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Electrical and thermomechanical properties of epoxy-POSS nanocomposites

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ABSTRACT

Two types of the epoxy-POSS nanocomposites were prepared and their electrical/dielectric and thermomechanical properties were determined. The mono- and octa-epoxyfunctionalized POSS (POSS,E1 and POSS,E8) were covalently incorporated in the epoxy network matrix DGEBA-3,3′-dimethyl-4,4′-diaminocyclohexylmethane (Laromin C260) as pendant units or as polyhedral junctions, respectively. While the POSS junctions are well dispersed in the hybrid network DGEBA-Laromin-POSS,E8, the pendant POSS aggregate to form large crystalline POSS domains.

The properties of the nanocomposites correlate with the morphology. The nanocomposites with inhomogeneously dispersed large aggregates of pendant POSS,E1 show poor properties, including low T_g and thermal stability, and the high dielectric loss factor at higher temperatures. On the contrary, the well homogeneous nanocomposites containing POSS,E8 dispersed units display improved electrical properties in the range of 1–10 wt.% POSS. The hybrid exhibits the high resistivity (1×10^{15} Ω m) and polarization index $p_i 1$ characterizing electrical relaxation, as well as the low dielectric loss factor tan δ, mainly at temperatures above 50 °C. Moreover, the material shows improved thermo oxidative stability and enhanced thermomechanical behavior. Consequently, this nanocomposite was proved to be a prospective insulation material particularly for a high temperature electrotechnical application. In contrast to electrical properties being the best at a low POSS content, the thermomechanical properties, such as rubbery modulus and T_g, are gradually improving with increasing POSS content due to growing crosslinking density.

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1. Introduction

Polymer nanocomposites show excellent mechanical and thermal properties, as well as a potential in application as electrical insulating material. Organic–inorganic polymer based nanodielectrics and electrical insulation systems have already attracted attention in the last decade [1]. Among a variety of polymer systems, such as polyamide, polyimide, polyethylene, etc., the epoxy networks belong to the most typical polymer matrices of the nanocomposites for a number of applications. The epoxy nanocomposites often meet the requirements on good mechanical properties and high thermal stability in addition to the electrical insulation and dielectric needs. Epoxy nanodielectrics are mainly based on epoxy-anhydride or amine systems filled with nanofillers such as layered silicates, silica, TiO_2, Al_2O_3 or ZnO nanoparticles. These nanocomposites were reported [2–5] to show good electrical insulation, higher breakdown voltage and resistance to partial discharges compared to neat epoxy networks or to the analogous systems filled with microsized fillers.

New types of nanofillers – well defined nanobuilding blocks – have appeared in the last time. Polyhedral oligomeric silsesquioxane (POSS) is one of the most prominent representative of this class of nanofillers. Incorporation of POSS units in a polymer matrix may result in a local reinforcement of a polymer chain [6]. The POSS containing polymer nanocomposites show an improvement of

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mechanical and thermal properties, reduced flammability and increased gas permeability. According to particular conditions, one can widely tune the properties. The POSS cage can act in a polymer either as a reinforcing filler or a plasticizing agent, thus increasing [7] or decreasing T_g [8] and modulus of a nanocomposite.

Some promising epoxy-POSS nanodielectrics have been reported lately as well. Horwath et al. [9] described the epoxy network (Epon 828-Jeffamine D400) containing physically blended POSS (trisilanolphenyl-POSS). The nanocomposite showed an increase in glass transition temperature by 2–4 °C and a significant improvement in corona endurance when exposed to a high electrical field. The low dielectric constant epoxy-POSS nanocomposite was prepared by Chen et al. [10] using octa(dimethylsilyl glycidyloxypropyl) POSS (OGDMS) and m-phenylenediamine (mPDA). The organic–inorganic network OGDMS- m-PDA involves the octa-functional POSS cage covalently bound as a junction of the network. The good dielectric properties resulted from presence of nanoporous POSS cages in the nanocomposite. Moreover, the highly crosslinked system displays a distinct increase in T_g by 80 °C compared to the reference epoxy network DGEBA- m-PDA. Takala et al. [11] have found that epoxy hybrids DGEBA-anhydride involving up to 10 wt.% of OGDMS or octa(glycidyloxypropyl)(OG) POSS units are promising in a high voltage application by a possible improvement of the breakdown strength. These nanocomposites exhibited a decrease in T_g with increasing POSS content due to a soft interphase formed by flexible substituents of OG or OGDMS.

Recently, we have studied the rubbery epoxy-POSS nanocomposites based on DGEBA – poly(oxypropylene)diamine (Jeffamine D2000) networks [12–14]. The monoepoxy and multiepoxy POSS monomers were used to prepare the hybrids DGEBA-D2000-POSS with POSS attached as pendant units on the network chain or as polyhedral junctions of the organic–inorganic network. The effect of topological placement (pendant or junction) and type of POSS organic substituents on formation, structure, thermomechanical properties and thermal stability of the rubbery nanocomposites was followed. In agreement with literature, we have found a good dispersion of POSS junctions in epoxy networks, while pendant POSS showed aggregation into amorphous or crystalline domains. Incorporation of the octaepoxy POSS monomer, octa(hexylepoxy) POSS, in the epoxy network led to an increase in rubbery modulus due to enhanced crosslinking density. T_g value, however, decreased as a result of the soft shell of POSS flexible organic substituents forming a soft organic–inorganic interphase. Hence, replacement of rigid DGEBA with POSS polyhedral junctions led to plasticization. In the case of the hybrid networks with pendant phenyl-substituted POSS units the POSS domains serve as physical crosslinks thus contributing to the reinforcement and increase in rubbery modulus. Thermal stability of the epoxy network was improved by introducing phenyl-POSS units, while POSS flexible junctions on the contrary facilitated a first thermal degradation step.

In this paper we have investigated glassy epoxy-POSS nanocomposites based on DGEBA – 3,3′dimethyl-4,4′diaminocyclohexylmethane (Laromin C260) network. The

phenyl-substituted monoepoxy POSS or octaepoxy POSS were introduced into the epoxy networks as pendant or crosslinks units. These systems were studied for possible application as electrical insulation materials. Therefore, determination of electrical and dielectric properties of the POSS containing nanocomposites was the main goal of the investigation. The effect of an epoxy matrix (glassy or rubbery), topology of POSS in a network and POSS content on electrical characteristics was studied. Moreover, we have followed the POSS influence on morphology, thermomechanical properties and thermal stability of the glassy hybrid networks, and compared the results with the rubbery DGEBA-D2000 based systems.

