New Nanocomposites based on Epoxy Resin and Modified Montmorillonite with Polyhedral Oligomeric Silsesquioxane-amine Compounds

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New reinforcing agents based on modified montmorillonite with different amines and polyhedral oligomeric silsesquioxanes were synthesized and characterized by different techniques like FTIR Spectrometry, Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC). DSC analyses show that the presence of the modified montmorillonite leads to an increase of epoxy resin reactivity due to the catalytic effect of the montmorillonite modifier which included amino groups. The glass transition temperature (T_g) for the final hybrid systems which contain modified montmorillonite with amines exhibits lower value than the epoxy systems without any reinforcing agent. The thermostability of the final hybrid systems was not influenced by the introduction of these reinforcing agents.

Keywords: epoxy, layered silicate, polyhedral oligomeric silsesquioxanes, glass transition temperature, nanocomposites.

In some cases, polymer nanocomposites exhibit significantly improved properties than conventional composites [1, 2]. The layered silicates are widely used as reinforcing agents for polymer systems. Because of its suitable layer charge density, montmorillonite is nowdays the most widely used clay as nanofiller [3]. A characteristic feature of montmorillonites is their ability to absorb certain cations and to retain them in an exchangeable state. In the normal state the montmorillonite is incompatible with a polymer matrix due to the hydrophilic character, so that it is required to modify the montmorillonite with certain organic cations in order to increase its hydrophobicity and thus to allow the dispersion of layered silicate into the polymer matrix. There are numerous modifiers used for the treatment of montmorillonite such as amino acids, alkylamines, dihydroimidazolines, silanes [4-11].

In the last years new modifiers based on polyhedral oligomeric silsesquioxanes were used for treatment of montmorillonite [12].

The term of Polyhedral oligomeric silsesquioxanes (POSS) is applied to hybrid compounds with the empiric formula $(RSiO_{1.5})_n$ and a 1-2 nanometer size, where R is hydrogen, alkyl, aryl or organofunctional derivative from alkyl or aryl group [13]. These compounds are called hybrids because they include in their structure an organic part (carbon-based) and an inorganic part based on silicon. The organic part of the POSS molecules ensures the compatibility with different resins, allowing the incorporation of the polyhedral oligomeric silsesquioxanes into the conventional organic resins. The inorganic part of the polyhedral oligomeric silsesquioxane molecules ($(SiO_{1.5})_n$ cage) increases the thermal and oxidative stability. Generally the POSS molecules may enhance the thermal, mechanical and dielectrical properties of traditional polymers [14].

The main purpose of this study is the synthesis and characterization of new reinforcing agents based on layered silicates and polyhedral assemblies of $(RSiO_{1,5})_n$ type designed for epoxy matrix.

Experimental part

Materials

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

The polyetheramines Surfonamine B 100 (B 100) and Jeffamine D230 (D 230) were provided by Huntsman. D 230 was used as crosslinking agent.

Sodium montmorillonite (MMT-Na) with a 92.5 mequiv./ 100g - Cationic Exchange Capacity (CEC) was supplied by Southern Clay Products (TX).

Benzylamine (BA) and Octadecylamine (ODA) were provided by Fluka and used without further purification.

Epoxy-POSS compound (3,7,14–tris {[3– (epoxy-propoxy)propyl]dimethylsilyloxy} 1,3,5,7,9,11,14 – heptacyclopentyl tricyclo[7.3.3.$1^{5,11}$] heptasiloxane) was received from Sigma-Aldrich.

The chemical structures of raw materials used are shown in scheme 1.

POSS modification

The Epoxy-POSS compound was modified with three amines - (B 100, ODA and BA) according to scheme 2. These modified POSS (POSS-B100, POSS-ODA and POSS-BA) were used in a protonated state as cationic agents for the montmorillonite.

The procedure for the synthesis of modified POSS with amines includes two steps. In the first step epoxy-POSS was treated with a stoechiometrical quantity of hydrochloric acid in order to open the epoxy rings. In the second step, a stoichiometric quantity of amine dissolved in tetrahydrofurane was added. The reaction mixture was heated at 60°C for 4 hours.

