SYNTHESIS AND CHARACTERIZATION OF ORGANIC-INORGANIC HYBRID MATERIALS REINFORCED WITH DIFFERENT POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS)

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Au fost sintetizate noi materiale hibride, având la baza două tipuri de ansambluri poliedrice de tip (RSiO1,5)n ca agenţi de ranforsare si diglicidil eterul bisfenolului A ca matrice polimeră. Aceste materiale hibride au fost caracterizate folosind Analiza Termogravimetrica (TGA) si Analiza Mecanică in Regim Dinamic (DMA) pentru a studia influenţa tipului substituenţilor ansamblurilor poliedrice de tip (RSiO1,5)n asupra proprietăţilor hibridelor obţinute. Rezultatele DMA arată că temperatura de tranziţie sticloasă a materialelor hibride este influenţată de tipul substituenţilor moleculelor de POSS şi deasemenea de concentraţia de POSS.

New hybrid materials based on two types of polyhedral oligomeric silsesquioxane used as reinforcing agents and diglycidyl ether of bisphenol A used as polymer matrix were studied. These hybrid materials were characterized using Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA) to identify the influence of different substituent types of the polyhedral oligomeric silsesquioxane on the properties of the hybrid obtained. The DMA results show that the glass transition temperature of the hybrid materials is influenced by the substituent type of the POSS molecules and also the POSS concentration.

Keywords: polyhedral oligomeric silsesquioxanes, glass transition temperature, hybrid material, epoxy

1. Introduction

The field of hybrid materials is in a continuos development and generates new materials with different properties given by the combination of the primary components in a single material [1].

Polyhedral oligomeric silsesquioxanes are a class of hybrid compounds with the empirical formula (RSiO1,5)n and nanometrical size (1 – 3 nm) [2 - 4].

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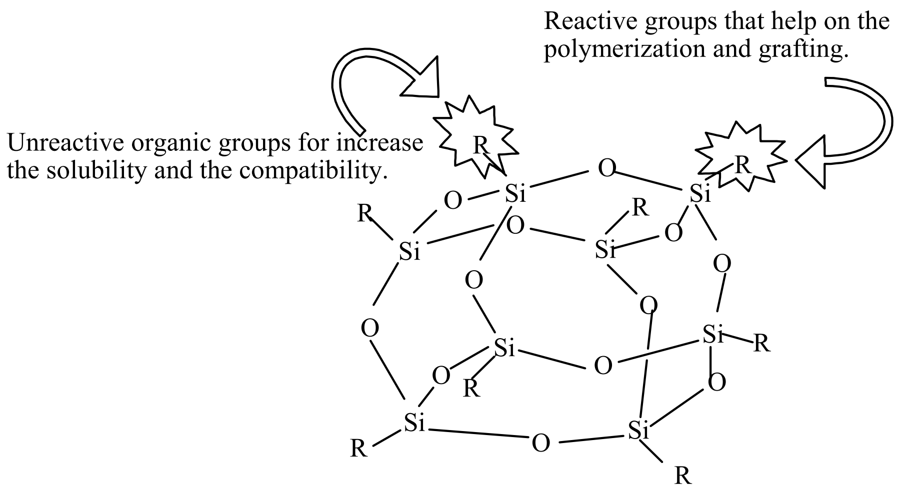


Fig. 1. Polyhedral oligomeric silsesquioxane [4].

Figure 1 shows the structure of the polyhedral oligomeric silsesquioxane. These compounds are called hybrids because they contain in their structure both an organic and an inorganic part. They may have a dual role, reinforcing agent and monomer. Generally the POSS molecules may enhance the thermal, mechanical and dielectrical properties of traditional polymers [4].

The epoxy resins are the most used thermosetting materials in the composites industry because they have excellent properties. However they exhibit some shortcomings in the applications due to the low stiffness and strength [5-7].

Incorporating the POSS in different polymers gives some improvements in the properties of these composites (reduced flammability, mechanical strength, sometimes higher Tg) [5, 8].

The goal of this work is to study the influence of different substituent types of the polyhedral oligomeric silsesquioxane on the properties of the obtained hybrid.