2. Experimental

2.1. Materials

Diglycidyl ether of Bisphenol A (DGEBA) (SYNPO a.s. Pardubice), phenylglycidyl ether (PGE), 3,3′-dimethyl-4,4′-diaminocyclohexylmethane (Laromin C260) and poly (oxypropylene) diamine (Jeffamine D2000, molecular weight M = 2000) (Huntsman Inc.) were used as received. POSS monomers were obtained from Hybrid Plastics: glycidyloxypropyl-heptaphenyl POSS (POSS$_{Ph}$E1) and octa(glycidyloxypropyl)POSS (POSS,E8).

2.2. Nanocomposite systems

List of the studied glassy epoxy-POSS nanocomposites, their composition and indication are given in Table 1. Characterization of the systems includes type and content of POSS defined as molar fraction x or as weight fraction. In addition the rubbery DGEBA-D2000-POSS,E8 hybrid was prepared for comparison.

2.3. Preparation of nanocomposites

The nanocomposites DGEBA-Laromin-POSS,E8 were prepared by bulk polymerization of the stoichiometric epoxy/amine mixture in a Teflon mould at temperatures 120 °C for 24 h, 150 °C for 3 h and 190 °C for 1 h. In the case of DGEBA-Laromin-POSS$_{Ph}$E1 networks the 50% suspension

Table 1
Epoxy-POSS nanocomposites.

System	x^a	wt.% POSS	Indication
DGEBA-Laromin	0	0	DL
DGEBA-Laromin-POSS,E8	0.015	1.1	DLE8(1.1)
	0.045	3.2	DLE8(3.2)
	0.09	6.5	DLE8(6.5)
	0.14	10	DLE8(10)
	0.2	14	DLE8(14)
	0.5	36	DLE8(36)
Laromin-POSS,E8	1	74	LE8(74)
DGEBA-Laromin-POSS$_{Ph}$E1	0.01	4	DLE1(4)
	0.02	8	DLE1(8)
DGEBA-Laromin-PGE	0.02^b	1.3^c	DLP

[a] x = [epoxy]$_{POSS}$/([epoxy]$_{POSS}$ + [epoxy]$_{DGEBA}$) – molar fraction of epoxy groups due to POSS monomer.
[b] molar fraction of epoxy groups in PGE.
[c] wt.% of PGE.

of the POSS monomer in toluene was admixed to the DGE-BA-Laromin mixture and prereacted under vigorous stirring at 60 °C in an open vessel before pouring into a mould and cured under the same thermal conditions as the POSS,E8 containing nanocomposite. The DGEBA-D2000 based nanocomposites were polymerized at 120 °C for 2 days.

All the samples prepared in the thickness of about 0.5 mm were transparent.

2.4. Experimental techniques

2.4.1. DC and AC electric measurements

For a complex classification of a dielectric material in terms of dielectric properties it is desirable to use both DC and AC evaluation methods. DC electric measurements were performed to study dielectric absorption and to determine polarization indexes, describing the phenomena occurring in dielectrics in the electric field. These measurements were implemented using High Voltage Supply 240A – Keithley, Solid State Electrometer 610C – Keithley. Special three-electrode system (30 mm in diameter, according to ČSN IEC 93 and ČSN IEC 250 standard) consisting of measuring voltage and shielding electrode were developed as shown in Scheme 1. The measurement took place using a volt-ampere method requiring a precise measuring equipment. Dielectric phenomenon was evaluated up to 900 s of applied voltage based on ČSN IEC 93 standard.

AC measurements were performed using Schering Bridge VKB BN3520 – Rohde & Schwarz for loss factor tan δ frequency dependences (42 Hz–300 kHz). Again three-electrode system was used to suppress an outer noise. Temperature dependence (30–160 °C) of the loss factor was measured by the automatic four-capacity bridge – High Volt, measuring computer LDV-5 – LDIC and heated electrode system – Tettex Instruments.

2.4.2. Dynamic mechanical analysis (DMA)

DMA was performed with a rheometer ARES (TA Instruments). The temperature dependence of the complex shear modulus of rectangular samples was measured by using oscillatory shear deformation at a frequency of 1 Hz. The dynamic shear storage modulus G' at rubbery state was determined at $T = 200$ °C. Temperature of glass transition T_g was evaluated from the maximum of loss factor tan δ ($= G''/G'$).

### 2.4.3. Transmission electron microscopy (TEM)

TEM was made with a microscope Tecnai G2 Spirit Twin 12. The samples were cut at room temperature using an ultramicrotome Leica Ultracut UCT. The 50 nm ultrathin sections were collected on a microscopic grid, covered with ca 4 nm carbon layer in order to limit sample damage in the electron beam and observed in the TEM microscope at 120 kV using bright field imaging.

2.4.4. Thermogravimetry (TG)

TG was performed as a part of Simultaneous Thermal Analysis with the analyzer SDT Q600 – TA Instruments. All samples were tested in air atmosphere at 5 °C/min temperature increase. The evaluation criteria for samples tested as electrical insulators was set up as three percent mass loss.

2.5. Samples conditioning

For evaluation of electrical properties of the dielectric material it is essential to ensure outer conditions of the

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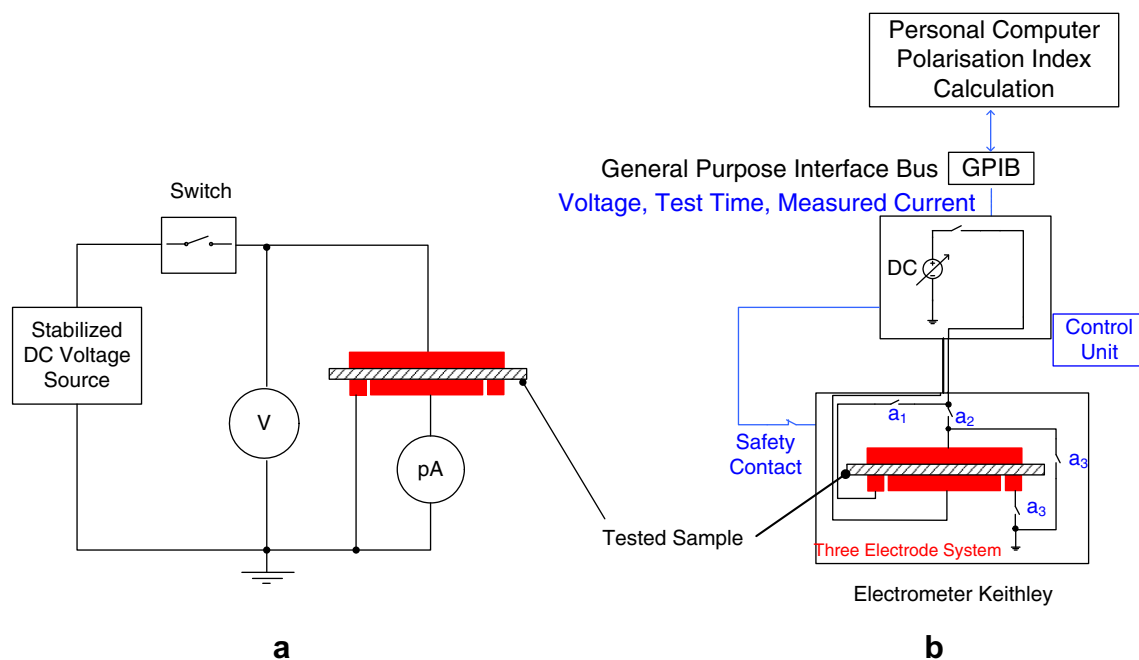
Scheme 1. Principal (a) and real (b) test set up for determination of polarization indexes. a_1, a_2, a_3 – are computer controlled switches for discharging of the sample and for measuring surface and volume resistivity (currents).

