



THERMAL CHARACTERISTICS OF THE EPOXY–METALLOSILOXANE COMPOSITIONS FILLED WITH PHENYLSILOXANE RESINS

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Abstract

A method for increasing the glass transition temperature of the compositions obtained by curing an epoxy-diane resin with a partially siloxy-substituted organo(alkoxy)(zirconium)siloxane by introducing phenylsiloxane resins is considered. The initial content of zirconium siloxane was 10 wt %. It is shown that the introduction of the siloxane resins in 10–50 wt % relative to the epoxy resin is capable of not only increasing the glass transition temperature of the material almost twice, but also enhancing the curing degree of the system.

Key words: curing, epoxy materials, metalloalkoxysiloxanes, thermal properties.

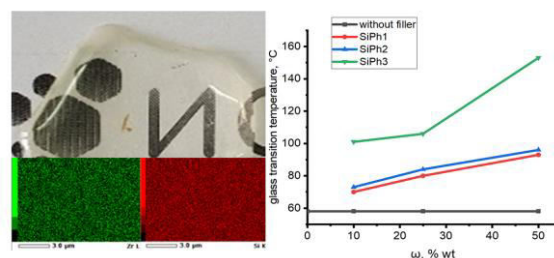
Introduction

The introduction of a siloxane component upon the formation of an epoxy material is known to improve its performance characteristics. Siloxane-containing compounds can be used both as the moieties incorporated into an epoxy matrix, in particular, as co-curing agents and as the fillers or filler modifiers for the intended material.

The use of silica as a siloxane filler is most widely considered in the literature. This is due to its high availability, variability of the sizes (nano/micro), and the possibility of additional functionalization for better compatibility with a matrix. In this respect, two main approaches to filling the epoxy matrix with silica can be distinguished: the direct introduction of the preformed and processed silica into an uncured matrix [1–3] and the formation of a silica component using sol-gel methods from siloxane precursors directly during the curing of an epoxy resin (ER) [4–6].

There are also reports on the formation of a silica phase from a soluble form of amino-epoxy-functionalized hyperbranched polyethoxysiloxane obtained by the preliminary sol-gel process of TEOS in the presence of the product of the reaction between glycidoxypropyltrimethoxysilane with aminophenyltriethoxysilane [7]. This approach significantly increases the glass transition temperature (T_g), the storage modulus, and the thermal stability of an epoxy matrix.

This work deals with the effect of phenylsiloxane resin additives on the thermal properties of the composites cured with partially siloxy-substituted zirconium siloxane. The effectiveness of curing an epoxy-diane resin with metallosiloxane oligomers has been shown earlier [8]. However, the resulting materials exhibited relatively low T_g values. At the same time, the very approach to the formation of such a material suggests the possibility of the uniform introduction of



phenylsiloxane resins, which can serve as a tool to increase the value of T_g .

Results and discussion

Phenylsiloxane resins were used as additives since they may exhibit high affinity for phenylsilyl-substituted metallosiloxane (MS) oligomers. For this purpose, two polycyclic oligomeric resins **SiPh1** and **SiPh2** were obtained by the condensation of ethoxyphenylsilanes in acetic acid, containing branching phenylsilsesquioxane $[(\text{Ph})\text{SiO}_{1.5}]$ and linear methylphenylsiloxane $[(\text{Me})(\text{Ph})\text{SiO}]$ units in an equimolar ratio. Moreover, **SiPh1** resin differed from **SiPh2** by the fact that half the molar amount of $[(\text{Ph})\text{SiO}_{1.5}]$ units were substituted for silica $[\text{SiO}_2]$ units owing to the use of tetraethoxysilane as a monomer during the synthesis. The third additive in use was hexol **SiPh3**, which was previously synthesized at ISPM RAS and represents an individual cyclic silanol compound [9]. **SiPh1** and **SiPh3** were solids, while **SiPh2** was a highly viscous substance at room temperature, being well soluble in organic solvents (toluene, THF) and capable of combining with the MS–epoxy mixture at a mixing stage (Fig. 1).

The chromatograms of **SiPh1** and **SiPh2** resins had a unimodal distribution and consistently differed in the molecular weight and polydispersity ($M(\text{SiPh1}) > M(\text{SiPh2})$) according to the differences in the elementary units (Fig. 2a). Hexol was characterized by the lowest molecular weight among the additives explored. However, all of them contained silanol groups to variable degrees, which potentially allowed them to bind to the growing MS network during the curing of the material (Fig. 2b). Partially (diethoxyphenyl)siloxy-substituted zirconium siloxane **Zr-Ph**(²⁻²) was chosen as the MS oligomer.