2. Experimental part

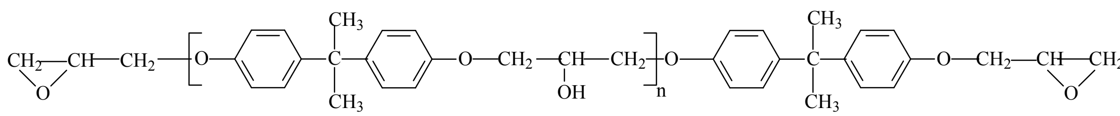
2.1. Materials

Diglycidyl ether of bisphenol A (Epilox A 19) epoxy resin type was purchased by Dow Chemical and used as received.

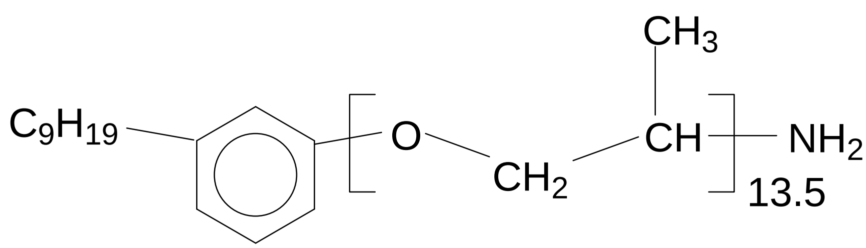
The polyetheramines Surfonamine B 100 (B 100) and Jeffamine D230 (D 230) were provided from Huntsman and used without prior purification. D 230 was used as crosslinking agent.

POSS – Cl (PSS – Octakis (2- (chlorodimetihylsily)ethyl) substituted) and POSS – H ((PSS – Octakis (dimethylsilyloxy) substituted 97 %) were provided from Sigma-Aldrich.

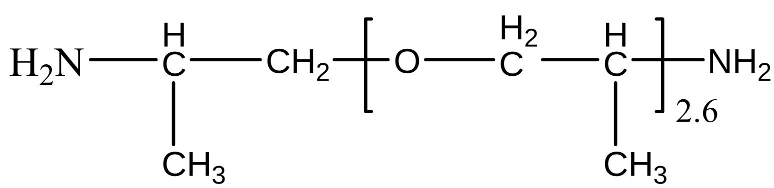
Scheme 1 shows the chemical structure of the raw materials:



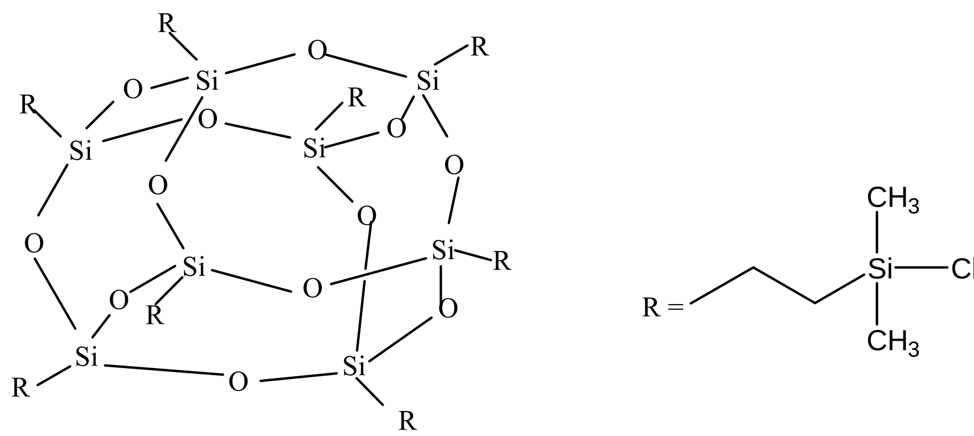
Diglycidylether of bisphenol A *(DGEBA)*