surrounding atmosphere. Therefore the samples were conditioned in the ambient laboratory before evaluation. Draining of any kind of surface potential from the samples before tests is a necessary condition especially for the DC test. It is performed by discharging surface charge by grounding the sample for a desirable time dependent on a material and dimensions. Placing the sample into measuring electrode systems needs to be done with a special concern to voltage induction during manipulation (e.g. using grounding bracelet).

3. Results and discussion

Both glassy and rubbery POSS containing epoxy nanocomposites have been prepared using DGEBA-Laromin and DGEBA-D2000 epoxy-amine network matrices. The monoepoxy (POSS,E1) and octaepoxy (POSS,E8) POSS monomers were introduced in the epoxy networks as pendant units or as network junctions. We have studied the nanocomposites with different POSS content ranging from 1.1 up to 74 wt.% (see Table 1).

Incorporation of the epoxy-functionalized POSS monomers into homogeneous epoxy-amine networks results in formation of nanostructured hybrids. In addition to a general trend, i.e. high tendency to aggregation of pendant POSS and a better dispersion of POSS junctions in a network [15], one has to take into account a kinetic factor. The epoxy-functionalized POSS monomers exhibit a lower reactivity compared to DGEBA [14], and hence they are incorporated in an epoxy-amine network only at a late stage of the reaction. Moreover, in the case of an incomplete reaction in a nanocomposite, mainly the less reactive POSS monomers remain unreacted and become phase separated. An important question is raised regarding an effect of these POSS units remaining unattached to the polymer and of an incomplete reaction generally on morphology of the nanocomposites and their properties.

It is well known that a polymer vitrification during polymerization is a typical phenomenon limiting the reaction conversion. The vitrification occurs when the

reaction temperature T_c is lower then the final T_g of the nanocomposite. Therefore, such a restriction of the conversion can be well controlled by the reaction conditions. In order to determine the effect of an incomplete conversion of POSS on morphology and mechanical, electrical as well as thermal properties of the nanocomposites, the two series of the hybrid systems were prepared by adapting the curing regime. The nanocomposites were (a) cured at sub-T_g temperatures, i.e. at T_c = 120 and 150 °C, and (b) postcured at T_c = 190 °C > T_g. We have taken into account that the glass transition temperature T_g of the DGEBA-Laromin network evaluated by DMA from maximum of the loss factor tan δ was found to be 177 °C as discussed below.

3.1. Morphology

POSS$_{Ph}$E1 is a crystalline monomer and the crystallinity is kept even after polymerization and incorporation in the epoxy network DGEBA-Laromin-POSS. WAXS analysis proved that about 70% of the POSS units remain in the crystalline form in the nanocomposite. TEM micrographs in Fig. 1a showed that POSS crystallites of the size 100 nm– 1 μm form loose agglomerates, while POSS,E8 monomer is well dispersed in the matrix forming small up to 5– 10 nm sized amorphous domains (Fig. 1b). Postcuring did not change morphology revealing that a slightly incomplete conversion and presence of the unbound POSS do not affect the nanocomposite morphology. Only in the case of the highest POSS content in the Laromin-POSS,E8 network (74 wt.% POSS) the postcuring resulted in the system homogenization as evidenced in Fig. 2.

3.2. Thermomechanical properties

Incorporation of POSS monomers in the epoxy matrix affects topology and structure of the network. Substitution of the diepoxide DGEBA by the octafunctional POSS,E8 results in an increase in crosslinking density of the network. On the contrary, covalent attachment of the monoepoxide POSS,E1 brings about formation of an imperfect network with a lower crosslinking density. Consequently, the net-
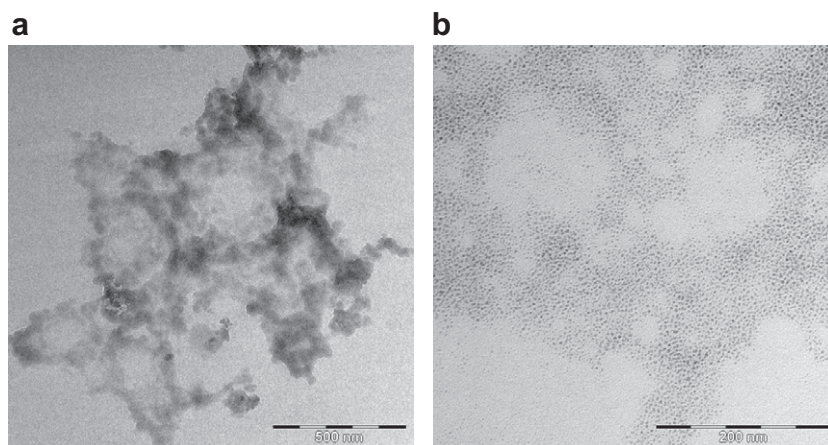

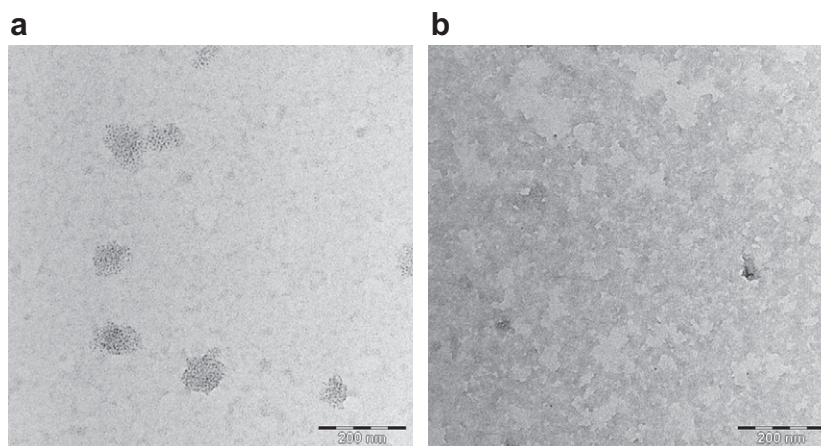**Fig. 1.** TEM micrographs of the nanocomposite DGEBA-Laromin-POSS. (a) DLE1(8), (b) DLE8(36).