The initial system $\{\text{Zr-Ph}(\text{2-2})\text{:KER-828} = 0.10\text{:1 parts by weight}\}$, featuring an incomplete degree of curing (gel fraction

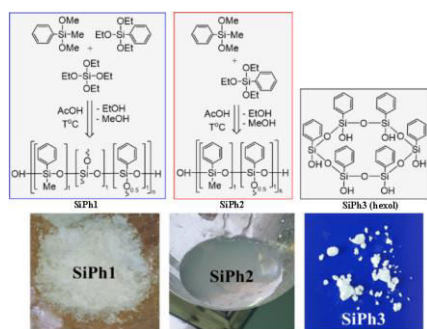


Figure 1. Synthesis and compositions of the phenylsiloxane additives explored.

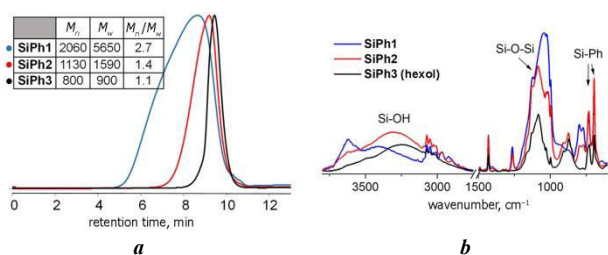


Figure 2. Chromatograms of the phenylsiloxane resins **SiPh** obtained in THF (*a*) and their IR spectra (*b*).

GF = 80 wt %) [8], was chosen as the main one. This system allowed us, first of all, to evaluate the effect of the siloxane additive on an increase in the GF value, and secondly, the presence of ethoxy groups of different types increased the probability of binding of the curing agent with the additive. In this case, the amount of **Zr-Ph**(²⁻²) relative to the ER remained unchanged, while the initial content of the additive varied within 10–50 wt % relative to the ER. The method for obtaining the composite samples was similar to that described previously [8].

The photographs of the samples (Fig. 3) revealed that almost all of them are transparent and homogeneous, except for the sample containing 50 wt % of hexol relative to the ER, which is characterized by opalescence. This indicates good compatibility of the final components of the material.

The data presented in Table 1 show that the introduction of the phenylsiloxane additives in all cases leads to an increase in the GF values relative to the initial system. Moreover, this value grows with an increase in the additive content from 10 to 25 wt % relative to the ER and then remains unchanged.

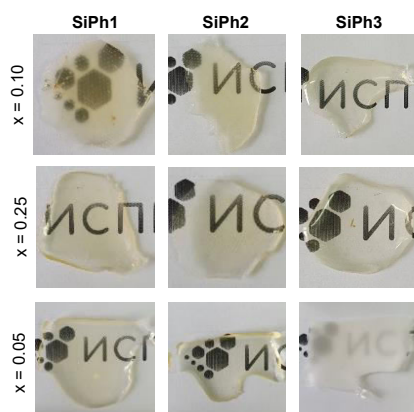


Figure 3. Photographs of the composite samples for the initial system {**Zr-Ph**(²⁻²):KER-828:SiPh = 0.10:1:*x* parts by weight}.

The greatest effect of the GF growth is characteristic of hexol. Thus, the addition of 10 wt % of hexol allows for obtaining the composition with GF = 96 wt %, which is 20% more than that of the reference sample. A value of this order is achieved when using the resins only at their maximum content; however, it allows obtaining transparent compositions. Presumably, the growth of the GF values is achieved owing to the catalytic binding of the additive and the epoxy matrix by silanol and hydroxy groups, respectively, and is determined by the number of silanol groups in the additive and, in turn, explains the greatest GF growth in the case of hexol. The data obtained on the GF values are in good agreement with the results of IR spectroscopic analysis of the samples: the intensities of the bands at 915 and 862 cm^{-1} significantly reduce relative to the spectrum of the initial ER (Fig. 4).

