

Epoxy Networks Reinforced with Polyhedral Oligomeric Silsesquioxanes (POSS). Thermomechanical Properties

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ABSTRACT: The rubbery epoxy network, based on diglycidyl ether of Bisphenol A (DGEBA) and poly(oxypropylene)diamine (Jeffamine D2000), was reinforced with a nanometer-sized inorganic building blocks—polyhedral oligomeric silsesquioxanes (POSS). The organic–inorganic networks contained POSS as pendant units of a network chain or as network cross-links of various functionality. Thermomechanical properties and thermal stability of the POSS-containing networks were determined by DMA and TGA. The strongest reinforcement was achieved in the networks with pendant POSS forming ordered crystalline domains, which act as physical cross-links. The POSS skeleton with “soft” flexible substituents, such as octyl, shows formation of weak aggregates only, which do not contribute to reinforcement. The rubbery modulus of the networks with POSS in a junction grows with increasing POSS functionality due to enhanced network cross-link density. These networks are more homogeneous, and the modulus of the network with the octafunctional POSS junction well agrees with theoretical prediction. The mechanical properties are affected mainly by POSS–POSS interactions while the POSS–network chain interactions are of minor importance.

Introduction

The polymer systems reinforced with well-defined nanosized inorganic clusters are an important class of polymer nanocomposites. Polyhedral oligomeric silsesquioxanes (POSS) are typical molecular nanobuilding blocks used to reinforce the polymer organic matrix. Functionalized POSS monomers are covalently bound to the polymer, leading to reinforcement of the system on molecular level.¹ The resulting nanocomposite shows improved mechanical properties and higher thermal stability which is determined by POSS–POSS and POSS–polymer interactions.^{2–4}

We have studied the POSS-modified epoxy–amine network based on diglycidyl ether of Bisphenol A (DGEBA) and poly(oxypropylene)diamine D2000 (Jeffamine). The POSS units were covalently bound to the network chain as pendant units or incorporated in the network as compact network junctions. Mono- and polyepoxy POSS monomers were used to prepare these two types of the organic–inorganic (O–I) networks with different topology of POSS. The formation and structure of these O–I networks were described in the preceding paper.⁵ Small- and wide-angle X-ray scattering (SAXS, WAXS) results reveal that POSS units located as the network junctions are slightly aggregated, which is in contrast to previous literature data.^{6,7} The extent of aggregation depends on the reaction conditions. In the initial reaction mixture, the POSSs aggregate, however, during cross-linking the aggregates are gradually broken, and the system becomes more homogeneous. Moreover, the degree of POSS aggregation decreases with increasing functionality of the POSS monomer due to steric restrictions around the forming POSS junction.⁵ On the contrary, strong aggregation and crystallization can occur in the case of POSS pendant on the polymer chain. The tendency to aggregation is determined by the POSS compatibility with the polymer matrix which is controlled by organic substituents of the POSS frame-

work. Significant crystallization occurs in the networks containing pendant POSS with phenyl or cyclopentyl substituents. POSS crystallization is not restricted by the network formation, and moreover, ordering of crystalline domains takes place during cross-linking. Lamellar crystalline structure or isotropic structure were determined in the networks with different pendant POSS units.⁵ The POSS monomer with isooctyl substituents shows higher miscibility with the epoxy–amine system, and hence the POSS–POSS interaction is weaker. As a result, only small amorphous irregularly arranged aggregates are present in the corresponding O–I network.

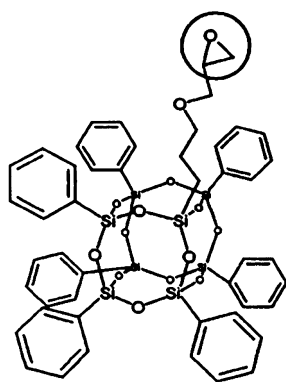
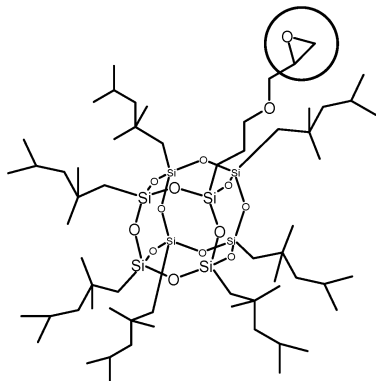
In this paper, thermomechanical properties of the POSS-reinforced epoxy networks are determined and discussed. We have followed mechanical behavior and thermal stability of the networks as functions of the POSS content, POSS topological localization in the network, and the type of substituents of the POSS framework. The hybrid systems were characterized by dynamic mechanical analysis (DMA) and thermal gravimetric analysis (TGA). The paper intends to explain the reinforcing effect of POSS and the relationships between structure and mechanical properties of the POSS-reinforced epoxy networks. On the basis of the structure analysis in the preceding paper⁵ and results of the mechanical properties, the mechanical behavior of the POSS-modified networks is interpreted. The role of the interactions POSS–POSS and POSS–polymer on mechanical behavior and thermal stability of the networks is explained.

