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Epoxy Compositions Cured with Aluminosilsesquioxanes: Thermomechanical Properties

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ABSTRACT: The aim of this study was to verify the influence of bis(heptaphenylaluminosilsesquioxane) (AlPOSS), used as a curing agent, on the thermomechanical properties of epoxy resin. Moreover, various curing conditions were taken into account. Epoxy casts were prepared from epoxy resin based on bisphenol A cured with different amounts of bis(heptaphenylaluminosilsesquioxane). The thermomechanical properties were investigated during dynamical mechanical thermal analysis (DMTA) in two cycles of heating. The storage modulus G' of the epoxy casts was found to be higher in comparison to the reference epoxy sample and significantly dependent on the POSS content. A correlation between the glass transition temperatures (T_g), the curing conditions and the amount of curing agents were closely related. The occurrence of the crosslinking process in epoxy matrix was proved by the FTIR spectroscopy. The structure of the epoxy casts was investigated using scanning electron microscopy (SEM). © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40672.

KEYWORDS: composites; crosslinking; mechanical properties; thermal properties

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INTRODUCTION

The application of polymeric materials especially modified for different industry types has considerably increased recently. Epoxy resins are an important group of these materials frequently used as a matrix for composites in the aviation, automotive, construction, and shipbuilding industry.[1–3] Epoxy composites have good mechanical and thermal properties and high chemical resistance. The incorporation of nanosize fillers and modifiers to polymers has contributed to obtaining the required properties of composite materials. Epoxy resins can be modified with different hardeners, accelerating agents, reinforcing fibers, or ionic liquids.[4]

New inorganic–organic modifiers and nano modifiers have recently been gaining ground among scientists as the main focus of scientific research.[5–10] The polyhedral oligomeric silsesquioxanes (POSS) which are new hybrid compounds, made of cube-octameric frameworks with inorganic silica like core and surrounded by eight organic corner groups, are one of the representatives of this group.[11] Various types of POSS are compatible with polymers or monomers and are added into common polymers via copolymerization, grafting or blending.[12,13] They may be used as additives, catalytic agent, reinforcement, processing aids, and flame retardants in the epoxy compositions.[14–19] Epoxy composites with POSS present improved thermomechanical properties and thermal stability.[16,20,21] Additionally, a lowering of the coefficient of volume thermal expansion (CVTE) has been reported, as a result of the presence of POSS particles in the cross-linked epoxy resin.[22] The epoxy resin composites prepared via the cocuring reaction with octaaminophenyl polyhedral oligomeric silsesquioxane are presented in an interesting way by Chen et al.[23] A series of flame-retardant epoxy resins proposed by Young et al.,[24] containing boron and silicon, were obtained through a crosslinking reaction, using tris (2-hydroxypropyl)borate together with octaaminophenyl POSS as curing agents. However, the mainly used curing agents for epoxy resins are: acid anhydride, organic and aromatic amines and aliphatic polyamines. The competition in improving the quality of epoxy products creates a necessity for the research on new types of curing agents. Metalized polyhedral oligomeric silsesquioxanes can be used as cure promoters, catalysts and initiators of ring-opening polymerization.[25,26] In our previous research,[27] a new method of curing epoxy resin using bis(heptaphenylaluminosilsesquioxane) was presented.

Therefore, the aim of this article was to study the influence of bis(heptaphenylaluminosilsesquioxane), applied as a curing

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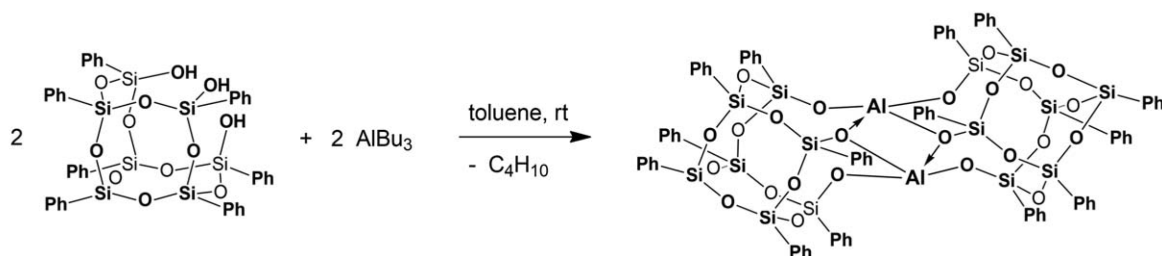

Figure 1. Formation of the Al(III) silsesquioxane complex.