MMT-Na modification

The MMT modification step was performed by a cationic exchange reaction between modified POSS or simply protonated amines and MMT-Na according to scheme 3 and scheme 4.

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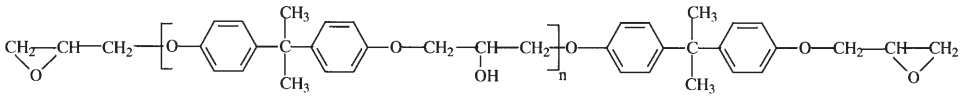
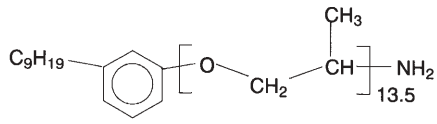
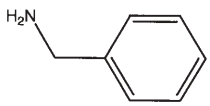


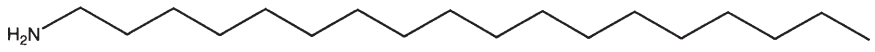
diglycidylether of bisphenol A(*DGEBA)*



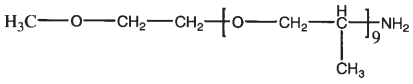
Surfonamine *(B100)*



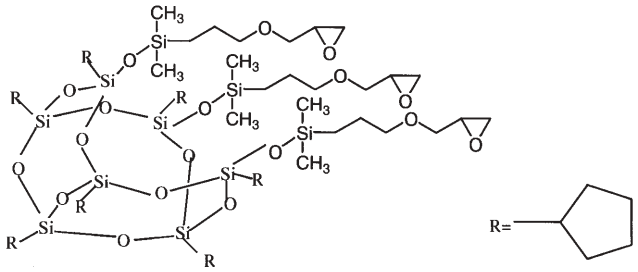
Benzylamine *(BA)*



Octadecylamine *(ODA)*

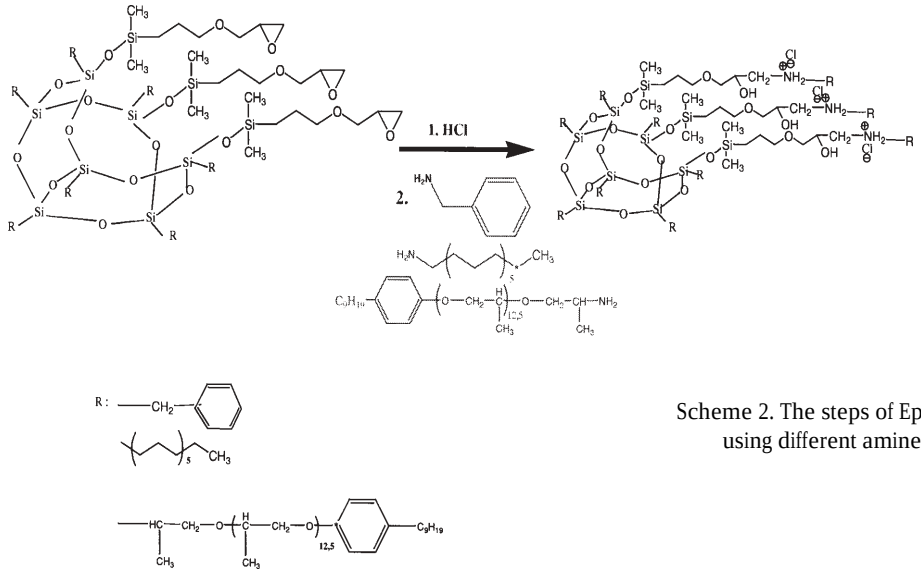


Jeffamine XTJ 505 (D230)