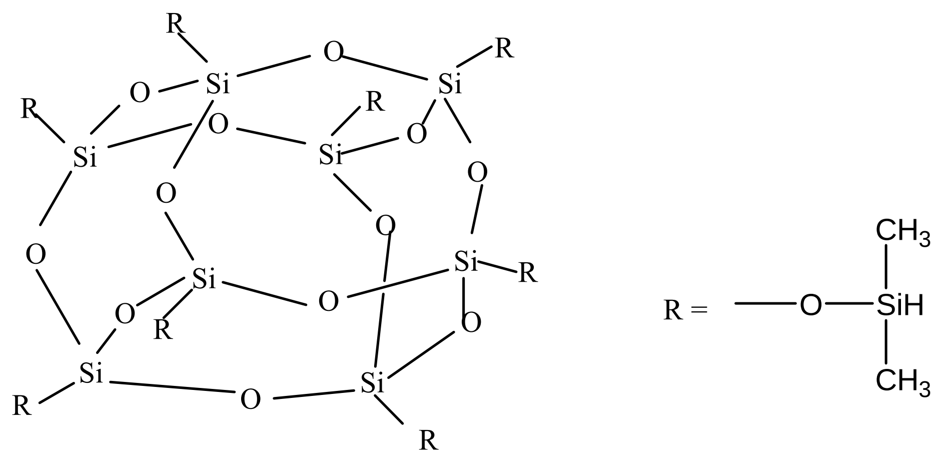
Surfonamine *(B100)*



Jeffamine (*D230*)



PSS – Octakis (2- (chlorodimetihylsily)ethyl) substituted (*POSS – Cl*)

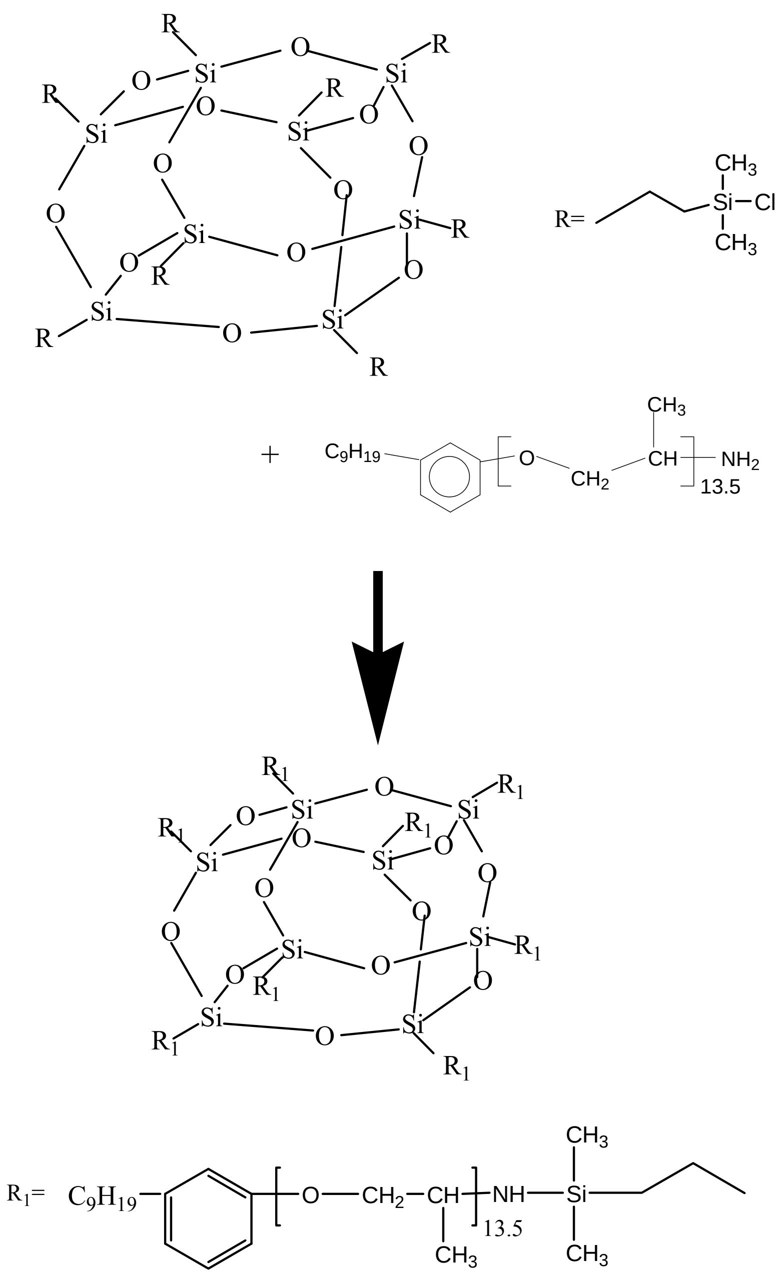


(PSS – Octakis (dimethylsilyloxy) substituted 97 % (*POSS – H*)

Scheme 1. Chemical structures of the raw materials.