Fig. 2. TEM micrographs of the nanocomposite DGEBA-Laromin-POSS,E8 (74%) cured at (a) T_c = 150 °C, (b) T_C = 190 °C.
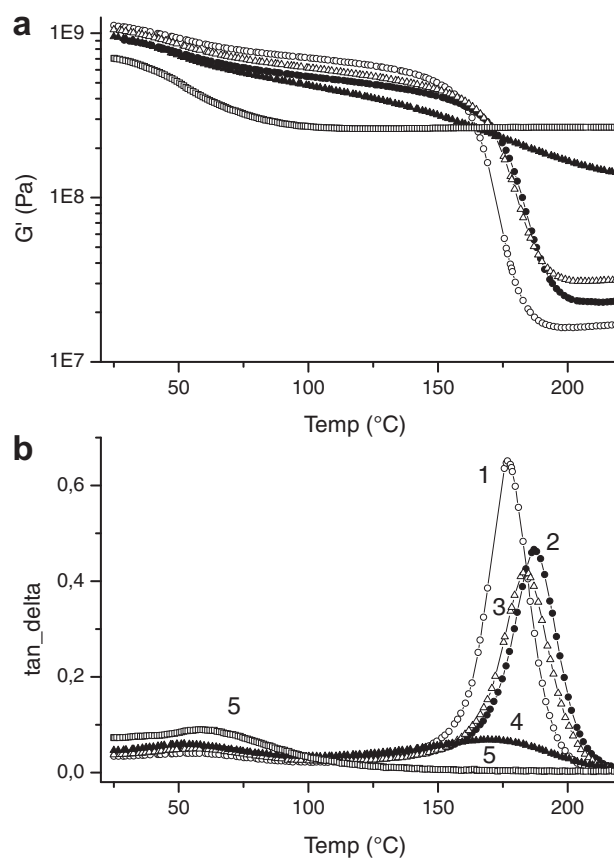

Fig. 3. Shear storage modulus G' (a) and loss factor tan δ (b) as a function of temperature of the DGEBA-Laromin-POSS,E8 nanocomposites with various content (wt.%) of POSS cured at T_C = 190 °C. 1- 0, 2- 6.5%, 3- 10%, 4- 36%, 5- 74%.

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work modification by POSS influences the main network characteristics, and thus it affects mechanical behavior of the system regardless of a phase structure and particular nanofiller effects. According to the theory of rubbery elasticity [16], the network crosslinking density v determines an equilibrium shear modulus of the material in a rubbery state G_e.

$G_e = AvRT$, where A is a front factor.

Figs. 3–5 show thermomechanical behavior of the DGEBA-Laromin-POSS nanocomposites. The rubbery storage modulus G' of the DGEBA-Laromin network is
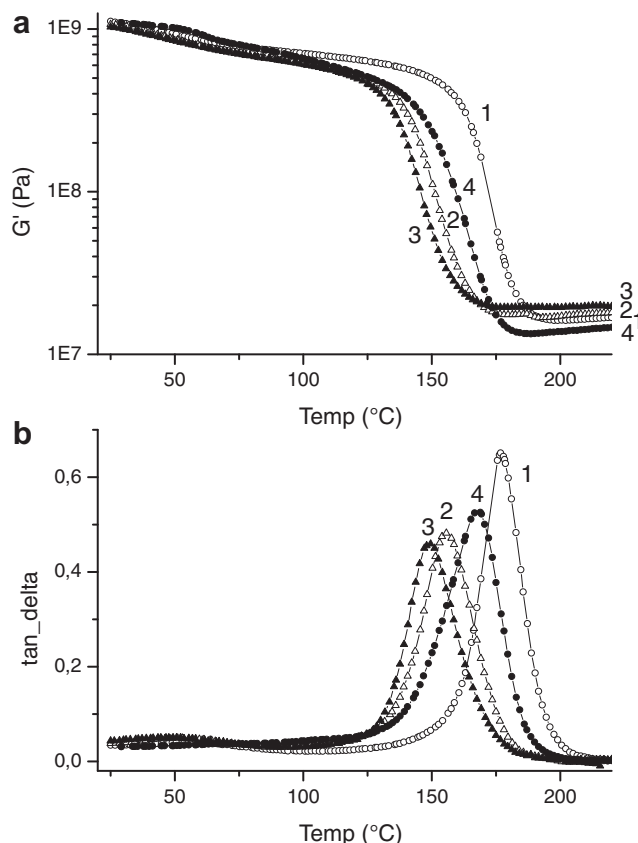
Fig. 4. Shear storage modulus G' (a) and loss factor tan δ (b) as a function of temperature of the DGEBA-Laromin- POSS$_{Ph}$E1 nanocomposites with various content (wt.%) of POSS cured at T_C = 190 °C. 1- 0, 2- 4%, 3- 8%, 4- DGEBA-Laromin- PGE (1.3 wt.%).

enhanced by introducing the POSS,E8 units in the same way as in the case of the DGEBA-D2000 based networks [13]. The modulus measured at T = 200 °C increases with growing POSS content from 1.1 wt.% up to 74 wt.% by more than an order of the magnitude (Fig. 3). Also T_g of these glassy networks grows by incorporation of POSS,E8. It is enhanced by 10 °C at 6.5 wt.% POSS. The relaxation peak corresponding to the glass transition broadens at a high POSS amount and at a content 74 wt.% POSS the glass transition of the nanocomposite even disappears. At such a high POSS content a phase inversion takes place and the continuous rigid inorganic POSS phase becomes dominating the properties of the system. The phase inversion is accompanied by a dramatic increase in modulus. The relaxation at 60 °C corresponds to a soft organic–inorganic interphase formed by the flexible organic POSS substituents. Glassy modulus of the nanocomposites decreases with increasing POSS content due to a large free volume introduced by a POSS cage.

In the hybrids with pendent POSS, i.e. DGEBA-Laromin-POSS$_{Ph}$E1 nanocomposites (DLE1), the rubbery modulus slightly increases with increasing POSS content, while T_g decreases with respect to the neat DGEBA-Laromin network as illustrated in Fig. 4. Two effects play a role in these systems; decrease in crosslinking density due to presence of the monoepoxide in the network and an

inherent influence of POSS domains. In order to separate these effects we have compared the nanocomposites with the reference network containing the same mol fraction of the POSS-free monoepoxide, phenylglycidylether (PGE). Fig. 4 reveals that presence of a small amount of the monoepoxide PGE (2 mol%) in the epoxy-amine composition leads to a decrease both in the rubbery modulus and T_g of the network DGEBA-Laromin-PGE (DLP) due to a diminished crosslinking density and formation of dangling short chains.