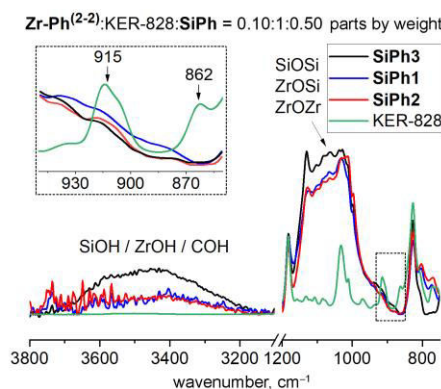


Figure 4. IR spectra of the samples obtained by curing the initial system {**Zr-Ph**(²⁻²):KER-828:SiPh = 0.10:1:0.50 parts by weight}.

The SEM micrographs show a high degree of homogeneity of the samples at the micro level (Fig. 5). It is obvious that, upon filling with the phenylsiloxane resins, all the components in the material are distributed uniformly, without the obvious presence of agglomerates, while upon filling with a large amount of hexol, the formation of individual nano and micron particles of complex shapes is clearly visible. The elemental maps revealed an increase in the silicon content, while the density and distribution of zirconium in all cases remained virtually unchanged, which is due to the affinity of the additive to the MS curing agent.

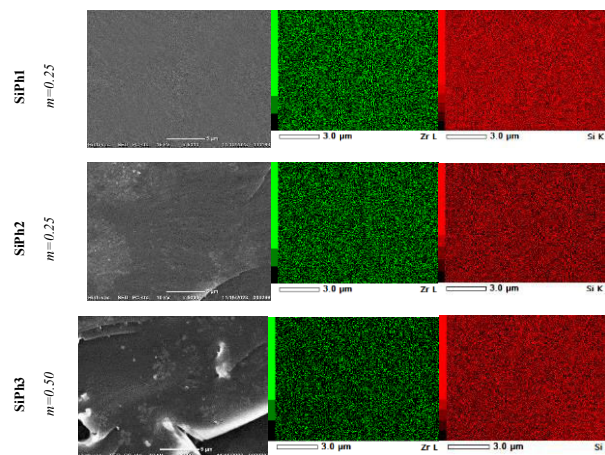


Figure 5. SEM micrographs and elemental maps of the samples obtained by curing the initial system {**Zr-Ph**(²⁻²):KER-828:SiPh = 0.10:1:*m* parts by weight}.

The glass transition temperature of the cured material was affected by both the amount and composition of the introduced phenylsiloxane additive (Table 1). In all cases, an increase in the amount of the introduced additive led to an increase in T_g relative to the reference sample. The greatest increase in T_g was observed in the case of hexol: the introduction of 10 wt % of the additive relative to the ER mass afforded an increase in T_g almost 2 times compared to the reference sample from 58 to 101 °C, and that of 50 wt %—to 153 °C. At the same time, the maximum content of hexol (**SiPh3**) in the system resulted in the appearance of two temperature transitions: at 68 and 153 °C. The former is likely to correspond to the T_g value of hexol itself and confirms the phase heterogeneity within the material.

Upon introduction of the phenylsiloxane resins, the close values were achieved only at their maximum contents explored; however, even at their content of 10 wt % relative to the ER, the value of T_g increased by 20–26%. The lower efficiency of the resins compared to hexol can be explained by their denser and more rigid three-dimensional structure, as well as a lower degree of binding to the matrix. This is in good agreement with the lowest observed effect in the case of **SiPh1** additive since it has a higher molecular weight and is more rigid due to the presence of silica [SiO₂] units in the structure.

It should be noted that the effect of increasing T_g is also observed in the case of the initially cured system {**Zr-Ph**⁽²⁻²⁾:KER-828 = 0.25:1 parts by weight}, which is demonstrated by the example of the introduction of hexol (Table 1).

Hence, the results obtained indicate the high efficiency of the introduction of the siloxane additives for increasing the value of T_g of the MS–epoxy compositions, and the approach of curing ER with MS oligomers allows one to fill the system with such additives in wide limits with the formation of a homogeneous material. In this case, the composition and structure of the additive can determine the degree of growth of T_g and be used as a tool to control the thermal properties of the material.

Experimental section

Materials

The solvents (toluene, ethanol) and acetic acid were dried according to the standard procedures and distilled under an argon atmosphere prior to use.

Methods

The elemental analyses were obtained on a Carlo Erba 1106 instrument (Italy). Silicon, carbon and hydrogen contents were determined by burning a sample (0.005–0.010 g) in an oxygen atmosphere at 950 °C. The error did not exceed 0.1 wt %.