2.2. POSS modification

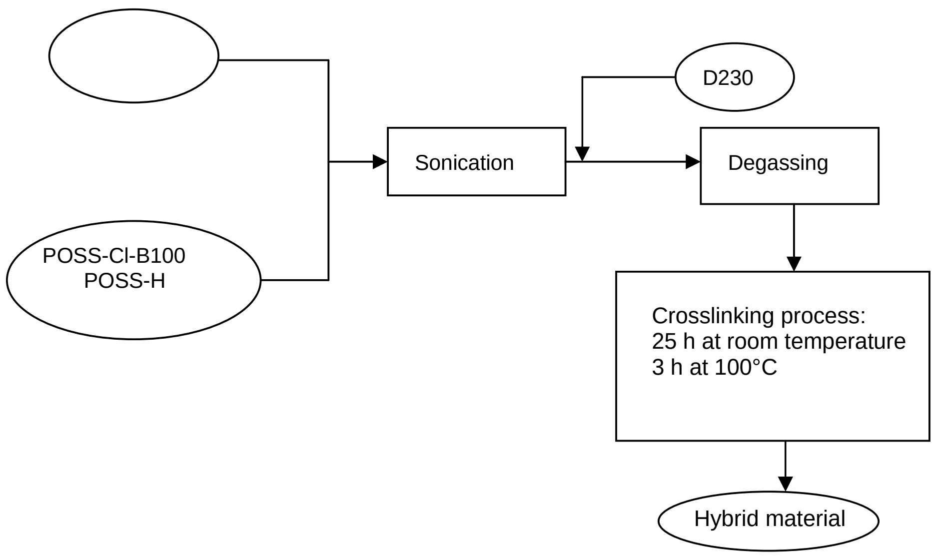
1 g POSS-Cl and a stoechiometrical quantity of amine B100 were introduced into a glass flask. The reaction mixture was heated at 40 °C for 3 hours and 24 hours at room temperature. The reaction is shown in Scheme 2.



Scheme 2. Reaction of the POSS- Cl with B100.

2.3. Synthesis of POSS-Cl-B100 and POSS-H hybrids

In this study two types of hybrid systems based on epoxy resin and POSS-Cl-B100 and POSS-H have been obtained. The synthesis of the hybrid materials was done according to Scheme 3.



Scheme 3. Synthesis of the hybrid systems reinforced with POSS-Cl-B100/POSS-H

A quantity of epoxy resin (1 g) was introduced into a glass tube and heated at 80oC in an ultrasound bath for 5 minutes. Then some different quantities of POSS (6, 15, 25 and 50 % wt.) were added and the mixture was sonicated for 30 minutes in order to allow a good dispersion of inorganic compounds into polymer matrix. The mixture was degassed for 5 minutes and then a stoichiometric amount of curing agent (D230) was added. The mixture was poured into a teflon mold. The mixture was crosslinked using the following temperature program: curing at room temperature for 25 hours and postcuring at 100 ^{o}C for 3 hours.

2.4. Characterization

Thermogravimetric analysis (TGA) was done on a Q 500 TA Instrument. A typical sample was heated from 20 to 750 ^{o}C at a heating rate of 10 ^{o}C /min under a constant nitrogen flow rate (40 ml/min).

Dynamic Mechanical Analysis (DMA) curves were recorded on a TRITEC 2000 B equipment. The samples were heated from 25 to 150 ^{o}C, using a heating rate of 10^{o}C /min and a frequency range between 0.316 and 3.16 Hz.

3. Results and discussion

3.1. Characterization of modified POSS-Cl

The modified POSS-Cl with B100 was characterized by TGA.