agent, on thermomechanical properties of epoxy casts. The thermomechanical properties were determined by dynamic mechanical thermal analysis (DMTA) in two cycles of heating. The FTIR spectroscopy was applied to monitor changes in chemical structures of the casts. The morphological structure of the epoxy casts was investigated using scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The following components were used in this study: epoxy resin Epidian 6 (EP6) based on bisphenol A (BPA) (epoxy number 0,510-0,540, viscosity 10,000–15,000 m Pas, density 116 g/cm^3), produced by Chemical Works Organika - Sarzyna in Nowa Sarzyna (Poland) and bis(heptaphenylaluminosilsesquioxane) (AlPOSS) $C_{84}H_{70}Al_2O_{24}Si_{14}$ (synthesis by Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Poland) as a curing agent. Another curing agent, Z1 (triethylenetetramine), also produced by Organika-Sarzyna, was used to prepare a reference epoxy sample. The synthetic route to bis(heptaphenylaluminosilsesquioxane) is shown in the Figure 1. It was prepared according to analogical procedure described by Feher et al.[28–30] (The NMR characterization of AlPOSS: ^{1}H-NMR(CDCl$_3$, ppm) 7.19 – 7,92 (C_6H_5-Si). ^{29}Si NMR(CDCl$_3$, ppm) −73.3, −74.2, −76.6, −76.9, −79.5 in a 1 : 2 : 2 : 1 : 1 ratio). The synthesis and manipulations were carried out under argon using standard Schlenk-line and vacuum techniques. The chemicals required for reactions were obtained from Sigma-Aldrich. All solvents and liquid reagents were dried and distilled under argon prior to use.

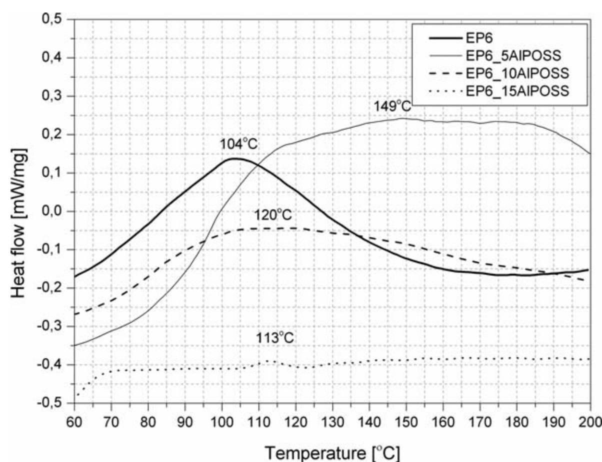

Figure 2. The DSC curves of the epoxy composites with AlPOSS cured at room temperature.

Sample Preparation

To achieve high dispersion of inorganic compounds in the polymeric matrix, AlPOSS was dissolved in acetone at the ratio 1:1. The epoxy resin with the 5, 10, or 15 wt % of AlPOSS, respectively to the total weight of the compositions, was mixed with the use of a high speed mechanical stirrer at 500 rpm for 5 min, 1000 rpm for 5 min, and 2000 for 5 min to produce homogeneous dispersion which was devolatilized for 10 min.

The compositions were cast to PTFE molds. The reference sample was prepared from epoxy resin Epidian 6 (EP6) cured with commercial Z1-triethylenetetramine (13 parts Z1 per 100 parts EP6 by weight), in the same way. The curing parameters were chosen on the basis of our previous works.[27,31] The samples were cured at room temperature for 24 h. Subsequently, the first group of samples was postcured for 2 h at elevated temperature indicated by DSC curves presented in Figure 2. This temperature was taken as the maximum of exothermic peak observed on the DSC curves. The temperatures of postcuring process were 104°C for EP6, 149°C for EP6_5AlPOSS, 120°C for EP6_10AlPOSS, 113°C EP6_15AlPOSS, respectively. The second group of samples was postcured for 2 h at the same temperature i.e., 150°C.

METHODS

The Scanning Electron Microscope (SEM) model Vega 5135MM produced by Tescan (Czech) was used to observe the dispersion of AlPOSS in epoxy matrix. The structure of epoxy cast was investigated with Secondary Electron (SE) signal with an accelerating voltage (15 kV) and the distributions of Si atoms in the matrix were taken from SEM EDX maps (X-ray Microprobe PGT Avalon). The points in the figure denote Si atoms.

The FTIR measurements were conducted by means of Fourier transform spectrometer Vertex 70, at ambient temperature (23°C). The samples were mixed with the KBr powder and pressed into pellets. In all cases a total 64 scans at resolution of 1 cm^{-1} were used to record the spectra.

The dynamic–mechanical properties of the postcured samples, with 10 × 4 × 35 mm^3 dimensions, were investigated using