Experimental Section

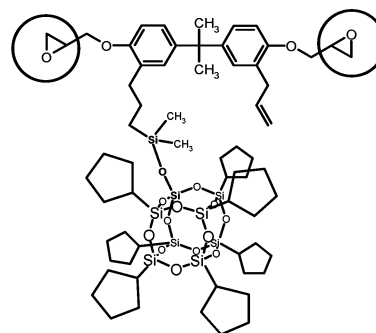
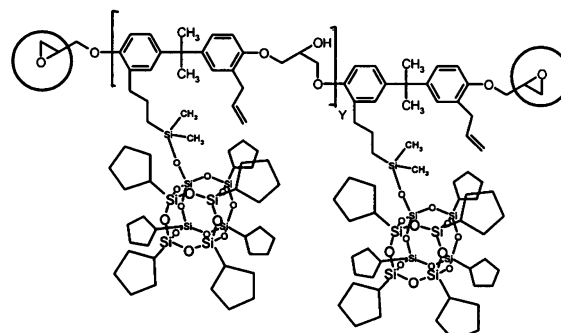
POSS-Modified Networks. The basic epoxy–amine network was prepared from diglycidyl ether of Bisphenol A (DGEBA) and poly(oxypropylene)diamine (Jeffamine D2000, molecular weight $M = 2000$) (Huntsman Inc.). The POSS-modified epoxy networks were prepared by using the epoxy-functionalized POSS monomers, POSS_REn, obtained from

Hybrid Plastics or synthesized in our laboratory.⁵ The POSS compounds with various number of epoxy functionalities, where $n = 1-8$, and various organic substituents R, were employed; R = phenyl (POSS_{ph}), isooctyl (POSS_{oct}), or cyclopentyl (POSS_{cpDGEBA}). Synthesis of the epoxy-POSS monomers and the modified epoxy networks was described in the previous paper.⁵ Composition of the epoxy networks was characterized by ratio of functional groups, r ($=\text{NH}/\text{epoxy}$).

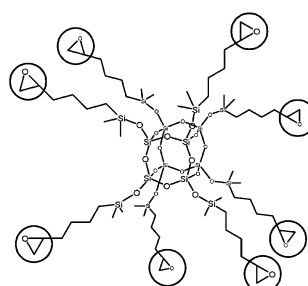
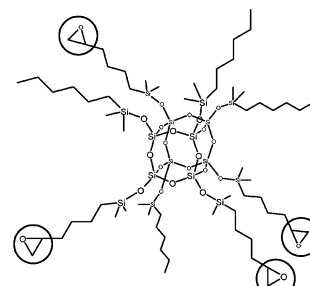
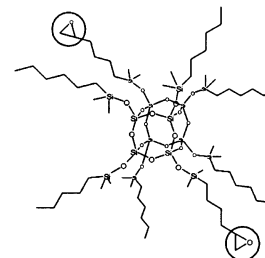
Networks with Pendant POSS. The O-I networks with POSS dangling on the network chain were formed by using the monoepoxide-POSS compound POSS_{E1}. A fraction x of the diepoxide DGEBA of the basic network DGEBA-D2000 was replaced by the monoepoxide, and the content of dangling POSS units in the modified epoxy network DGEBA(1- x)-POSS_{E1}(x)-D2000 was controlled by the ratio of both epoxy monomers. The total concentration of epoxy groups was kept constant and equal to the concentration of NH groups in D2000. The monoepoxide-POSS with phenyl (POSS_{ph}E1) or isooctyl (POSS_{oct}E1) substituents was used. Incorporation of the monofunctional monomer into the epoxy network, however, leads to a decrease in cross-linking density compared to the DGEBA-D2000 network.

POSS_{ph}E1POSS_{oct}E1

To keep a constant cross-linking density, the epoxy networks with pendant POSS were prepared also using diepoxide DGEBA containing the cyclopentane-substituted POSS unit, POSS_{DGEBA} (Hybrid Plastics). In this case, the network POSS_{DGEBA}-D2000 shows no decrease in cross-linking density compared to the reference DGEBA-D2000 network. The amount of pendant POSS was varied by varying the ratio of the epoxy monomers, POSS_{DGEBA} and DGEBA, in the network DGEBA-POSS_{DGEBA}(x)-D2000. In addition to the POSS-modified DGEBA monomer (POSS_{DGEBA,mon}), we have used also POSS-modified DGEBA oligomer (POSS_{DGEBA,olig}). The POSS_{DGEBA,mon} and POSS_{DGEBA,olig} contain on average 1.6 or 4.3 POSS units per molecule, respectively.


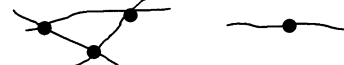
POSS_{cpDGEBA,mon}POSS_{cpDGEBA,olig} ($y=3.3$)

Networks with POSS in Junction or Backbone. The epoxy networks containing POSS units as network junctions of various functionality were prepared from multifunctional epoxy-POSS monomers: octaepoxides (POSS_{E8}) and tetraepoxides (POSS_{E4}). Diepoxide-POSS monomer POSS_{E2} was incorporated in the backbone of the network. Monomers POSS_{E4} and POSS_{E2} are statistical mixtures of a multifunctional POSS with an average functionality of 4 and 2 epoxy groups per POSS molecule, respectively. The epoxy groups are attached to the POSS skeleton through flexible hexyl spacers (see previous paper⁵).

POSS_{E8}POSS_{E4}POSS_{E2}

Methods. Dynamic Mechanical Analysis (DMA) was performed with a rheometer ARES (Rheometric Scientific). The temperature dependence of the complex shear modulus of rectangular samples was measured by using oscillatory shear

Table 1. Composition of POSS-Modified Epoxy Networks^a

network with dangling POSS	POSS wt %	Si-O skeleton wt %
		
DGEBA – POSS _{ph} E1($x=0.33$) – D2000	0.25	0.097
DGEBA – POSS _{ph} E1($x=0.67$) – D2000	0.48	0.19
DGEBA – POSS _{oct} E1($x=0.33$) – D2000	0.30	0.094
DGEBA-POSS _{DGEBA,mon} ($x=0.33$)-D2000	0.27	0.114
DGEBA – POSS _{DGEBA,mon} ($x=0.5$) – D2000	0.35	0.15
POSS _{DGEBA,mon} – D2000	0.50	0.21
POSS _{DGEBA,olig} – D2000	0.50	0.21
network with POSS in junction or backbone		
		
POSS ₈ E8 – D2000	0.31	0.13
POSS ₄ E4 – D2000	0.47	0.20
POSS ₂ E2 – D2000	0.64	0.27
reference network		
DGEBA-D2000	0	0
DGEBA-PGE($x=0.33$)-D2000	0	0

^a x ($= n_{\text{epoxy-POSS}}/(n_{\text{epoxy-POSS}} + n_{\text{DGEBA}})$) is the molar fraction of the epoxy-POSS monomer or x ($= n_{\text{PGE}}/(n_{\text{PGE}} + n_{\text{DGEBA}})$) is the molar fraction of the monoepoxide PGE.

deformation at a frequency of 1 Hz. Relaxation of modulus was carried out by a rapid, preselected deformation of the sample followed by measurement of the stress required to maintain the strain over time.