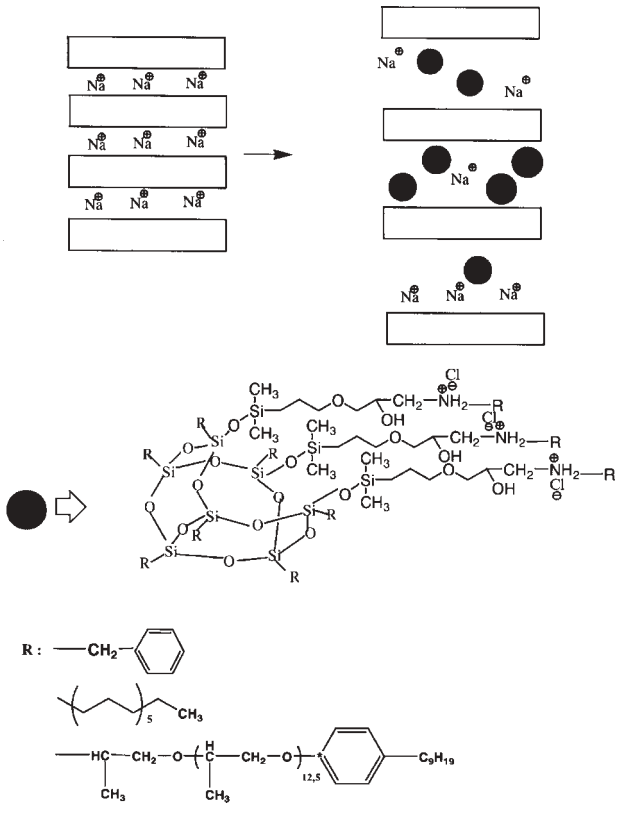
POSS – epoxy (3,7,14 – tris {[3 – (epoxypropoxy) - propyl]dimethylsilyloxy}
1,3,5,7,9,11,14 – heptacyclopentyl tricyclo[7.3.3.1^{5,11}] heptasiloxane

Scheme 1. Chemical structures of the raw materials

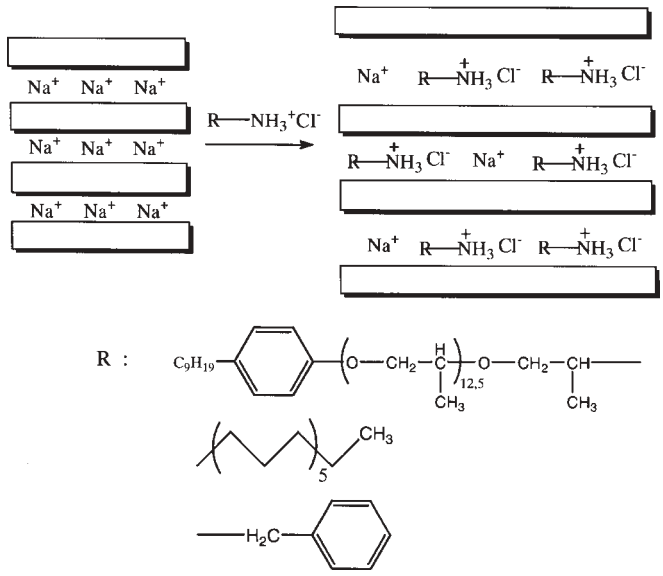


Scheme 2. The steps of Epoxy-POSS modification using different amines (BA, B100, ODA)

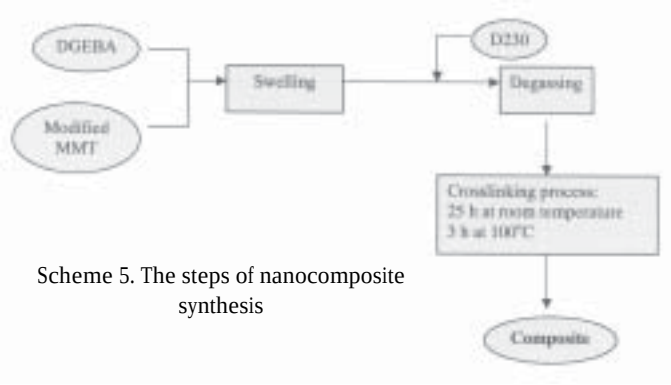
The protonated amines or modified POSS were added to 2.5 g MMT-Na already swollen in 400 ml hot deionized water for 1 h at 80 °C. The suspension was maintained at 80 °C for 4 h. Then the modified montmorillonites were isolated and washed with hot deionized water until no chloride ions were detected by one drop of 0.1 N $AgNO_3$ solution. The product was dried for two days at 80°C and then ground to produce powder.