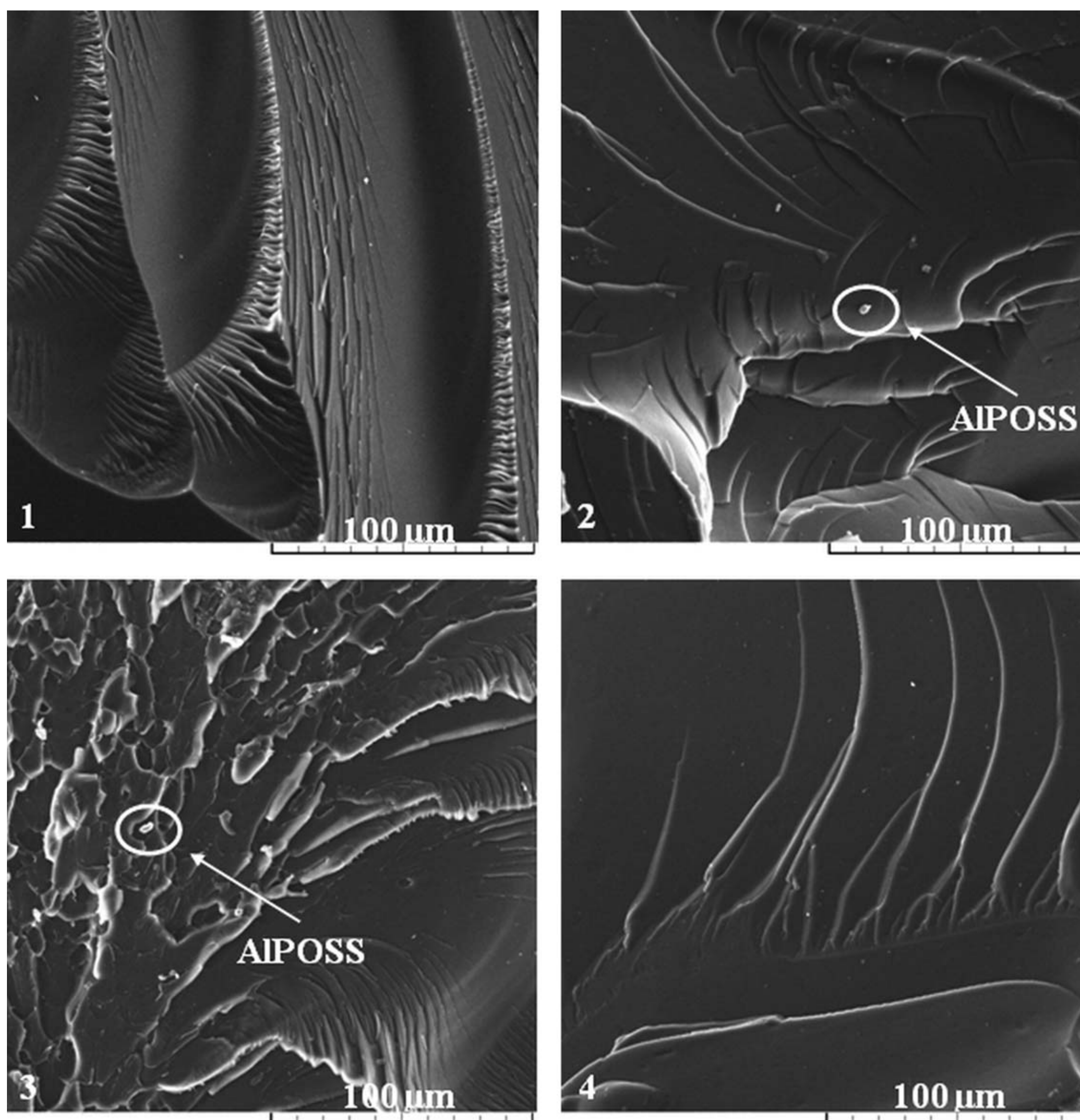

Figure 3. SEM microphotographs of the fracture surfaces of epoxy casts: 1- EP6; 2- EP6_5AlPOSS; 3- EP6_10AlPOSS; 4 - EP6_15AlPOSS.

DMTA methods in a torsion mode, operating at frequency $f = 1$ Hz in the temperature range between 25°C and 200°C, and at heating rate 2°C min. These methods applied very small sinusoidally varying strains to test the material at constant frequency and constant heating rate. The stress is defined as storage modulus G', loss modulus G'' and loss factor tan δ.[32–34] The position of tan δ at its maximum was taken as the glass transition temperature. The samples were heated from 25 to 200°C (first heating cycle) and then quenched to 25°C, followed by reheating to 200°C (second heating cycle). The reheating of the samples was carried out in order to evaluate the changes of the glass transition temperature. The temperature of exothermic peak, characterizing the postcuring process, was determined using Phoenix DSC 204 F1 Netzsch, in standard conditions, i.e., samples of about 5 mg closed in aluminum crucible were heated from 20 to 200°C under protected nitrogen atmosphere, with a flowing rate of 30 mL min^{-1}. ^{1}H, ^{29}Si-NMR spectra were recorded on Brucker Avance 400 MHz and 500 MHz in benzene-d_6 and $CDCl_3$.