Thermal Gravimetric Analysis (TGA). Mass-loss/temperature curves were obtained with a Perkin-Elmer TGA7 device. The samples were measured at a heating rate 10 °C/min. Nitrogen or air was used as a purge gas.

Results and Discussion

The rubbery epoxy-amine network DGEBA–D2000 was reinforced with POSS units of variable types, amounts, and topological location in the network. Table 1 shows composition of the POSS-modified epoxy networks including weight fraction of the POSS molecule and of the cage-like Si–O skeleton without organic ligands.

1. Thermomechanical Properties. 1.1. Networks with Pendant POSS. Thermomechanical properties of the POSS-modified epoxy networks were determined by DMA. Figures 1 and 2 depict dynamic shear storage G' and loss G'' moduli and loss factor $\tan \delta$ ($= G''/G'$) as functions of temperature for the networks containing pendant POSS units. The thermomechanical properties are summarized in Table 2. A significant reinforcement of the DGEBA–D2000 epoxy network was achieved mainly by an incorporation of cyclopentyl-substituted POSS frameworks using POSS_{DGEBA} (see Figure 1). In our paper,⁵ it was found that strong interactions between dangling POSS units in this network lead to formation of ordered lamellar crystalline domains (see Scheme 2 in our paper⁵). These domains serve as physical cross-links, which is the reason for the rein-

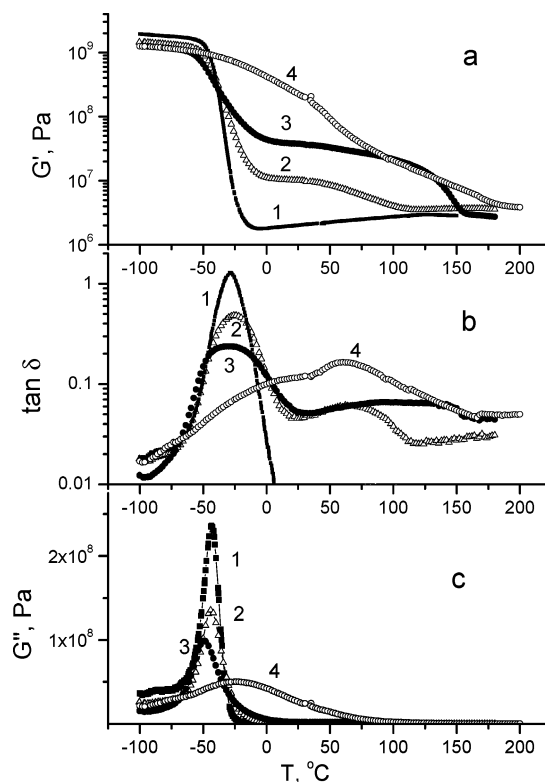


Figure 1. Shear storage modulus G' (a), loss factor $\tan \delta$ (b), and loss modulus G'' (c) of the networks with pendant POSS as functions of temperature. 1: DGEBA–D2000; 2: DGEBA–POSS_{DGEBA,mon}($x=0.5$)–D2000; 3: POSS_{DGEBA,mon}–D2000; 4: POSS_{DGEBA,olig}–D2000.

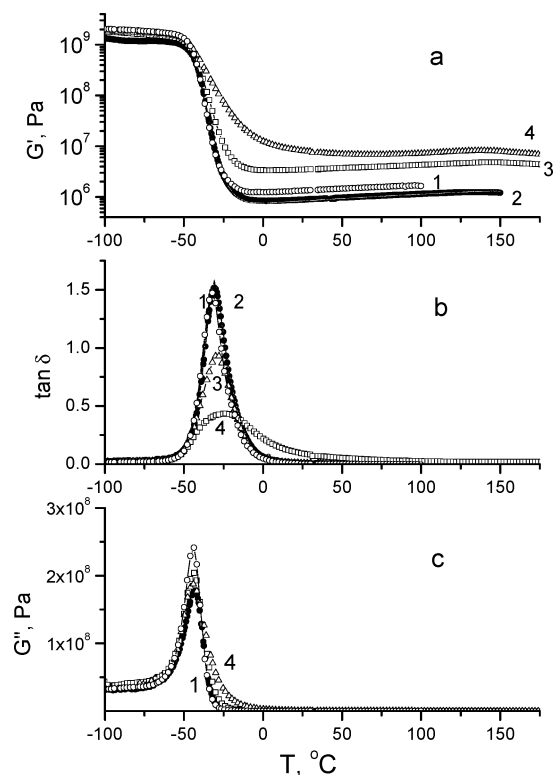


Figure 2. Dynamic shear storage modulus G' (a), loss factor $\tan \delta$ (b), and loss modulus G'' (c) of the networks with pendant POSS as functions of temperature. 1: DGEBA-PGE($x=0.33$)-D2000; 2: DGEBA-POSS_{oct}E1($x=0.33$)-D2000; 3: DGEBA-POSS_{ph}E1($x=0.33$)-D2000; 4: DGEBA-POSS_{ph}E1($x=0.67$)-D2000.