The different thermomechanical behavior of the two networks DLP and DLE1(8) with the same molar amount (2 mol%) of the monoepoxide can be assigned to the effect of the POSS units. Under ideal case the DLE1 networks should display a lower crosslinking density because of dilution of the system by bulky POSS units. The observed reinforcement, i.e. the higher modulus by 40%, of the POSS containing network DLE1(8) with respect to DLP is a result of physical crosslinking through hard crystalline POSS domains in the network. The modulus is even higher than in the case of DGEBA-Laromin network meaning that low chemical crosslinking of the hybrid network due to a presence of the monoepoxide is more than compensated by the physical crosslinking. Such a physical reinforcement was previously observed also in the rubbery DGEBA-D2000-POSS$_{Ph}$E1 networks [13]. In the glassy nanocomposite
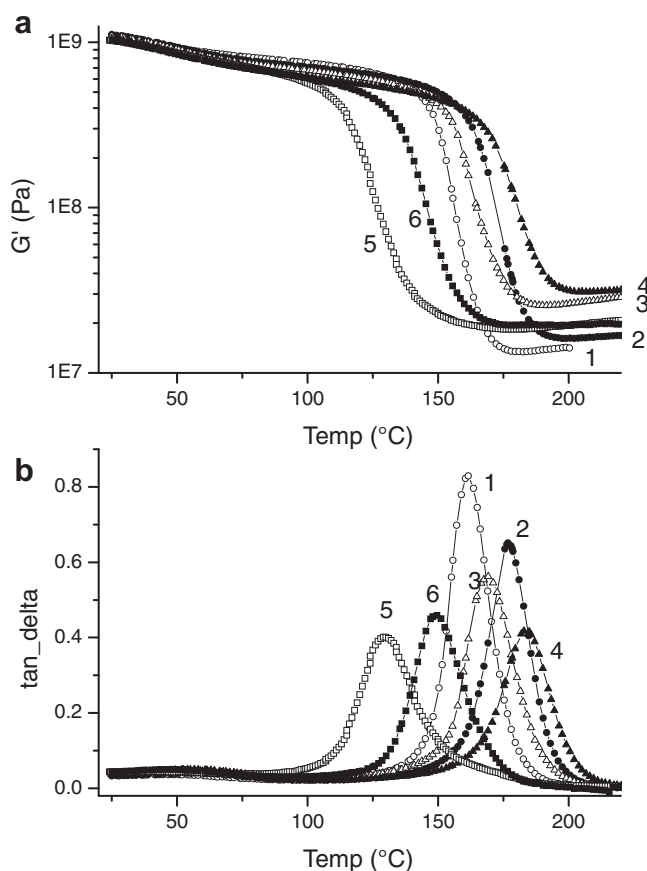
Fig. 5. Effect of postcuring. Shear storage modulus G' (a) and loss factor tan δ (b) as a function of temperature of the epoxy-POSS nanocomposites cured at T_C = 150 °C and 190 °C. 1- DL T_C = 150 °C, 2- DL T_C = 190 °C, 3- DLE8(10) T_C = 150 °C, 4- DLE8(10) T_C = 190 °C, 5- DLE1(8) T_C = 150 °C, 6- DLE1(8) T_C = 190 °C.

based on DGEBA-Laromin the reinforcement is obvious only in the rubbery state. The volumineous POSS$_{Ph}$ unit contributes by a large free volume and does not display any strong interaction with the polymer chains of the network as proved both by NMR [17] and DMA (Fig. 4b). As a result, T_g of the nanocomposite decreases with respect to DGEBA-Laromin network and with increasing POSS amount. The cage POSS$_{Ph}$E1 in the glassy network thus acts as a plasticizer.

Due to vitrification during the reaction the DGEBA-Laromin based networks are incompletely cured at a reaction temperature T_c = 150 °C. The postcuring at T_c = 190 °C results in a significant increase in T_g as well as in the rubbery modulus in both neat network and hybrids as illustrated in Fig. 5. Enhancement of the modulus reflects growth of the crosslinking density in the postcured networks. In the case of DGEBA-Lar-POSS$_{Ph}$E1 hybrid the modulus is not changed or even decreases because it is mainly affected by physical crosslinks and to a lesser extent by chemical crosslinking density determined by conversion.

3.3. Thermal oxidative stability

A positive effect of POSS on thermal and mainly thermo oxidative stability of polymer materials is well known [18].

In addition to a high thermal stability of the Si-O based POSS cage also a type of organic substituents of a POSS unit is of importance. The aromatic groups show high thermal resistance and we have also previously found [13] that POSS$_{Ph}$E1 unit increases thermal stability of the rubbery DGEBA-D2000 network.

The thermogravimetric results of the glassy DGEBA-Laromin based hybrid networks cured at 150 or 190 °C are shown in Table 2 and Fig. 6. For the thermooxidative stability of dielectrics in electrotechnical application there is a criterion of 3% mass loss for a material to be usable. The polymer nanocomposites are therefore characterized in Table 2 by temperature T_3, at which a sample exhibits 3% loss of a mass in the air atmosphere. The thermal stability of the nanocomposites (T_3) shows the same trend like the corresponding T_g values and increases in the series DLE1 < DL < DLE8. The POSS,E8 unit improves the initial thermal resistance of the epoxy network and an increasing POSS content plays a slightly positive role in DLE8 hybrids. On the contrary, POSS$_{Ph}$E1 brings about a faster initial polymer decomposition and the stability of DLE1 nanocomposites is worsened by the growing POSS amount. While the initial thermooxidative degradation is related to the homogeneity of POSS dispersion, the bulk polymer decomposition in the later heating stage (above 25% mass
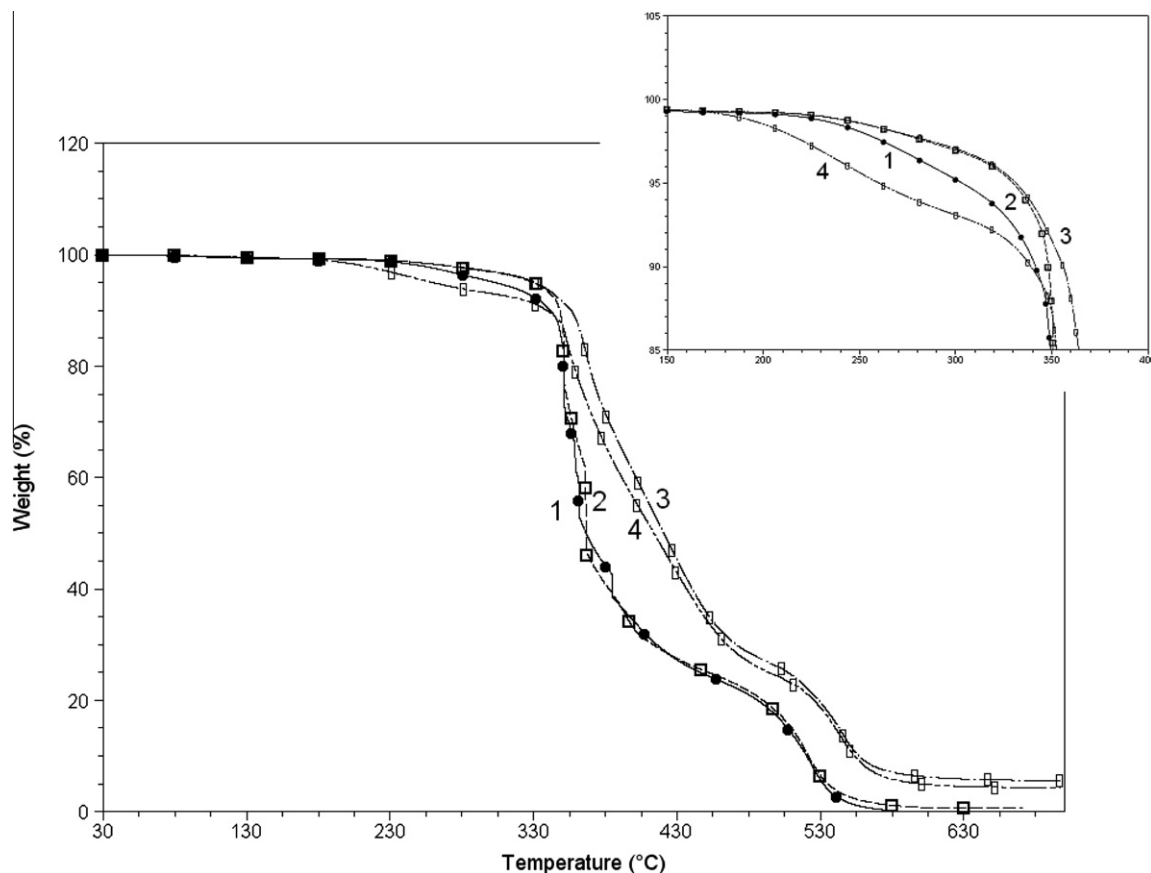
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Fig. 6. Thermogravimetric curves of the nanocomposites in the air. 1- DL, 2- DLE8(1.1), 3- DLE8(14), 4- DLE1(8).