RESULTS AND DISCUSSION

Morphology of Epoxy Casts

The SEM micrographs of the epoxy casts with AlPOSS are presented in Figure 3. In these photographs the smooth gray regions correspond to epoxy matrix while, the white domains correspond to AlPOSS.[35] The bulky nanocages of AlPOSS were uniformly dispersed in epoxy matrix however, in some parts phase separation was observed. This effect is usually induced by polymerization which can occur as a result of curing reaction.[11,36,37] In the Figure 4 the representative EDX Si map of epoxy cast is presented. As described by Ni et al.[38] the dynamic mechanical properties, fracture toughness, and thermal stability

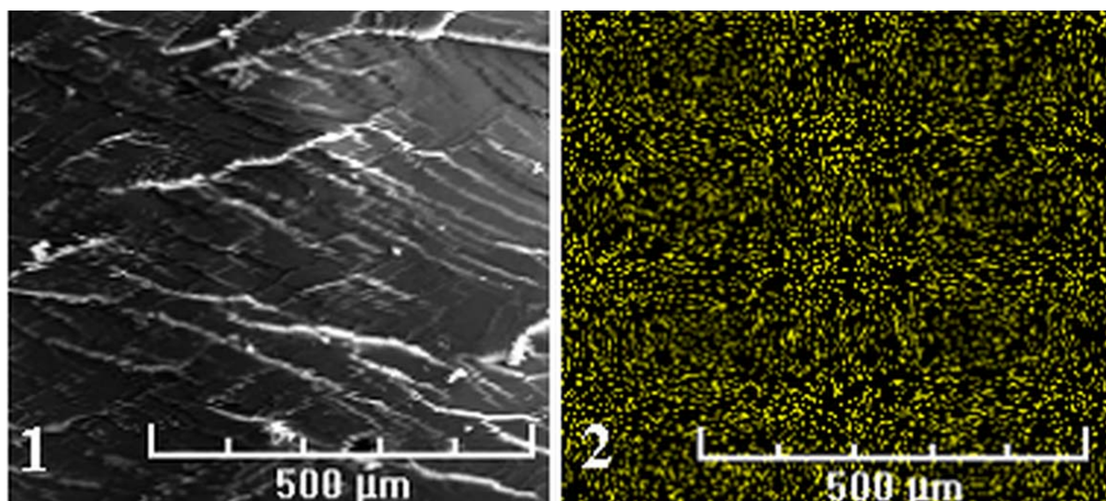

Figure 4. SEM microphotograph and Si-map of the fracture surfaces EP6_5AlPOSS sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the epoxy materials were dependent on the types of pendant groups in POSS and structures between epoxy matrix and silsesquioxane. The addition of POSS at high concentration into the polymer matrix significantly decreases the glass transition temperature. On the other hand, the rigid structures of AlPOSS cages can act as a reinforcement for epoxy matrix.[20,38] In accordance to Xu et al. the formation of irregular clusters may be explained by AlPOSS-AlPOSS or AlPOSS-epoxy chains interactions. Moreover, POSS particles tend to form random aggregations to reduce interfacial energy.[39]

Chemical Structure of Composites Measured by FTIR

An aluminosilsesquioxane gel was first prepared and described by Abbenhuis et al.[40] This silsesquioxane can be considered polymeric Lewis acid[41] and used as a catalyst for the Diels-Alder reactions of enones with butadienes to form substituted cyclohexenes. As a result, the increasing rate of the reactions was observed. In our work, however, aluminosilsesquioxane was applied as a curing agent for epoxy resin. In order to evaluate changes in chemical structures of the casts, FTIR analysis was conducted for the samples prostcured at 150°C. In Figure 5 spectra of all the compounds and composites are presented. For AlPOSS, a characteristic peak corresponding to Si-O-Si bond was noted at 1100 cm^{-1}. The peak at 915 cm^{-1}, attributed to the C—O deformation of the oxirane group (Figure 5), was applied to follow the development of the epoxy group. An augmented part of Figure 5 was presented in Figure 6 in order to highlight the changes between epoxy resin cured with AlPOSS and epoxy resin cured with amine.

The choice of the resin curing agent depends on the manufacturing process, the application, and the desired properties. It is noteworthy that bis(heptaphenylaluminosilsesquioxane) may catalyze the open-ring process and provoke homopolymerization of epoxy groups. This type of aluminosilsesquioxanes may act comparably to the aluminum triacetylacetonate, described by Liu et al., used as accelerator in the reaction of epoxy

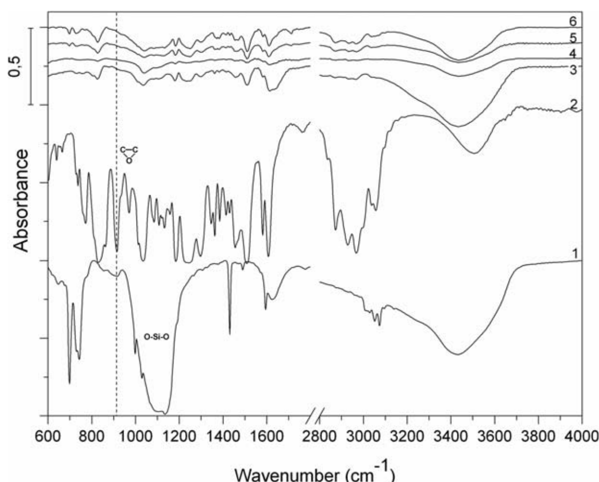

Figure 5. Comparison of IR spectra for the composition 1- AlPOSS; 2- BPA (uncured epoxy resin); 3- EP6; 4- EP6_5AlPOSS; 5- EP6_10AlPOSS; 6- EP6_15AlPOSS.