forcement. Modulus G' above the glass transition temperature T_g of the O-I networks in Figure 1a increases with increasing content of POSS in the system. The network POSS_{DGEBA,mon}-D2000 containing 50 wt % POSS units (curve 3) shows an increase in modulus by 1.5 orders of magnitude with respect to the reference network DGEBA-D2000 (curve 1). However, above T_g the modulus slightly decreases with increasing temperature and finally drops more or less steeply to an equilibrium value. The steep decrease in modulus at heating is observed at temperatures $T \sim 50$ and ~ 125 °C in the case of the networks DGEBA-POSS_{DGEBA,mon} ($x=0.5$)-D2000 containing 35 wt % POSS (curve 2) and POSS_{DGEBA,mon}-D2000 with 50 wt % POSS (curve 3), respectively. This thermomechanical behavior is reversible. By cooling the hybrid system to the glass transition temperature, its modulus grows in contrast to the DGEBA-D2000 network. We assume that the modulus decrease at heating is a result of disordering of reinforcing crystalline domains. The higher the POSS content in the network, the higher is the temperature of the modulus drop, corresponding to the increasing thermal stability of the domains and to the temperature of their disordering. The equilibrium rubbery modulus of the POSS-modified networks at a temperature above breaking of crystalline domains is close to that in the POSS-free network (see Figure 1a). It implies that the reinforcing effect of POSS is disappearing at a high temperature and that the permanent chemical cross-linking density is similar to that in the DGEBA-D2000 network.

The glass transition temperature, characterized by the position of the maximum of $\tan \delta$, is surprisingly not significantly affected by the presence of POSS in

the network POSS_{DGEBA,mon}-D2000 (see Figure 1b). However, the amplitude of the loss modulus G'' , which is a measure of the amount of relaxing chains, decreases in the networks with increasing POSS content (Figure 1c). The reduction and broadening both of the $\tan \delta$ and G'' peaks in Figure 1b,c imply a diminishing fraction of free epoxy network chains due to POSS-network chain interaction. A remarkable increase in T_g by ~ 50 °C occurs in the network containing oligomer POSS_{DGEBA,olig} (curve 4) instead of monomer POSS_{DGEBA,mon}. However, determination of T_g in this case is difficult because of an overlap of $\tan \delta$ maximum, corresponding to the glass transition and the maximum resulting from disordering of crystalline domains. The transition is very broad, and the network chain mobility is severely restricted. This O-I hybrid contains long sequences of the POSS units of the oligomer POSS_{DGEBA,olig} (see Scheme 1 in the Experimental Section). The presence of stiff blocks of the epoxy resin and an interaction of POSS with the network chain result in an increase in T_g . A detailed description of the POSS_{DGEBA}-based networks is given in the next paper.

Effect of POSS Substituents. The effect of substituents of the inorganic POSS core on mechanical properties of the networks with pendant POSS is apparent from Figure 2. In this figure the networks prepared from the monoepoxide-POSS with phenyl or isooctyl ligands are compared. The networks DGEBA-POSS_{E1} ($x=0.33$)-D2000 contain 33 mol % of the monoepoxide instead of diepoxide. The presence of a monofunctional monomer leads to chain termination and formation of defects in the network resulting in reduction of cross-linking density and the rubbery modulus compared to DGEBA-D2000. Therefore, the effect of POSS on the network properties was determined by a comparison with the reference POSS-free network of a similar cross-linking density prepared using the same molar fraction of the monoepoxide phenyl glycidyl ether (PGE), DGEBA-PGE($x=0.33$)-D2000. The theoretical decrease in the equilibrium rubbery modulus G_e of the networks due to the presence of various monoepoxides is shown in Figure 3. The modulus was calculated assuming an affine network model,⁸ $G_e = A\nu RT$, where ν is network chains density and $A = 1$. The difference in theoretical curves for various networks is given by the dilution effect due to different molecular weights of monoepoxides; $M_{\text{PGE}} = 150$, $M_{\text{POSSoct,E1}} = 1324$, $M_{\text{POSSph,E1}} = 1071$.

Figure 2a illustrates that the two POSS_{E1} monomers strongly differ in their reinforcing effect. The network with phenyl ligands, DGEBA-POSS_{ph}E1($x=0.33$)-D2000 (curve 3), exhibits an increase in the rubbery modulus G' relative to the reference network (curve 1). On the contrary, the network DGEBA-POSS_{oct}E1($x=0.33$)-D2000 with isooctyl-substituted POSS (curve 2) shows a lower modulus than the DGEBA-PGE($x=0.33$)-D2000 network (cf. also Figure 3). Experimental moduli of the networks containing PGE or POSS_{oct}E1 monoepoxides well agree with the theoretical prediction for the affine network in Figure 3, while the modulus of DGEBA-POSS_{ph}E1($x=0.33$)-D2000 network is appreciably higher compared to the theory. The results can be explained as follows, taking into account the network structure revealed by X-ray scattering in part I.⁵

Phenyl-substituted POSS units bonded to the polymer chain tend to a strong POSS-POSS interaction. The

Table 2. Thermomechanical Properties and Thermal Stability of the O–I Networks^a

	$G'(25\text{ }^{\circ}\text{C}), \text{Pa} \times 10^6$	$T_g, ^{\circ}\text{C}$	$G(t = 2\text{ h})/G(t = 0)$	$T_{5\%}, ^{\circ}\text{C}$
DGEBA–D2000	2.0	–29	0.989	296
POSS,E8–D2000	3.8	–45	0.975	280
DGEBA–POSS _{ph} E1($x=0.33$)–D2000	3.4	–30	0.937	315
DGEBA–POSS _{oct} E1($x=0.33$)–D2000	0.88	–31	0.995	299
DGEBA–POSS _{DGEBA,mon} ($x=0.33$)–D2000	5.0	–26	0.82	319
POSS _{DGEBA,mon} –D2000	38	–24	0.74	325
POSS _{DGEBA,olig} –D2000	230	20	0.43	355

^a T_g is the temperature of the maximum of the loss factor $\tan \delta$. $G(t = 2\text{ h})/G(t = 0)$ is the relative decrease in modulus $G(t)$ by stress relaxation at $T = T_g + 85\text{ }^{\circ}\text{C}$ in 2 h. $T_{5\%}$ is the temperature corresponding to 5% loss of mass in air atmosphere.