Scheme 3. The MMT-Na modification with POSS-amines



Scheme 4. The MMT-Na modification with protonated amines



Scheme 5. The steps of nanocomposite synthesis

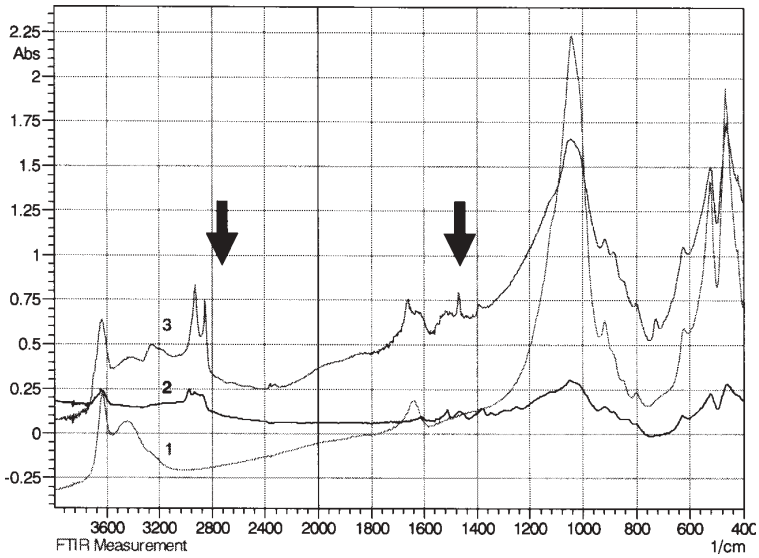


Fig. 1. FTIR spectra of unmodified montmorillonite (MMT-Na) and modified MMT with different amines: 1- MMT-Na, 2- MMT-B100, 3-MMT-ODA

Synthesis of epoxy-montmorillonite hybrids

Several types of hybrid systems based on epoxy resin (DGEBA) and different modified MMT (MMT-B100, MMT-ODA, MMT-BA, MMT-POSS-B100, MMT-POSS-ODA, MMT-POSS-BA) were synthesized according to scheme 5.

Thus, a certain amount of epoxy resin (3 g) was introduced into a glass tube and heated at 80°C in an ultrasound bath for 5 minutes. Then the modified montmorillonite (5 wt. %) was added and the mixture was sonicated for 1 hour in order to achieve a good swelling of the montmorillonite with epoxy resin.

After the degassing step (30 min) a stoechiometrical quantity of Jeffamine D230 was added. The final mixture was crosslinked using the following temperature program: curing at room temperature for 25 h and postcuring at 100°C for 3 h.

Characterization

FTIR spectra were recorded on a SHIMADZU 8900 equipment using 30 scans and 4 cm^{-1} resolution. The samples were analyzed from KBr pellets.

Thermogravimetric analyses were performed on a Q 500 TA Instruments. A typical sample was heated from 20 to 750°C at a heating rate of 10 °C /min under a constant nitrogen flow rate (40 mL/min).