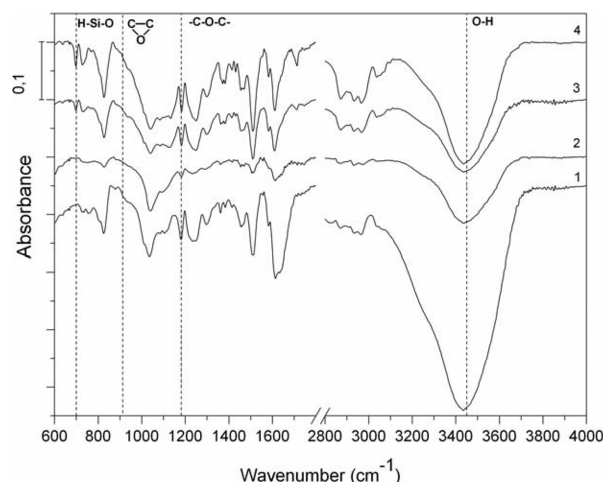

Figure 6. An augmented part of IR spectra for the composites 1- EP6; 2- EP6_5AlPOSS; 3-EP6_10AlPOSS; 4- EP6_15AlPOSS.

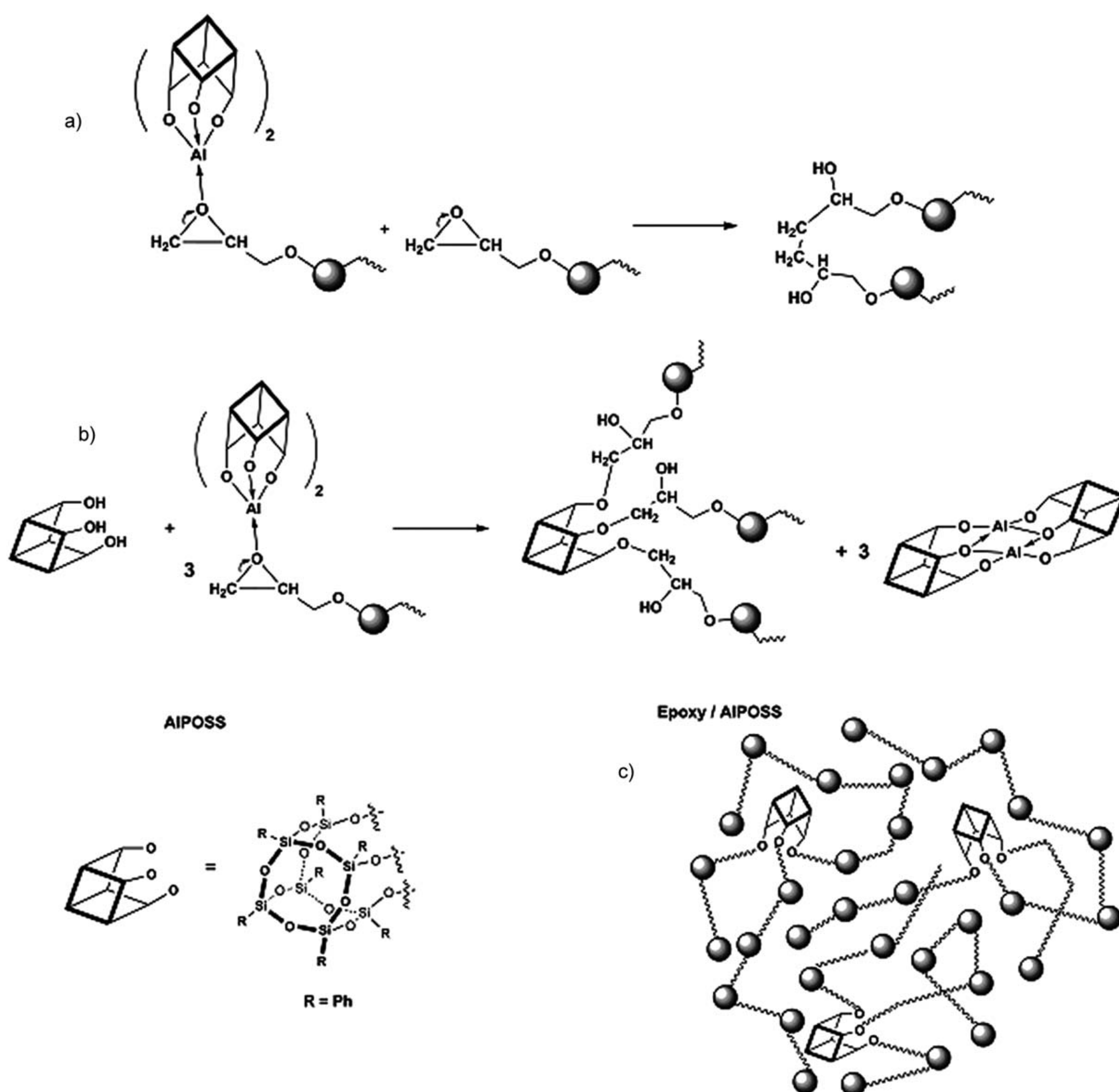

Figure 7. Schematic drawing illustrating the predicted interactions between the reagents: (a,b) AlPOSS + epoxy monomer and (c) the microstructure resulting of the epoxy resin cured with AlPOSS.