Scheme 1. Structure Model of DGEBA–POSS_{ph}E1–D2000 Network

formed crystalline POSS domains, proved in part I,⁵ act as polyfunctional POSS clusters and create physical cross-links depicted in Scheme 1. These crystalline junctions are responsible for the reinforcement of the epoxy network. In the network DGEBA–POSS_{ph}E1($x=0.67$)–D2000 with a higher monoepoxide–POSS content, the chemical cross-linking density is severely reduced as illustrated by the theoretical curve in Figure 3. However, Figures 2 and 3 show that the experimental modulus of the DGEBA–POSS_{ph}E1($x=0.67$)–D2000 network is even higher than that of the network with a lower monoepoxide–POSS content, $x = 0.33$. The modulus increase is a result of the higher concentration of POSS crystalline physical cross-links. Unlike the POSS_{DGEBA}–D2000 network, the physical junctions are effective even at a very high temperature. Only a slight decrease in modulus above $140\text{ }^{\circ}\text{C}$ in Figure 2a (curve 4) is caused by a gradual breaking of physical junctions.

On the contrary, no crystallization occurs in the DGEBA–POSS_{oct}E1–D2000 network,⁵ and the detected amorphous aggregates of POSS presumably are too weak to form stable physical cross-links. Hence, the modulus approaches the theoretical value for a homogeneous system (see Figure 3). The increased miscibility of POSS substituents with the organic matrix, which is the case of POSS_{oct}E1, does not necessarily lead to an increase in modulus and T_g as found by Phillips et al.⁹ In the case of flexible POSS substituents in POSS_{oct}E1, the weak POSS–network chain interaction affects neither modulus nor the glass transition temperature.

Figure 2b shows that there is no shift of T_g in the POSS-modified networks. Only a high content of phenyl-substituted POSS ($w_{\text{POSS}} = 0.48$, $x = 0.67$) results in broadening of the $\tan \delta$ peak (curve 4). The maximum of the loss modulus G'' in Figure 2c changes negligibly by the POSS presence in the networks, which implies that a fraction of mobile free network chains is not significantly reduced. For characterization of network flexibility often also the compliance J'' is used instead of G'' . This quantity is more sensitive to the transition details close to rubbery state while G'' characterizes better the transition motion close to glassy state. The results reveal that a very high amount of POSS_{ph} is

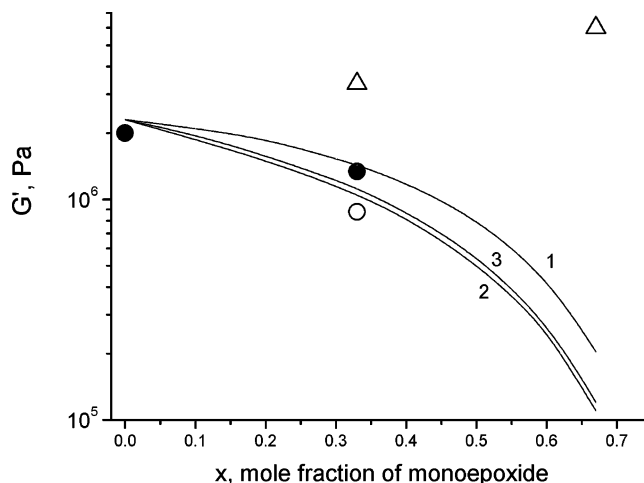


Figure 3. Shear modulus of the networks DGEBA–monoepoxide–D2000 at $25\text{ }^{\circ}\text{C}$ as a function of composition: \circ , DGEBA–POSS_{oct}–D2000; \triangle , DGEBA–POSS_{ph}–D2000; \bullet , DGEBA–PGE–D2000. Theoretical curves: 1, DGEBA–PGE–D2000; 2, DGEBA–POSS_{oct}E1–D2000; 3, DGEBA–POSS_{ph}E1–D2000.

necessary to partially affect the polymer chain mobility. At moderate POSS contents, the POSS–chain interaction is negligible and the POSS–POSS interactions dominate, being crucial for mechanical properties.

1.2. Networks with POSS in Junction or in the Backbone. The networks with POSS as network junctions units or in the backbone show an increase in rubbery modulus with increasing epoxy–POSS functionality in the series POSS,E2–D2000 < POSS,E4–D2000 < POSS,E8–D2000, as depicted in Figure 4 (curves 4, 3, and 2). To keep the stoichiometric ratio of functional groups in the system, the content of POSS units in the networks differs and rises with decreasing functionality of the POSS cross-links (see Table 1). From Figure 4 one can see that the POSS content is not crucial for modulus. It is clear that the modulus is determined by cross-linking density, which grows with rising functionality of the POSS cross-linker. As revealed by X-ray scattering,⁵ the POSS_{En} units aggregate in the network; however, the extent of aggregation decreases with increasing POSS functionality. The POSS,E8–D2000 network shows a relatively good dispersion of POSS cross-links. Therefore, this O–I network could be approximately treated by the classical theory of network formation assuming a homogeneous system. We have found a reasonable agreement of experimental and theoretical values of the modulus of POSS,E8–D2000 network (see Figure 5). Figure 5 shows also an effect of network composition on the equilibrium modulus. Generally, in epoxy–amine networks the stoichiometric composition, $r = 1$, leads to the highest cross-linking density and the highest rubbery modulus. In this case we assume the absence of polyetherification reaction