The IR spectra were recorded on Bruker Vertex 70v and Bruker Tensor 27 spectrometers (Germany) in the ATR mode in the range of 550–4000 cm⁻¹.

The GPC analysis was performed on a Shimadzu LC-10A chromatograph (Japan). Phenomenex columns (USA) filled with phenogel sorbent (eluent THF) were used for the separation.

The TMA data were obtained on a TMA Q400 instrument (USA). The experiments were performed by the penetration method at a load of 1 N, with the probe diameter of 2.5 mm and at a heating rate of 5 deg/min.

Table 1. Characteristics of the composite samples obtained by curing the initial compositions {**Zr-Ph**⁽²⁻²⁾:KER-828: SiPh = x:1:m parts by weight}

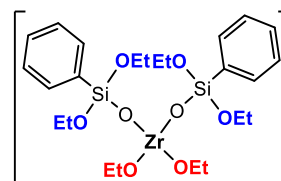
| x, parts by weight | SiPh | m, parts by weight | GF, % | T_g , °C |
|--------------------|-------------------------|--------------------|--------|------------|
| 0.1 | – | – | 80 | 58 |
| | SiPh1 | 0.10 | 87 | 70 |
| | | 0.25 | 93 | 80 |
| | | 0.50 | 98 | 93 |
| | SiPh2 | 0.10 | 91 | 73 |
| | | 0.25 | 96 | 84 |
| | | 0.50 | 95 | 96 |
| | SiPh3 (hexol) | 0.10 | 96 | 101 |
| | | 0.25 | 98 | 106 |
| | | 0.50 | 98 | 68/153 |
| 0.25 | – | – | 99 | 77 |
| | SiPh3 (hexol) | 0.1 | | 101 |
| 0.5 | | | 65/100 | |

The SEM studies were carried out using a JCM-6000 PLUS microscope (Japan).

The GF values were determined by extracting a soluble portion of the sample with hot ethyl acetate.

Syntheses

Diethoxy-bis-(diethoxyphenylsiloxy)zirconium **Zr-Ph**⁽²⁻²⁾ was obtained according to the published method [10].



The phenylsiloxane resins were obtained by heating a solution of a mixture of alkoxy silanes in anhydrous acetic acid at 120 °C for 10 h. Then toluene (40 mL) was added and the resulting mixture was washed with aq. NaCl until the neutral pH value of the washings (5–6 times). The organic layer was dried over anhydrous Na₂SO₄ for 24 h, then filtered and evaporated (1 Torr, 60 °C) to constant mass. The resulting residue was analyzed.

SiPh1 was obtained from TEOS (3.55 g, 0.0168 mol), PTEOS (4.09 g, 0.0168 mol), MPDMS (3.53 g, 0.0168 mol), and acetic acid (25 mL). Yield: 5.53 g (101%). The dry product was a colorless brittle solid. ¹H NMR (CDCl₃): δ –0.33–0.73 (br., 3H, SiMe), 6.55–7.94 (br., 10H, SiPh) ppm. IR (ν/cm⁻¹): 3200–3750 (SiOH). GPC (THF, 40 kDa, PSS): M_n = 2060, M_w = 5650, M_w/M_n = 2.7.

SiPh2 was obtained from PTEOS (6.08 g, 0.0253 mol), MPDMS (5.32 g, 0.0253 mol), and acetic acid (25 mL). Yield: 6.70 g (100%). The dry product was a colorless transparent highly viscous liquid. ¹H NMR (CDCl₃): δ –0.20–0.72 (br., 3H, SiMe), 6.77–7.92 (br., 10H, SiPh) ppm. IR (ν/cm⁻¹): 3200–3750 (SiOH). GPC (THF, 40 kDa, PSS): M_n = 1130, M_w = 1590, M_w/M_n = 1.4.

The samples for investigations were prepared according to the published procedure [8].

Conclusions

The introduction of three polycyclic phenylsiloxane resins into the zirconium siloxane–epoxy material at the stage of mixing the initial components afforded the materials that feature higher glass transition temperatures than the sample without the additives (an increase of up to 50 °C). At the same time, owing to the nature of the curing agent, good compatibility of the components of the cured system was observed in a wide range of concentrations of the introduced additives, and the resins themselves contributed to an increase in the degree of curing at a lower content of the metallosiloxane.

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