monomer with phenyltrisilanol polyhedral oligomeric silsesquioxane.[11] Moreover, aluminum complexes are excellent initiators of the living polymerizations of monomers such as: epoxides, lactones alkyl methacrylates, and alkyl acrylates.[42] Metal complexes used as latent catalysts to cure epoxies usually require high cure temperature or cocatalysts.[43] In this work, bis (heptaphenyl aluminosilsesquioxane) was used both as a modifier and as a curing agent at ambient temperature. It is highly probable that the applied amount of active aluminum atom present in AlPOSS, which initiated the epoxy monomer oxirane group opening, was appropriate to favor the crosslinking process at ambient temperature. In Figure 7 schematic drawing illustrating the predicted interactions between the reagents are presented. The predicted first step of the reaction involves the opening of the monomer oxirane group and homopolymerization of epoxy groups. The second step assumes a reaction between AlPOSS particles and epoxy monomer.

The disappearance of an asymmetrical epoxy ring stretching peak at 915 cm^{-1} in all samples with AlPOSS proved the occurrence curing reaction and network formation. While, the increase in the intensity of the peak at 1200 cm^{-1} (C—O—C stretching of aliphatic linear ester) is connected with the homopolymerization of epoxy groups. With AlPOSS as a curing agent, epoxy homopolymerization could take place, however at higher temperatures than in case of the reference sample.[44] For epoxy samples with AlPOSS peak at 800–700 cm^{1} (probably cause by H—Si—O bonds) was noted unlike the reference sample.[45,46] The epoxide ring opening process was indirectly proved by the occurrence of the peak at a wavenumber of 3500 cm^{-1} (corresponding to the O—H stretching vibration) for all epoxy casts. The intensity of this band increased with the increase of AlPOSS addition (Figure 6). This effect might be related to the following factors: the presence of OH groups inherent to neat epoxy resin; the interaction of each active Al atom with epoxy

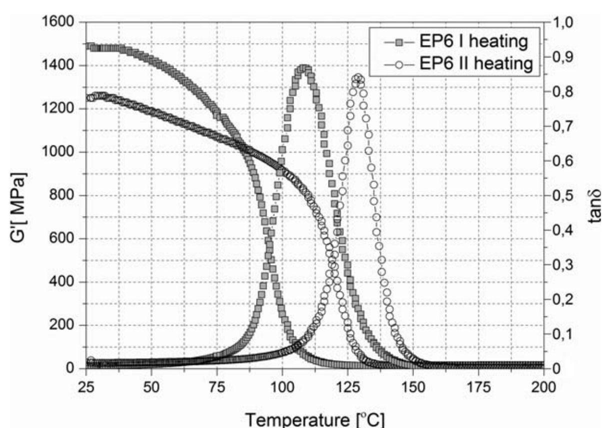

Figure 8. The DMTA curves of storage modulus and tan δ of the EP6 sample cured at 104°C (during the first and the second heating).

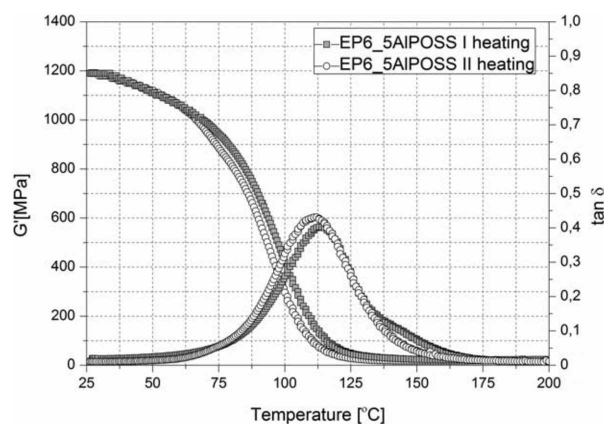

Figure 9. The DMTA curves of storage modulus and tan δ of the EP6_5AlPOSS sample cured at 149°C (during the first and the second heating).

groups or the creation of OH groups between AlPOSS particles and epoxy monomers.[47] According to Supanchaiyamat et al., the appearance of this band may also be a result of epoxide ring opening followed by protonation of the resultant and negatively charged oxygen intermediate.[48]