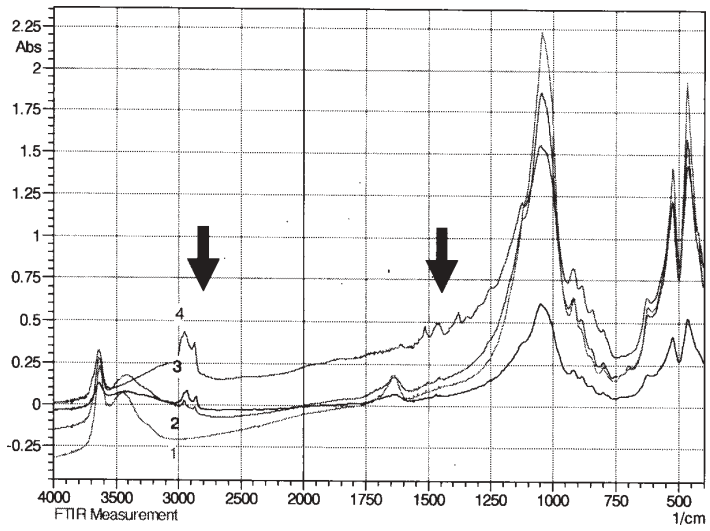


Fig. 2. FTIR spectra of unmodified montmorillonite (MMT-Na) and modified MMT with different POSS: 1- MMT-Na, 2- MMT-POSS-B100, 3-MMT-POSS-ODA, 4-MMT-POSS-BA

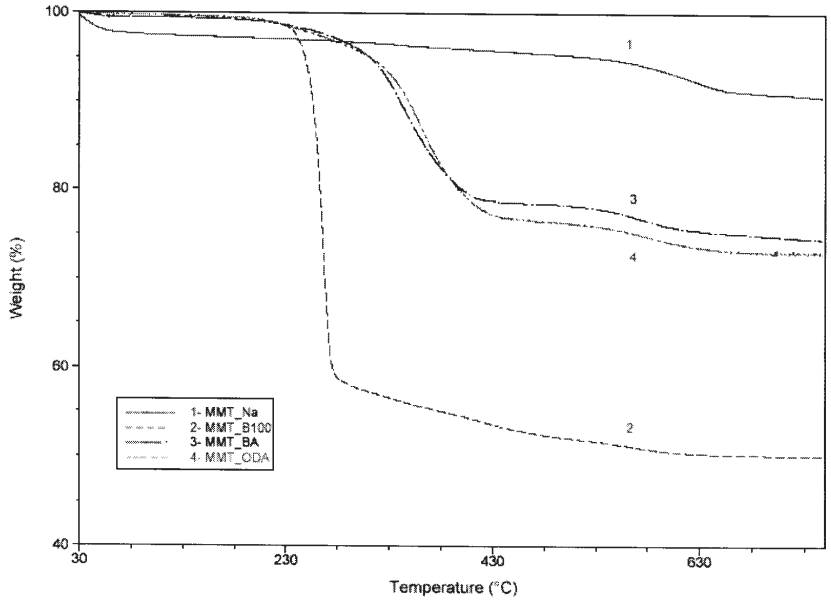


Fig. 3. TGA curves of 1-unmodified MMT (MMT-Na) and modified MMT with different amines (2-MMT-B100; 3-MMT-BA; 4-MMT-ODA)

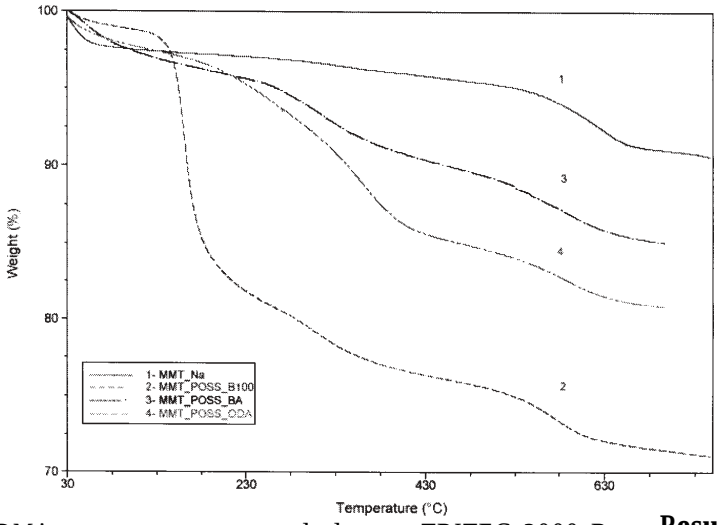


Fig. 4. TGA curves of 1-unmodified MMT (MMT-Na) and modified MMT with different POSS (2-MMT-POSS-B100; 3-MMT-POSS-BA; 4-MMT-POSS-ODA)

DMA curves were recorded on a TRITEC 2000 B equipment. The samples were analyzed in a single cantilever bending mode. The samples were heated from 25 to 150°C, using a heating rate of 10°C /min and a frequency range between 0.316 and 3.16 Hz.