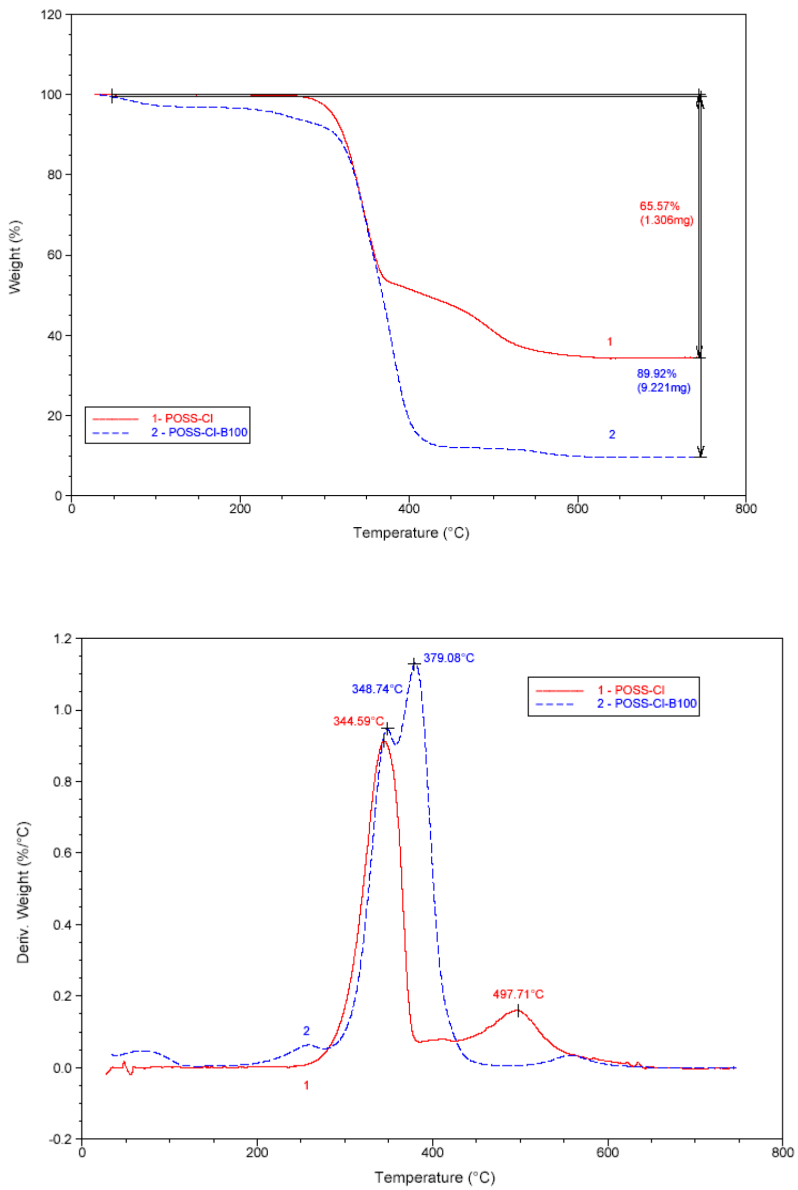


Fig. 2. TGA and DTG curves of POSS-Cl and POSS-Cl-B100.

From Fig. 2 one may observe that the weight loss for the POSS-Cl-B100 is higher that for POSS-Cl and this may be explained by the presence of the organic chain from B100 that causes a higher mass loss for the modified POSS.

3.2 Characterization of hybrid materials

3.2.1. Thermal stability of hybrid materials

TGA tests were done in order to study the influence of the POSS type and concentration on the thermal stability of hybrid materials.

Fig. 3 presents the TG and DTG curves for the hybrid materials with different concentrations of POSS-Cl-B100.

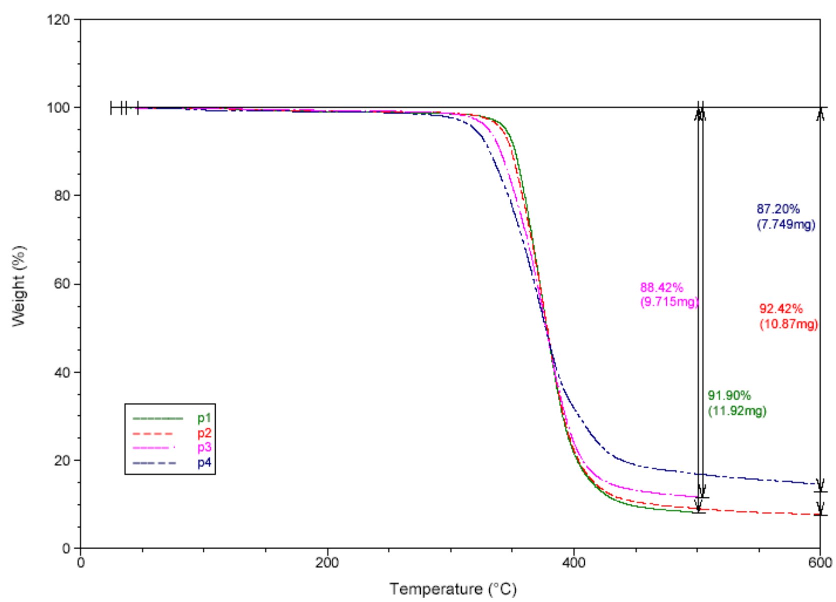


Fig. 3. DTG and TGA curves for DGEBA/ POSS-Cl-B100 hybrid materials (1)