Thermomechanical Properties

Samples Postcured at the Temperature Indicated by DSC Curves. The dynamic mechanical−thermal analysis was conducted to determine the influence of the curing agent and curing conditions on the epoxy casts' viscoelastic behavior, described by dynamic and damping properties.[49,50] DMTA measurements with different modes (torsion, tension, and three-point bending) are usually applied to characterize it. Because of the fact that in DMTA with torsion mode small forces are required to deform the sample this particular method was used herein.[34,51–53] Moreover, this method allows to avoid destruction or changes in the structures of the investigated materials, such as brittle epoxy composites.[54] The thermomechanical properties of resins directly depend on crosslinking density achieved due to the curing process as well as the curing temperature.[55] It is worth noticing that the values of the temperature of maximal heat flow observed on the DSC curves decrease simultaneously with the increase of AlPOSS content (Figure 2).The characteristic exothermic peaks, which prove the occurrence of the post-curing process, were noteworthy for all samples with the exception of EP6_15AlPOSS. The introduction of 15 wt % AlPOSS may allow to obtain crosslinked epoxy samples at ambient temperature, The minimal exothermic peak on the DSC curve for EP6_15AlPOSS sample proves this effect.

Plots of the storage modulus G' and tan δ versus temperature T for representative types of casts obtained during the first and the second heating are shown in Figures 8 and 9. The values of storage modulus G' of the composites at 25 and 50°C are presented in Table I. It is worth noticing that up to 10 wt % of AlPOSS, the values of the G' epoxy cast increased simultaneously with AlPOSS content. While, in case of 15 wt %, the values of G' (at 25°C during I heating) were lower than the ones for EP6_10 AlPOSS sample (Table I). The highest value of G' (1580 MPa) was noticed for EP6_10AlPOSS in comparison with the reference sample (1490 MPa). This effect may be attributed to the molecular reinforcement effect achieved via the POSS molecules cage used as a hardener.[20] In addition, the AlPOSS samples indicated more constant properties (G' at 25°C) during both heating cycles when compared with the reference sample (Table I).

The glass transition temperature T_g determined in the first heating cycle, was 85°C and 72°C for EP6_10AlPOSS and EP6_15AlPOSS, respectively, while the T_g of the reference sample was 109°C (Table I). The addition of the bulky POSS group may give rise to the increase in the distance between epoxy chains which can result in lower values of T_g, in a good agreement with Yang et al.[24] During the second heating cycle the changes in the value of T_g were observed for all composites (Table I), with the exception of EP6_5AlPOSS. Also, T_g values for EP6_10AlPOSS, EP6_15AlPOSS were 109°C and 81°C respectively and for the reference sample 129°C. The increase of the epoxy casts glass transition temperature indicated that the

Table I. The Values of Epoxy Composites Storage Modulus and Glass Transitions Obtained During the First (I h) and the Second Heating (II h) for the Samples Postcured at the Temperature Indicated by DSC

Name	POSS wt %	G' (MPa) at 25°C I h	G' (MPa) at 25°C II h	G' (MPa) at 50°C I h	G' (MPa) at 50°C II h	T_g (°C) I h	Maks tg δ I h	T_g (°C) II h	Maks tg δ II h
EP6	0	1490	1250	1180	1040	108	0.87	129	0.84
EP6_5AlPOSS	5	1190	1190	780	852	112	0.43	113	0.40
EP6_10AlPOSS	10	1580	1510	1117	996	85	0.73	109	0.52
EP6_15AlPOSS	15	1400	1530	1030	1150	72	0.46	81	0.46

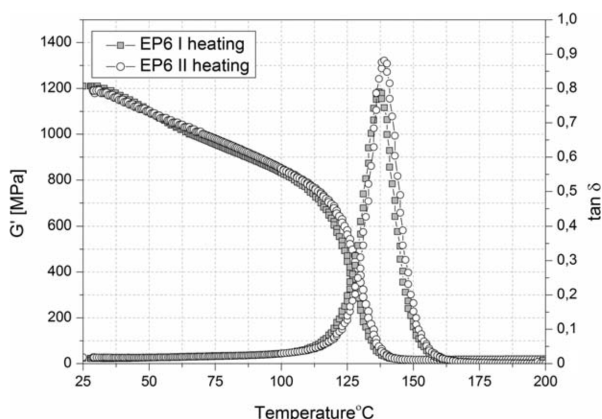

Figure 10. The DMTA curves of storage modulus and tan δ of the EP6 sample cured at 150°C (during the first and the second heating).