Table 2
Nanocomposite thermal stability – 3% mass loss (electrotechnology criteria).

System	T_3, °C
DGEBA-Laromin	271
DGEBA-Laromin-POSS,E8	
DLE8(1,1)-T150	299
DLE8(1,1)-T190	298
DLE8(3.2)-T150	299
DLE8(10)-T150	307
DLE8(14)-T150	301
DGEBA-Laromin-POSS,E_{Ph}1	
DLE1(4)-T150	263
DLE1(4)-T190	263
DLE1(8)-T150	229
DLE1(8)-T190	256

Heating rate 5 °C/min. T150 – curing at 150 °C, T190 – curing at 190 °C.

loss is governed mainly by the total POSS content as shown in Fig. 6. In most cases it is retarded by increasing POSS amount. The deep thermal degradation of the nanocomposite DLE8(14) with a high POSS,E8 content is more significantly slowed down compared to the initial decomposition. The T_{50} value (temperature of the 50% loss of a mass) is enhanced by 60 °C. The figure also reveals that

POSS$_{Ph}$E1 nanofiller retards the bulk polymer decomposition (T_{50}) despite the initial fast degradation process of the DLE1(8) nanocomposite.

Interpretation of the data is based on the close relationship between the thermal stability and the nanocomposite morphology. POSS,E8 units are well homogeneously dispersed in the networks providing a protective silica layer on a polymer surface and slowing down the decomposition. On the contrary, the POSS$_{Ph}$E1 cages form large crystalline aggregates, inhomogeneously dispersed in a matrix. As a result, a part of the polymer becomes unprotected and easily decomposed. After degradation of the unscreened polymer, however, the remaining organic phase is protected by the very efficient phenyl-containing silica layer, thus being decomposed in a slower rate [7,19].

Table 2 shows also the effect of the curing temperature. While the thermal stability of the DLE8 nanocomposites with the small POSS content is not affected by the curing temperature, the T_3 value of the hybrid DLE1(8) is increased by 27 °C after postcuring. Possibly, homogeneity of a POSS dispersion is slightly improved by postcuring of the hybrid with a high POSS content.

3.4. Electrical/dielectrical properties

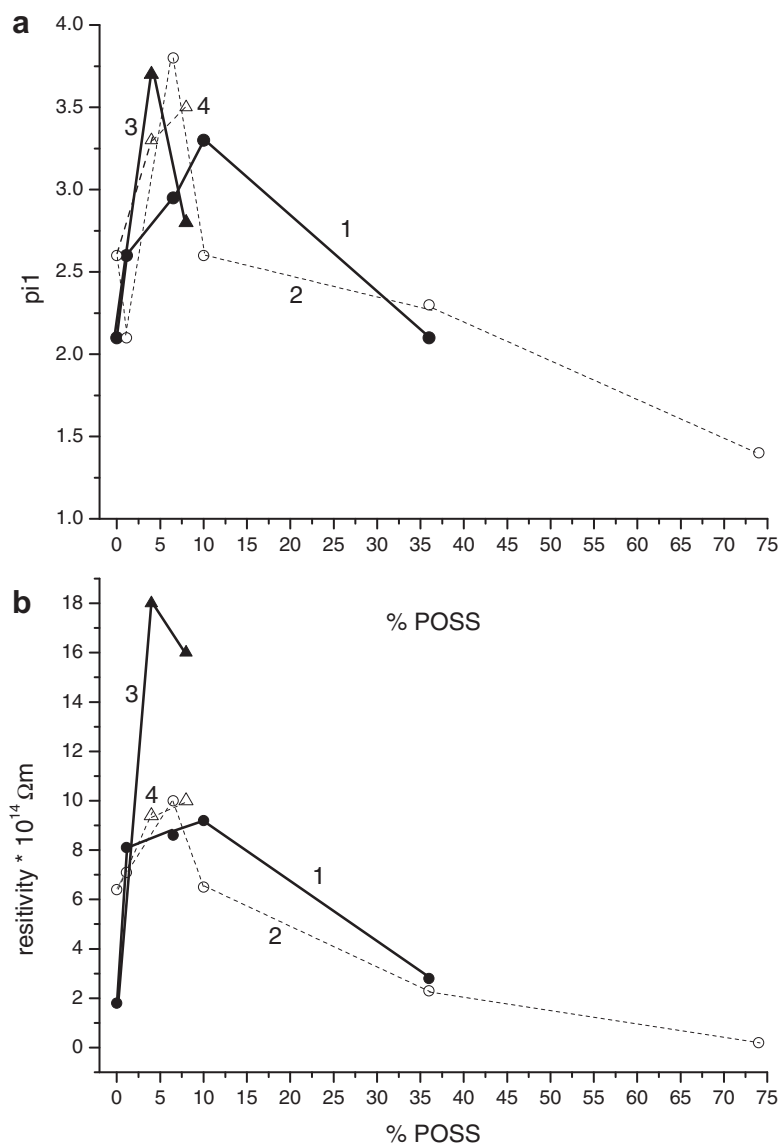We have followed three electrical parameters to characterize the hybrid systems as an insulation material.