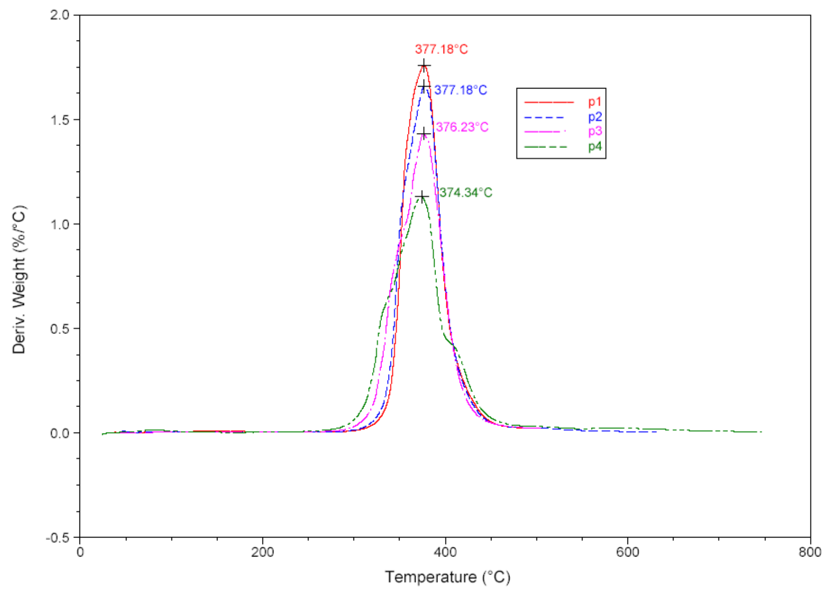


Fig. 3. DTG and TGA curves for DGEBA/ POSS-Cl-B100 hybrid materials (2)

The POSS concentration = 6% (p1); 15% (p2); 25% (p3); 50% (p4).

Table 1

The weight loss and Tmax determined from TGA and DTG for hybrid materials with POSS-Cl-B100

Hybrid system	Weight loss (%)	T_{max} (°C)
DGEBA/ POSS-Cl-B100 6%	92	377
DGEBA/ POSS-Cl-B100 15%	92	377
DGEBA/ POSS-Cl-B100 25%	88	376
DGEBA/ POSS-Cl-B100 50%	87	374

Table 2

The weight loss and Tmax determined from TGA and DTG for hybrid materials with POSS-H

Hybrid system	Weight loss (%)	T_{max} (°C)
DGEBA/ POSS-H 6%	86	378
DGEBA/ POSS-H 15%	87	380
DGEBA/ POSS-H 25%	88	380

The introduction of POSS-Cl-B100 does not significantly influenced the thermal stability of the hybrid materials even at high POSS concentrations (50 %)

(Table 1). Similar results were obtained for the hybrid materials which contain POSS-H at different concentrations (Table 2).

3.2.2. Glass transition temperature of hybrid materials

The glass transition temperature was determined using Dynamical Mechanical Analysis (DMA) which gives the Tan δ against temperature curves.

In the case of the hybrid materials with POSS-Cl-B100 the influence of the concentration of the reinforcing agent on glass transition temperature of the obtained hybrids was studied. Fig. 4 shows the curves of Tan δ-temperature dependence for the hybrids including different concentrations of reinforcing agent (6%, 15%, 25% and 50%).