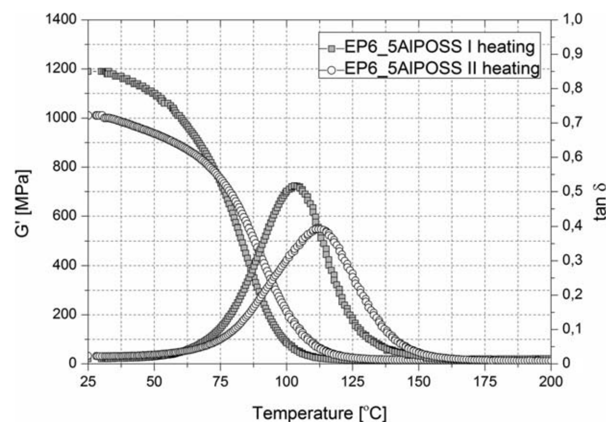

Figure 11. The DMTA curves of storage modulus and tan δ of the EP6_5AlPOSS sample cured at 150°C (during the first and the second heating).

postcuring process had occurred. It is worth noticing that no changes of T_g values were observed for the EP6_5AlPOSS sample, which may prove that accurate curing conditions were applied for this composite.

Samples Postcured at Equal Temperature Conditions. The investigated casts are rather unexplored materials and the selection of curing parameters was experimental therefore the second group of samples was postcured at 150°C. The representative plots of the storage modulus G' tan δ versus temperature T obtained during the first and the second heating for this group of samples are shown in Figures 10 and 11. In these cases, the values of G' for epoxy resin cured with AlPOSS increased simultaneously with the increase of AlPOSS content (from 1190 to 1500) while, the G' value of the reference sample was 1210 MPa. This effect could result from partial degradation of the reference sample in high temperature. To facilitate the analysis, the data were collected in Table II. Moreover, the epoxy samples cured with AlPOSS indicated more stable properties after the second heating cycle in comparison with the reference sample. The changes in G' values of these materials were slight comparing to EP6 sample. The T_g determined in both heating cycles (Table II), for this group of samples proved more constant than for the samples postcured at the temperature indicated by DSC curves. This may indicate that the curing temperature at 150°C was appropriate for the epoxy samples with AlPOSS.

For all samples cured with AlPOSS, regardless of the curing conditions, the introduction of the silsesquioxane resulted in the decrease of the T_g values (from 113 to 77°C). The G' values of the samples cured with AlPOSS below T_g depended on the AlPOSS concentration. The main observed tendency below T_g was the increase of G' values together with the increase of AlPOSS content. Still a different trend was observed for this material above T_g where the G' values decreased simultaneously with AlPOSS concentration. The results of DMTA confirmed that the silsequioxane used as a curing agent influenced the viscoelastic properties of the epoxy samples by changing the mobility of epoxy segments in the AlPOSS particles vicinity.[56,57]

A similar phenomenon of the increased the Young's modulus increased and the decreased glass transition temperature for epoxy resin with functionalized POSS was described Pellice et al.[58] The authors associated the relation between the module increase and the T_g decrease with a higher cohesive energy density, which can correlate with the rigid structure of POSS as well as the increase in the percolation of the three-dimensional network of the resin.[58] In this work the introduction of bis(heptaphenylaluminosilsesquioxane) improved the organic epoxy matrix stiffness due to AlPOSS rigid structures of inorganic cage. Therefore, the increase of the G' values was observed. On the other hand, nanocages of AlPOSS increased the distance between the epoxy chains and lowered glass transitions of the epoxy composites.[11]

CONCLUSIONS

The epoxy resin was modified by bis(heptaphenylaluminosilsesquioxane) used as a curing agent. Phase separation in the epoxy casts induced by the reaction between epoxy monomers and AlPOSS was obtained. The occurrence of the curing reaction

Table II. The Values of Epoxy Composites Storage Modulus and Glass Transitions Obtained During the First (I h) and the Second Heating (II h) for the Samples Postcured at Equal Temperature Conditions

Name	POSS wt %	G' (MPa) at 25°C I h	G' (MPa) at 25°C II h	G' (MPa) at 50°C I h	G' (MPa) at 50°C II h	T_g (°C) I h	Maks tg δ I h	T_g (°C) II h	Maks. tg δ II h
EP6	0	1210	1180	932	1100	137	0.79	139	0.88
EP6_5AlPOSS	5	1190	1010	1100	936	103	0.52	111	0.39
EP6_10AlPOSS	10	1460	1460	1100	1070	82	0.49	84	0.55
EP6_15AlPOSS	15	1500	1410	965	740	75	0.52	77	0.53

and network formation was confirmed by FTIR. Therefore, the modified epoxy casts exposed relatively good mechanical properties. The storage modulus of these materials presents higher values than the reference epoxy sample. These results may be ascribed to the reinforcement effect achieved by the AlPOSS particles dispersion in the epoxy resin. It was found that the value of glass transition temperature of the casts decreased simultaneously with the increase of AlPOSS content. This phenomenon occurred due to the increase in the distance between epoxy chains. The advantageous curing conditions however, were defined for these materials. A higher resistance against temperatures changes i.e. heating was noted for the epoxy casts with AlPOSS in comparison to the reference sample. Concluding, it may be stated that bis(heptaphenylaluminosilsesquioxane) can be used as a curing agent for epoxy resin. Finally, it should be acknowledged that because silsequioxanes show no toxicity, we may assume that they are safe for industrial applications. Probably, these new materials can be used as coating materials with good mechanical properties and resistance to temperature changes.

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