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Fig. 7. Polarization index p_i1 (a) and resistivity in 900 s after application of the DC voltage (b) as a function of POSS content in the hybrid networks DLE8 and DLE1 cured at 150 °C and 190 °C, respectively. 1- DLE8, T_C = 150 °C, 2- DLE8, T_C = 190 °C, 3- DLE1, T_C = 150 °C, 4- DLE1, T_C = 190 °C.

Dielectric absorption and resistivity of the material were determined by DC methods, and losses of the electrical energy in the system were measured by AC methods.

With respect to the neat epoxy network the glassy nanocomposites have been found to show an improvement of the corresponding electrical properties at a low POSS content, while a worsening at a high amount of POSS. On the contrary, the rubbery nanocomposites based on DGE-BA-D2000 exhibit very poor electrical properties. These hybrids are quite unsuitable for electrotechnical application and will not be further discussed.

3.4.1. Dielectric absorption and the material resistivity

Dielectric absorption is a phenomenon responsible for changing of time characteristics of DC current after application of DC voltage to a dielectric material. Such a material is unable to follow a leap change of an applied voltage. The electric relaxation slowed-down a response of a dielectric to the electric field due to relatively slow polarization processes. Consequently, from time dependences of the current it is possible to identify properties of the material – polarization mechanisms and presence of the free charge carriers. The mechanism can be described by using the polarization indexes. This technique is used to easy compare values from all measurement data. The indexes p_i1 and p_i10 are often observed electrical insulation parameters in the case of a material evaluation. They are defined as a ratio between DC currents, I_{time}, passing through the dielectric subjected to DC voltage ($p_i1 = I_{60s}/I_{15s}$ – minute polarization index and $p_i10 = I_{600s}/I_{60s}$).

Particular test setup – principal and real used is described in the Experimental part in Scheme 1. The polarization indexes are defined for example in IEEE Std. 43–2000. The higher polarization index of the observed material means better insulation properties. A good electrical insulation material shows the polarization index higher than 1, e.g. 2–4.

In Fig. 7a one can see an increase in the polarization index p_i1 at small amounts of nanofiller in the hybrids both with POSS,E8 and POSS$_{Ph}$E1. The optimum POSS content was found to be in the range of 4–10 wt.%. The corresponding nanocomposites show the values of p_i1 = 2.6–3.8, which is comparable to classical insulation materials. While the DC measurement is widely used for a dielectric evaluation, there is no reference available as to the polarization indexes measurement of the POSS nanocomposites. According to our information our results are the first to evaluate the POSS nanocomposites using this method. The paper by Wintle [21] could serve as an example of a general description of the method.
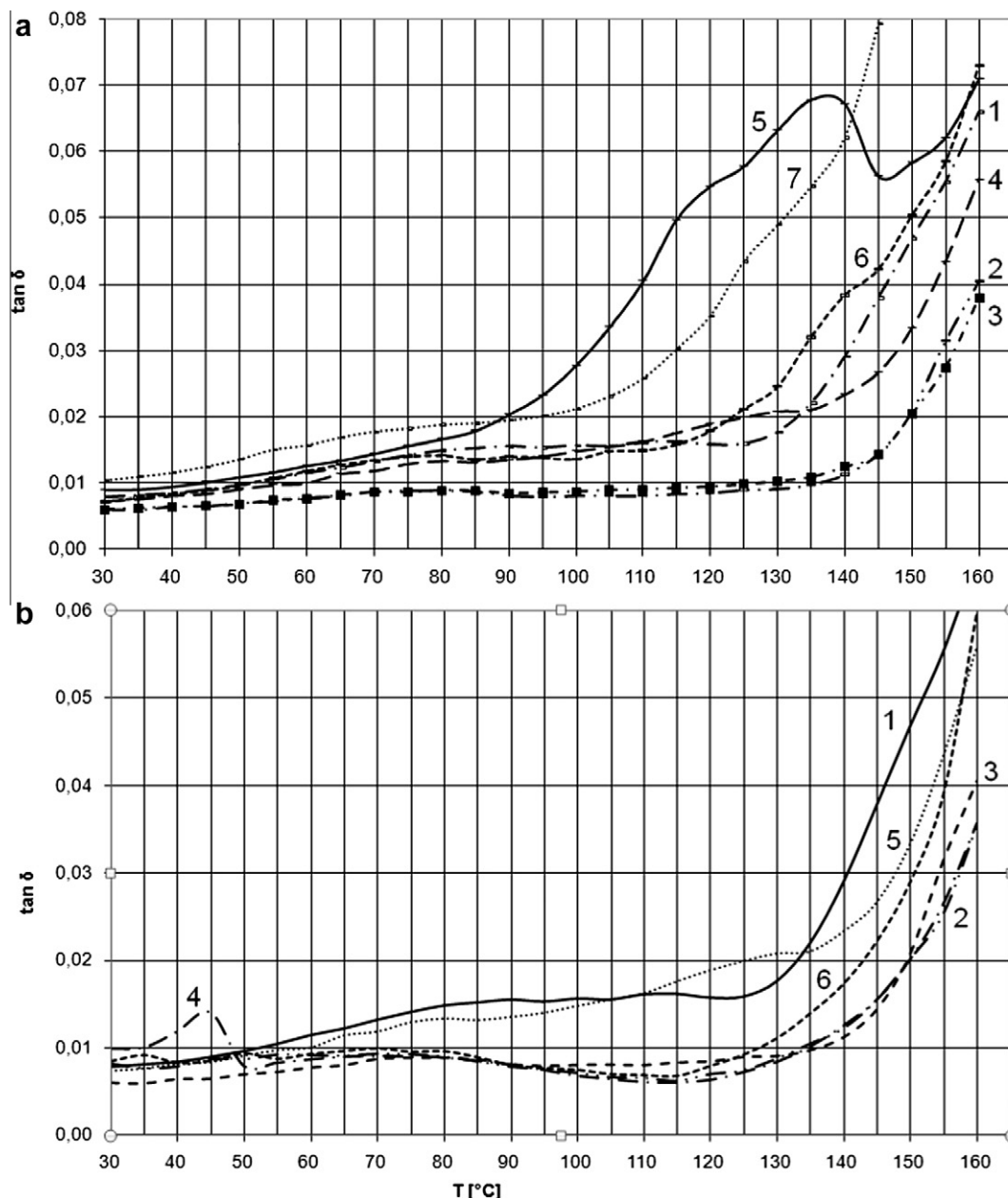

Fig. 8. Loss factor tan δ measured at a frequency 50 Hz as a function of temperature for the epoxy network DL and nanocomposites DLE8 and DLE1 cured at T_C = 150 °C (a) and comparison of curing at T_C = 150 °C and at T_C = 190 °C (b). (a) 1- DL, 2- DLE8(1.1), 3- DLE8(6.5), 4- DLE8(10), 5- DLE8(36), 6- DLE1(4), 7- DLE1(8), (b) 1- DL, T_C = 150 °C, 2- DL, T_C = 190 °C, 3- DLE8(1.1), T_C = 150 °C 4- DLE8(1.1) T_C = 190 °C, 5- DLE8(10), T_C = 150 °C 6- DLE8(10) T_C = 190 °C.