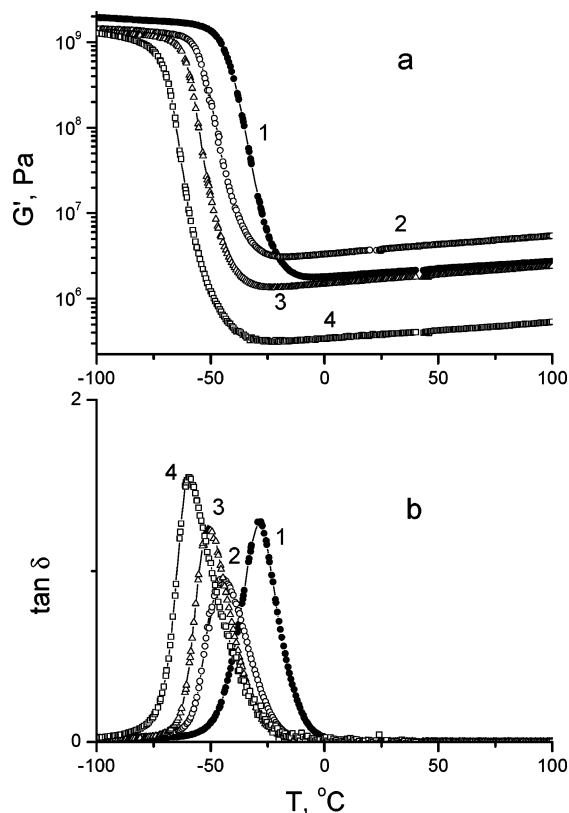


Figure 4. Dynamic shear storage modulus G' (a) and loss factor $\tan \delta$ (b) of the networks with POSS in junctions or in the backbone: 1, DGEBA–D2000; 2, POSS,E8–D2000; 3, POSS,E4–D2000; 4, POSS,E2–D2000.

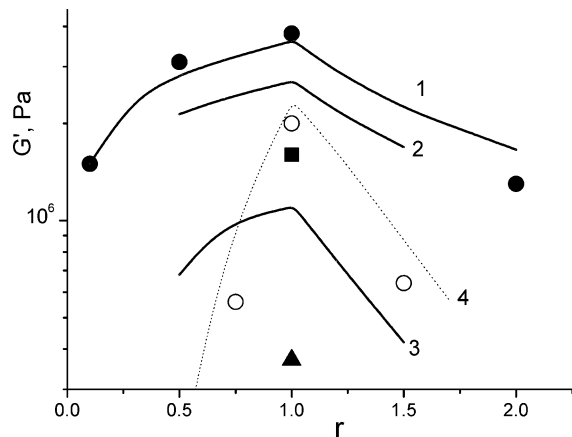


Figure 5. Dynamic shear storage modulus of the networks with POSS in junction or backbone at 25 °C as a function of the system composition r ($= \text{NH/epoxy}$): ●, POSS,E8–D2000; ■, POSS,E4–D2000; ▲, POSS,E2–D2000; ○, DGEBA–D2000. Theoretical curves: 1, POSS,E8–D2000; 2, POSS,E4–D2000; 3, POSS,E2–D2000; 4, DGEBA–D2000.

taking place under a high-temperature regime in the system with epoxy in excess.¹⁰ The experimental data of POSS,E8–D2000 networks, both with epoxy excess, $r < 1$, and amine excess, $r > 1$, correlate quite well with the theoretical prediction of the affine model. The experimental G' value measured at a frequency of 1 Hz was assumed to be an equilibrium value as no significant modulus relaxation was observed (see below and Table 2).

On the contrary, the experimental moduli of the networks with POSS of a lower functionality in junctions or backbone, POSS,E4 and POSS,E2, are signifi-

cantly lower compared to the theory (Figure 5). These networks show a higher extent of aggregation,⁵ which increases with decreasing POSS functionality. The inhomogeneity of the system results in a deviation from the theory; the larger the higher is the extent of aggregation. Because of the POSS aggregation, some epoxy functionalities are not sterically accessible to the reactant, and an incomplete conversion leads to a lower cross-linking density. Moreover, one has to take into account that the monomers POSS,E4 and POSS,E2, are statistical mixtures of products with an average functionality of 4 and 2, respectively. Particularly in the case of POSS,E2, the presence of non- and monofunctional monomers would result in an appreciable lowering of the modulus. A high fraction of the sol determined in the corresponding networks, $w_s(\text{POSS,E4-D2000}) = 0.10$ and $w_s(\text{POSS,E2-D2000}) = 0.32$, points to an incomplete conversion or the presence of nonfunctional reagents. Figure 5 shows also a slight deviation from the simple theory even for the reference network DGEBA–D2000. Lower experimental values of the modulus are a result of cyclization taking place in this system.¹⁰ The cyclization leads to an imperfect network and presence of the sol fraction, $w_s = 0.04$, in the reference stoichiometric network.

The epoxy networks with POSS in the junctions exhibit in Figure 4 a decrease in the glass transition temperature with respect to the DGEBA–D2000 network. The multifunctional POSS units contain flexible, hexyl substituents and act as a “soft” junction in the network. As a result, the network chain mobility is less restricted by flexible POSS cross-links than by stiff DGEBA moieties in the DGEBA–D2000 network, leading to a lower T_g . In addition, T_g drops with decreasing functionality of the epoxy-POSS monomer because of enhancing content of the plasticizing soft POSS unit and decreasing cross-linking density.