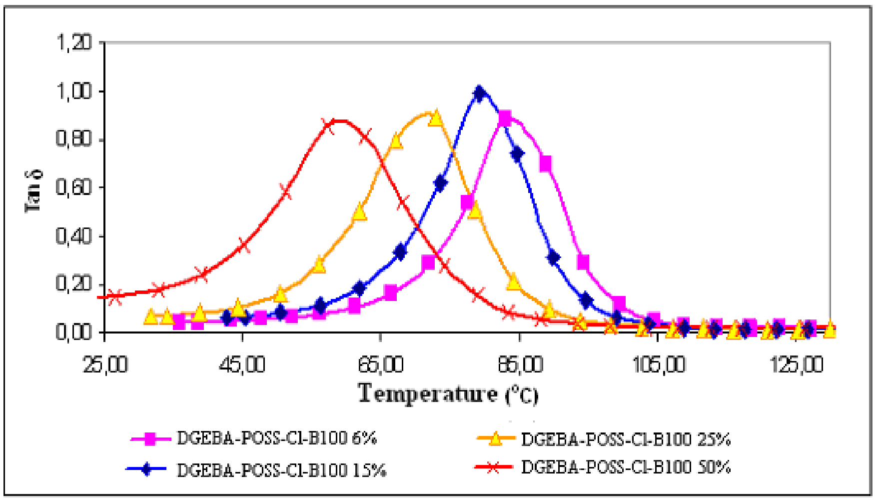


Fig. 4. The dependence of Tan δ against Temperature for different hybrid materials. Frequency =1 Hz

Table 3

The value of glass transition temperature determined from DMA curves

Hybrid system	T_g (°C)
DGEBA/POSS-Cl-B100 5 %	89
DGEBA/POSS-Cl-B100 15 %	79
DGEBA/POSS-Cl-B100 25 %	73
DGEBA/POSS-Cl-B100 50 %	63

In case of the epoxy systems reinforced with POSS-Cl-B100 a significant decrease of glass transition temperature may be noticed. In comparison with the reference (DGEBA-D230) which exhibits a glass transition temperature of 95 ^{o}C the epoxy hybrid that contains 5 % POSS-Cl-B100 gives a decrease of Tg with 6 ^{o}C. As the POSS-Cl-B100 concentration increases, the value of Tg strongly decreases (Table 3) probably due to the presence of the polyether chains of B100 which act as a plasticizer on the final material.

In case of the hybrid materials that contain POSS-H as reinforcing agent, the introduction of the POSS-H causes a low change of the glass transition temperature (Fig. 5, Table 4). Even at a high concentration of POSS-H (50 %) the Tg increases only with 3 °C which means that POSS-H exhibits a low effect as reinforcing agent.

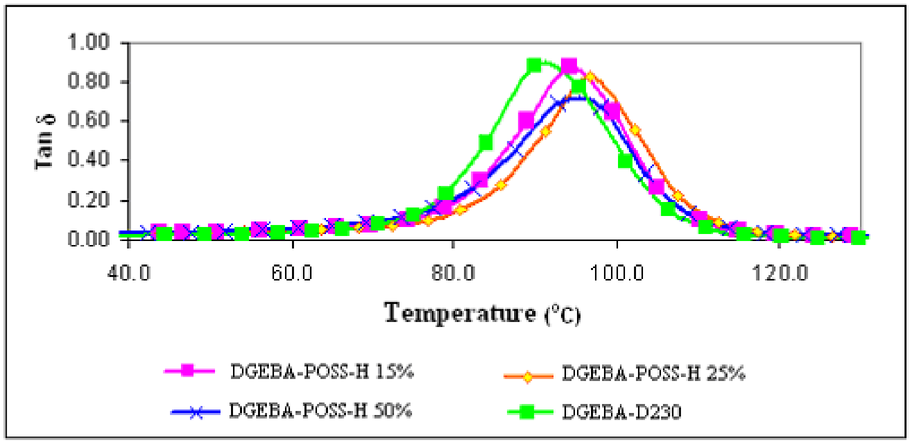


Fig. 5. The dependence Tan δ against Temperature for different hybrids. Frequency =1 Hz

Table 4.

Glass transition temperature determined from the DMA curves

Hybrid system	T_g (^{o}C)
DGEBA/ POSS-H 15 wt. %	94
DGEBA/ POSS-H 25 wt. %	97
DGEBA/ POSS-H 50 wt. %	98

4. Conclusions

New hybrid materials based on different polyhedral oligomeric silsesquioxane and epoxy resins were synthesized.

The glass transition temperature for the hybrid materials strongly depends on the POSS type and concentration.

The thermal stability of the crosslinked epoxy compound is not influenced by the presence of the POSS-H and also POSS-Cl-B100.

R E F E R E N C E S

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