Resistivity of a material is another key parameter in terms of electrical properties. For characterization of a dielectric material the resistivity is measured in the time when all polarization processes after application of the DC voltage have finished. In our experiment it is in 900 s. Fig. 7b shows a significant increase in resistivity in the hybrids with respect to the neat epoxy network. The resistivity of the material enhances at optimum POSS content (1–10 wt.%) by an order of the magnitude or even more and reaches the value of $1 \times 10^{15} \, \Omega$ m and $1.8 \times 10^{15} \, \Omega$ m for DLE8 and DLE1, respectively. The comparison of the hybrids cured at 150 °C and those postcured at 190 °C in figure reveals that an incomplete conversion due to vitrification has no appreciable effect on the material resistivity.

3.4.2. Loss factor tan δ

AC methods for a dielectric material exhibit mainly losses of the electrical energy in the bulk material in an alternating electrical field. Generally low losses in a material are required. Fig. 8 exhibits the loss factor tan δ measured at 50 Hz as a function of temperature for samples without and with nanofiller. 50 Hz is the frequency widely used in the energy supply network, hence most of the measured electrical insulating materials have a corresponding loss factor value in the material specification. Comparison in Fig. 8b includes also the effect of vitrification and lowering of the loss factor with the increasing curing temperature.

The dielectric losses were found to be severely related to a homogeneity of the nanounits dispersion in the epoxy medium. While the nanocomposites with the poorly dispersed POSS$_{Ph}$E1 display a high dissipation factor, the small amount of POSS,E8 in the network results in the well homogeneous hybrid and lowering of tan δ factor compared to the neat network, mainly at temperatures above 50 °C. The increasing POSS content, however, leads to deterioration of the dielectrical behavior. This is in contrast to the results of Nagendiran et al. [20] who found a decreasing trend of a dielectric constant and dielectric loss at increasing POSS loading in the network DGEBA-DDS-octa-aminophenyl POSS. In our case the hybrid DLE8(1.1) with the POSS content 1.1 wt.% exhibits the best properties in terms of the dissipation factor. 36 wt.% of POSS in the network dramatically worsen the properties above $T = 50$ °C. Loss factor gradually increasing with growing temperature overrun the value tan $\delta = 0.01$ at the temperature $T \sim 50$ °C in the case of the epoxy network. For the hybrid DLE8(1.1) the temperature to reach such a value of the loss factor is extended up to 136 °C.

Fig. 8b proves that postcuring leads to a significant lowering of the dissipation factor at higher temperatures both in the neat epoxy network and in the nanocomposites with a higher POSS content (10%). The effect is negligible in the case of the hybrids with a low POSS amount. It is obvious that a large amount of the unreacted monomer due to vitrification in the nanocomposites leads to an increase in dissipation factor mainly at higher temperatures.

The samples with POSS nanoparticles proved better or similar values of the loss factor compared to systems with classical inorganic fillers such as polyethylene filled with SiO_2, TiO_2 and Al_2O_3 [22]. Takala et al. [11] studied the epoxy-POSS nanocomposites based on the epoxy-anhydride matrix. These POSS nanocomposites showed a slightly lower loss factor at 50 Hz and $T = 30$ °C compared to our epoxy-amine based POSS nanocomposites though, however, the resistivity was by almost three orders of the magnitudes lower ($\sim 10^{12} \, \Omega$ m). Another advantage of the studied epoxy-amine-POSS systems consists in a higher T_g by ~ 60–70 °C. In addition, the hybrids show good high temperature dielectric characteristics; low dielectric losses at a high temperature allowing a high application temperature of an insulation material.

4. Conclusions

It has been demonstrated that the glassy epoxy-POSS nanocomposites based on DGEBA-Laromin network represent promising insulation material for electrotechnical applications. The electrical properties of the two studied POSS containing hybrids are closely related to the morphology.

The octa-epoxy POSS monomer (POSS,E8) is well homogeneously dispersed in the epoxy network as a polyhedral junction. The homogeneous nanocomposite DGEBA-Laromin-POSS,E8 exhibits significantly improved properties including the electrical ones. While the thermomechanical properties, i.e. T_g and rubbery modulus are getting better gradually with increasing POSS content in the nanocomposite, the improved electrical behavior requires the optimum POSS amount in the range 1–10 wt.%. The best electrical properties were achieved in the case of the hybrid containing 1.1–6.5 wt.% POSS. This nanocomposite shows a high resistivity ($\sim 1 \times 10^{15} \, \Omega$ m) and polarization index p$_i$1 (3.8), as well as a low loss factor. Relatively low dielectric losses at temperatures above 50 °C make the system interesting as nanodielectrics for use at high temperatures. Tan δ factor oversteps the value 0.01 only at 136 °C. Moreover, the nanocomposites display improved thermomechanical properties (T_g and rubbery modulus) and thermal stability by 28 °C with respect to the neat epoxy network. The electrical properties are downgraded at a higher POSS content and mainly in the case of an incomplete conversion. Postcuring of such systems leads to a significant lowering of the loss factor. The selected nanocomposites with an optimal composition will be subjected to the dielectric breakdown test to determine the material dielectric strength in the next stage of the study.

The electrical properties are worse in the case of the hybrid network DGEBA-Laromin-POSS$_{Ph}$E1 with pendant mono-epoxy POSS forming inhomogeneously dispersed aggregates in the epoxy medium. The nanocomposite with a small amount of POSS (4 wt.%) shows a high resistivity ($1.8 \times 10^{15} \, \Omega$ m) and polarization index (3.7). However, the dielectric properties exhibit a larger deterioration, i.e. the high loss factor, at increasing temperature compared to the DLE8 nanocomposite. In addition, a low thermal stability for electrotechnical application (T_3) and a low T_g compared to DLE8 system make this system less applicable.

Incorporation of POSS in the epoxy network resulted in an increase in rubbery modulus. The reinforcement of the

nanocomposites with respect to the neat epoxy network was interpreted by increasing crosslinking density in the DLE8 network containing octa-functional POSS junctions, and by physical crosslinking through hard POSS crystalline domains in the case of DLE1 hybrid.

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