2. Structure Rearrangement under Strain. The results reveal that the reinforcement is mainly achieved in the networks with pendant POSS showing a strong POSS–POSS interaction, which results in crystallization and supermolecular ordering.⁵ Breaking of these crystal domains arrangement in the POSS_{DGEBA}–D2000 network at a high temperature leads to a decrease in the modulus, as illustrated in Figure 1. We have also followed stability of the reinforcing domains under strain by determination of relaxation of the modulus $G(t)$ in a rubbery state at $T = T_g + 85$ °C. A significant long-term slow modulus relaxation was observed in the case of networks with dangling POSS, DGEBA–POSS_{ph}E1–D2000 and mainly in DGEBA–POSS_{DGEBA}–D2000. The extent of the effect is characterized in Table 2 by the relative decrease in the modulus $G(t)$ within 2 h. The effect grows with increasing content of POSS, the highest effect being in the POSS_{DGEBA,olig}–D2000 network.

Slowing of chain relaxation by the bound POSS was observed by several authors.^{11–13} It is assumed that the interaction between POSS on different polymer chains, forming a physical junction, leads to a partial immobilization of the corresponding chains. The role of the interaction between POSS units (POSS–POSS interaction) and the interaction between POSS and the polymer chain (POSS–chain interaction) in affecting the hybrid system behavior was a subject of study in the last time. Romo-Uribe et al.¹² assume that retardation of the chain motion could be a result of inertia effect of a large mass

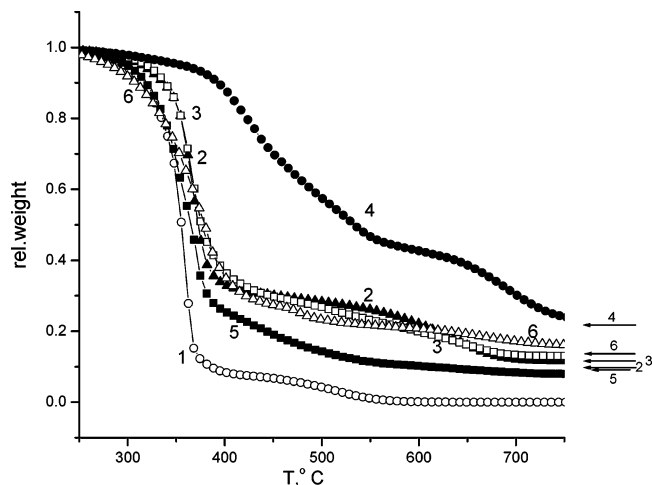


Figure 6. TGA curves of the networks in air: 1, \circ DGEBA-D2000; 2, \blacktriangle DGEBA-POSS_{ph},E1($x=0.33$)-D2000; 3, \square DGEBA-POSS_{DGEBA.mon}($x=0.33$)-D2000; 4, \bullet POSS_{DGEBA.olig}-D2000; 5, \blacksquare DGEBA-POSS_{oct},E1($x=0.33$)-D2000; 6, \triangle POSS_{E8}-D2000. Arrows indicate the theoretical residual SiO_2 .

POSS molecule acting as an anchor on the chain. Also, theoretical simulations¹⁴ agree with the effect of POSS as an anchor point. According to the simulations, the POSS aggregation is not necessary for slowing down of the chain motion. On the contrary, Lichtenhan et al.¹⁵ assume that the interaction between POSS units is dominant and determine properties of the POSS-containing systems.

In our networks, DGEBA-POSS_{ph}E1-D2000 (cf. Scheme 1), the strong POSS aggregation and formation of POSS physical junctions seem to restrict the network chain mobility. In the networks, however, this effect is less pronounced compared to the thermoplastics, as is obvious from small changes in T_g of our systems. On the contrary, in the POSS_{DGEBA.olig}-D2000 network and mainly in the POSS_{DGEBA.olig}-D2000 system, there is a very strong influence of POSS crystalline domains on the chain mobility, as evidenced by high T_g in Figure 1. In addition to this POSS-chain interaction, the observed slow modulus relaxation in the POSS_{DGEBA}-D2000 network is assumed to be also a result of a gradual breaking or disordering of the POSS structures. Both phenomena are reflected in the loss factor peak in Figure 1. The broadness of this peak is given by an overlap of the effects corresponding to the glass transition and a structure change due to disordering of the POSS crystalline domains.

No slow relaxation was observed in the networks with nonaggregating or weakly aggregating POSS units, POSS_{E8}-D2000 or DGEBA-POSS_{oct}E1-D2000. The results seem to disprove an interpretation of the POSS-modified polymers behavior by the anchoring effect.¹⁴ The heavy POSS_{oct}E1 unit bound to a polymer chain does not affect the mechanical and relaxation behavior. Obviously a strong POSS-POSS interaction plays a crucial role.