The X-ray Diffraction (XRD) analysis was performed on a XRD 6000 SHIMADZU Diffractometer.

DSC thermograms (non-isothermal curves) were registered on a Linseis PT 10 instrument. from 30 °C to 300 °C using a 10 °C/min heating rate.

Results and discussion

The modification of MMT was initially proved by FTIR analysis (fig. 1 and fig. 2).

The appearance of the new peaks at 2925 cm^{-1} and 2854 cm^{-1} assigned to C-H stretching vibration from CH_2 groups and the peak at 1450 cm^{-1} assigned to the C-H deformation vibration from CH_2 group represents the first evidence of the exchange process. All the clays exhibit the peaks corresponding to the hydroxyl group stretching vibration from the Si-OH group. In the case of MMT-B100 and MMT-

Table 1
THE WEIGHT LOSS OF UNMODIFIED MMT (MMT-NA) AND MODIFIED MMT DETERMINED BY THERMOGRAVIMETRICAL ANALYSIS

Montmorillonite type	Weight loss (%)
MMT-Na	6
MMT-B100	50
MMT-BA	25
MMT-ODA	27
MMT-POSS-B100	29
MMT-POSS-BA	15
MMT-POSS-ODA	19

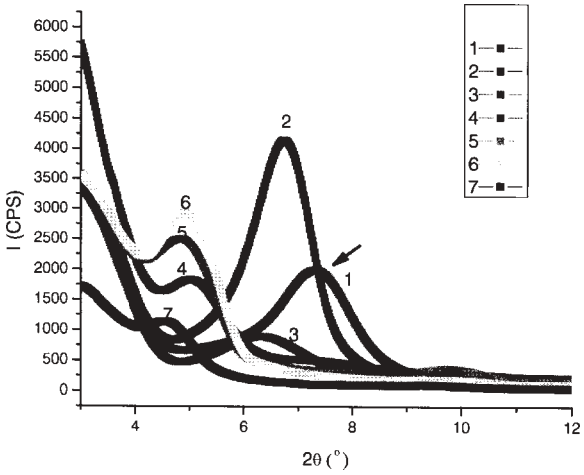


Fig. 5. XRD curves of 1-unmodified MMT (MMT-Na) and modified MMT with different agents: 2-MMT-BA; 3-MMT-POSS-BA; 4-MMT-B100; 5-MMT-POSS-B100; 6-MMT-ODA; 7-MMT-POSS-ODA

Table 2
THE BASAL DISTANCES OF UNMODIFIED MONTMORILLONITE (MMT-NA) AND MODIFIED MONTMORILLONITE WITH DIFFERENT AGENTS

Montmorillonite Type	Basal distance (Å)
MMT-Na	11.9
MMT-BA	12.9
MMT-POSS-BA	13.5
MMT-B100	16.6
MMT-POSS-B100	17.1
MMT-ODA	16.9
MMT-POSS-ODA	17.1

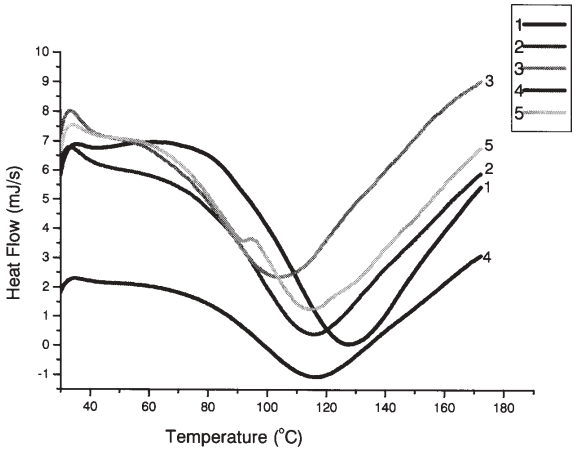


Fig. 6. DSC curves of epoxy systems which contain modified MMT with different agents: 1- DGEBA/D230; 2-DGEBA/MMT-B100/D230; 3-DGEBA/MMT-POSS-B100/D230; 4-DGEBA/MMT-ODA/D230; 5-DGEBA/MMT-POSS-ODA/D230

