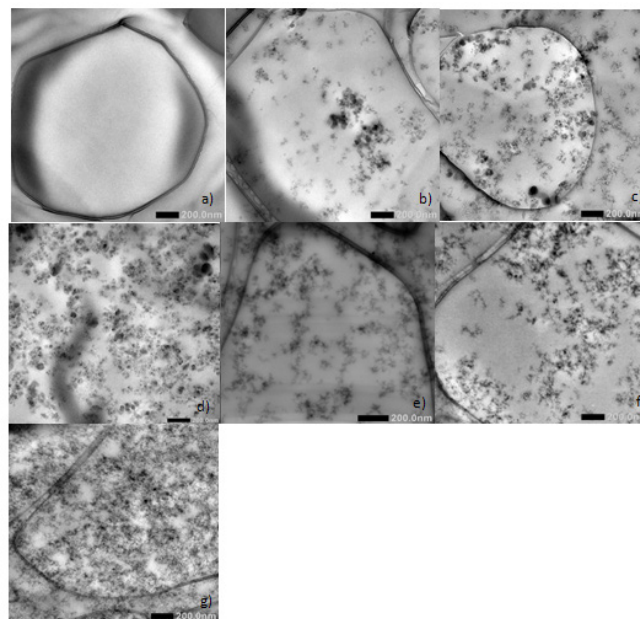

Figure 7. TEM images of a) pure elastomer Siloxane-El, b) Siloxane-1-phobSil-10Mb, c) Siloxane-10-phobSil-10Mb, d) Siloxane-20-phobSil-10Mb, e) Siloxane-1-philSil-10Mb, f) Siloxane-10-philSil-10Mb and g) Siloxane-20-philSil-10Mb (scale bar = 200 nm)

Conclusion

A new class of cross-linked siloxane materials based on different network precursors, α, ω-divinylpoly(dimethyl disiloxane) (ViPDMS) and poly(methylhydrogensiloxane) (HPDMS), was synthesized. In order to properly structure the siloxane hybrid materials, nanofillers of silicon(IV)oxide with a hydrophilic and hydrophobic surface were used as additional reinforcement of the obtained elastomers. To further strengthen the obtained hybrid materials, a masterbatch was added in amounts of 5 and 10 wt% relative to the weight of the reactants. The structures of the obtained siloxane elastomer and siloxane-based nanocomposites were confirmed by FTIR spectroscopy and showed that with the addition of the masterbatch there is no movement of the bands in relation to the nanocomposites without the masterbatch. The masterbatch contains hydrophobic fillers which affect the mechanical properties due to the simplified interaction with the hydrophobic matrix, which is especially visible when adding 10 wt% masterbatch. DSC results show that the addition of fillers and masterbatch to the polymer matrix leads to phase separation and melting at temperatures of about -50 to -60 °C, indicating that these cross-linked materials can be used in different fields. Also, by examining the thermal properties of the obtained siloxane materials, it can be concluded that the addition of a masterbatch reduces the thermal stability because the stoichiometry is disturbed.

Acknowledgements

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Izvod

UTICAJ NANOPUNILA I MASTERBAČA NA SVOJSTVA SILOKASNIH MATERIJALA

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Sintetisani su nanokompoziti na bazi siloksana i nanočestica silicijum(IV)oksida (sa hidrofobnom i hidrofilnom modifikacijom površine) da bi se dizajnirala željena finalna svojstva kompozitnog materijala. Da bi se poboljšale mehaničke osobine i topologija siloksanskih mreža, dodat je masterbač (koji sadrži vinil funkcionalne siloksane i silicijum(IV)oksid punila). U sintezi nanokompozita korišćen je silicijum(IV) oksid u količinama od 1, 5, 10 i 20 tež% i masterbač u količinama od 5 i 10 tež% da bi se ispitao efekat punila i masterbača. Hemijska struktura dobijenih materijala analizirana je infracrvenom spektroskopijom sa Furijeovom transformacijom. Transmisiona elektronska mikroskopija (TEM) je korišćena za ispitivanje disperzije čestica punila u siloksanskim nanokompozitima. Karakteristični fazni prelazi sintetisanih nanokompozita ispitivana su diferencijalnom skenirajućom kalorimetrijom (DSC) dok je toplotna stabilnost dobijenih materijala proučavana termogravimetrijskom analizom (TGA). Dodavanje masterbača nije dovelo do značajne razlike u temperaturi topljenja, ali je poremećena stehiometrija, što je smanjilo termičku stabilnost u poređenju sa uzorcima bez masterbača. Dodavanje masterbača nanokompozitima sa hidrofilnim punilima povećava i zateznu čvrstoću i izduženje pri kidanju. Na osnovu dobijenih rezultata može se zaključiti da kombinacija masterbača i nanopunila utiče na svojstva siloksanskih materijala, što bi moglo da omogući dobijanje materijala sa željenim osobinama.