3. Thermal Stability. An improvement of thermal stability of epoxide systems by incorporation of POSS is illustrated in Figure 6, showing the TGA results. The stability of the epoxy networks is ameliorated at heating mainly in the air, implying an improved thermal oxidation resistance, while in nitrogen the effect is much smaller. Thermal stability, characterized by the temperature $T_{5\%}$ at which 5% loss of mass occurs (see Table

2), increases with increasing POSS content in the networks with pendant POSS. $T_{5\%}$ of the networks with phenyl- and cyclopentyl-substituted POSS ($w_{\text{POSS}} \sim 0.25$) (curves 2 and 3) in the air is higher by 20–25 °C compared to the reference network (curve 1). The maximum increase in the thermal stability of 60 °C was observed for the network POSS_{cp}-DGEBA_{olig}-D2000 (curve 4). “Soft POSS” in the network, containing isooctyl ligands, increases the $T_{5\%}$ only by 3 °C (curve 5). On the other hand, a drop of $T_{5\%}$ appears in the networks with POSS in junction units (curve 6). The faster initial thermal degradation corresponds to a higher mobility of network chains and lower T_g (cf. Table 2). Moreover, the POSS in junction contains the core Q8M8H8 (octakis(dimethylsilyloxy)-T8-silsesquioxane) (see Experimental Section in part I⁵), which is less thermal stable than T8 core involved in the studied networks with pendant POSS. However, in the case of the POSS_{E8}-D2000 network, a significant retardation of decomposition occurs after initial mass loss. The temperature of maximum decomposition rate is shifted to a higher value with respect to the reference network. The residue at 750 °C in the hybrid networks corresponds to the content of a pure Si-O skeleton of the POSS without the organic substituents (cf. Table 1, Figure 6).

The decompositions in nitrogen were at higher temperatures than in air. This difference was significant mainly in systems with POSS acting as a softener, while in the case of the POSS_{cp}-DGEBA-D2000 network the decomposition temperatures in nitrogen and in air were almost the same. The organic groups of POSS_{cp}-DGEBA and POSS_{ph} units seem to undergo some pyrolytic condensation in nitrogen, which leads to heat resistant materials as indicated by the relatively high final weights of these samples at 850 °C. In air an oxidation of these groups takes place at elevated temperatures (650–700 °C), which is distinguishable as a second decomposition step in Figure 6.

The high thermal stability of the POSS_{cp}-DGEBA_{olig}-D2000 network may be explained by a strong POSS-network chain interaction, which is absent in other studied O-I systems. Because of this interaction, the organic chain is shielded by the inorganic structure. In this case, however, also a high content of aromatics in the POSS oligomer can be responsible for high thermal stability of the hybrid network. Consequently, mainly the POSS-chain interaction, in addition to the POSS content and nature of the POSS ligands, are the factors governing thermal stability of the POSS-containing networks.

Conclusions

The rubbery epoxy network DGEBA-D2000 was reinforced by nanosized inorganic POSS units. Mechanical properties of the O-I networks are determined by topological localization of the POSS within the organic matrix and by morphology of the nanocomposite. The POSS-POSS interaction is crucial for mechanical properties of POSS-containing networks. Efficient reinforcement was observed mainly in the case of networks involving pendant POSS with a high propensity to crystallization. The POSS crystalline domains in the networks form physical cross-links, thus increasing cross-linking density and rubbery modulus. In the network POSS_{DGEBA}-D2000 with pendant POSS (50 wt %), the modulus increases by 1.5 orders of the magnitude relative to the DGEBA-D2000. The POSS crys-

tallites in this network are ordered in a lamellar structure as proved by SAXS and TEM;⁵ however, the supermolecular ordering is perturbed at high temperatures. Rearrangement and disordering of crystalline domains at increasing temperature result in a loss of the reinforcing effect. Thermal stability of the ordered domains increases with enhancing amount of POSS. Also in the DGEBA-POSS_{ph}E1-D2000 network the interaction between dangling phenyl-substituted POSS leads to reinforcement due to formation of crystalline physical cross-links. The networks with pendant POSS having isooctyl substituents do not exhibit any reinforcement. In this case only small, weak POSS aggregates are formed which are not strong enough to act as physical cross-links.

The POSS moieties built-in in the network as junctions are better dispersed in the matrix. The POSS dispersion and system homogeneity increase with increasing POSS functionality. Therefore, the network POSS,E8-D2000 with high-functional POSS cross-links is relatively homogeneous, and its mechanical properties can be predicted by the mean-field statistical theory of network formation and theory of rubber elasticity. The rubbery modulus of these networks is determined by cross-linking density. Hence, the modulus enhancement in POSS,E8-D2000 network compared to DGEBA-D2000 is a result of the high POSS functionality, governing the cross-link density. No specific reinforcing effect of the POSS was observed, which is in agreement with the results of Li et al.⁷ and Choi et al.¹⁶ However, in the networks with low-functional POSS cross-links or the POSS units in the backbone, the POSS dispersion is poor and small amounts of POSS aggregates remain in the network. The aggregation leads to steric shielding of the reactive POSS-epoxy groups in the networks POSS,E4-D2000 and POSS,E2-D2000. This fact results in a possible lower epoxy conversion, lower cross-linking density, and deviations from the theory. The aggregates of POSS with flexible hexyl substituents (see Experimental Section) are weak as in the case of POSS_{oct}. They break easily under stress and do not contribute to an increase in modulus.

The studied POSS-containing networks show a slight POSS-network chain interaction. Pendant POSS in the networks prefer more or less aggregation and do not significantly interact with the chain. Only a very high POSS content results in some immobilization of network chains. Therefore, the T_g of a majority of systems is not affected, and only a broadening of the transition is observed in some cases. The POSS as a network junction unit contains flexible hexyl substituents, which leads to a lower restriction of network chain mobility compared to stiff DGEBA units in the DGEBA-D2000

network. As a result, T_g decreases with increasing POSS content. POSS with flexible substituents behaves like a diluent and decreases the glass transition temperature of the network. The only system exhibiting strong interactions between POSS and organic chains is the POSS_{DGEBA,olig}-D2000 network. The network shows an increase in T_g by 50 °C due to a POSS-chain interaction and the presence of a long stiff oligomer sequence involving several POSS units.

Thermal stability of the O-I networks increases with POSS content depending on an extent of protection of organic chains by inorganic structures. The system with strong POSS-chain interactions, POSS_{DGEBA,olig}-D2000, shows the highest thermal stability.

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