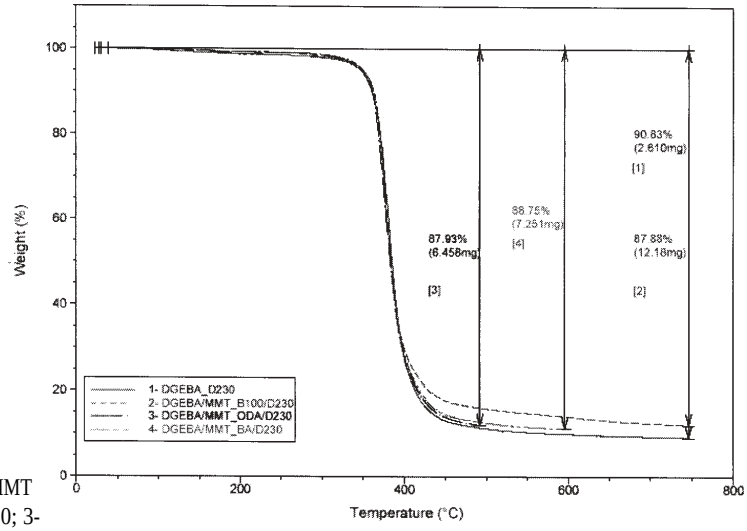


Fig. 7. TGA curves of epoxy systems reinforced with modified MMT with amines

POSS-B100 a new peak at 1500 cm^{-1} corresponding to the C-H stretching vibration from aromatic ring was also identified.

The presence of the modifier agent into the silicate layers after the cationic exchange process took place was also proved by thermogravimetrical analysis.

Figures 3 and 4 show the TGA curves of unmodified MMT and modified MMT with different agents (amines and modified POSS).

From figure 3 and figure 4 one may notice that in the case of unmodified MMT a small weight loss assigned to the adsorption water elimination was observed. Also a weight loss assigned to the aluminosilicate dehydroxilation

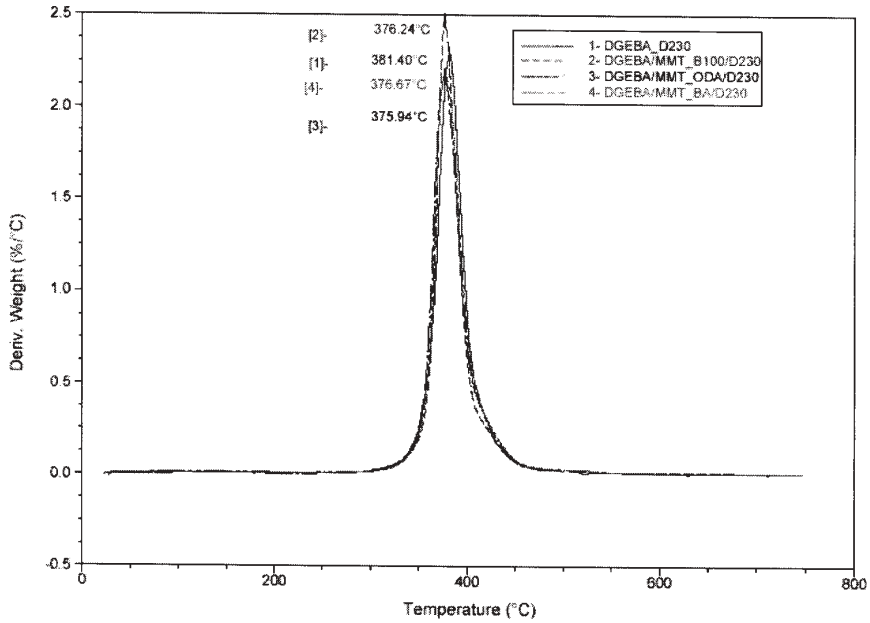


Fig. 8. DTG curves of epoxy systems which contain modified MMT with amine

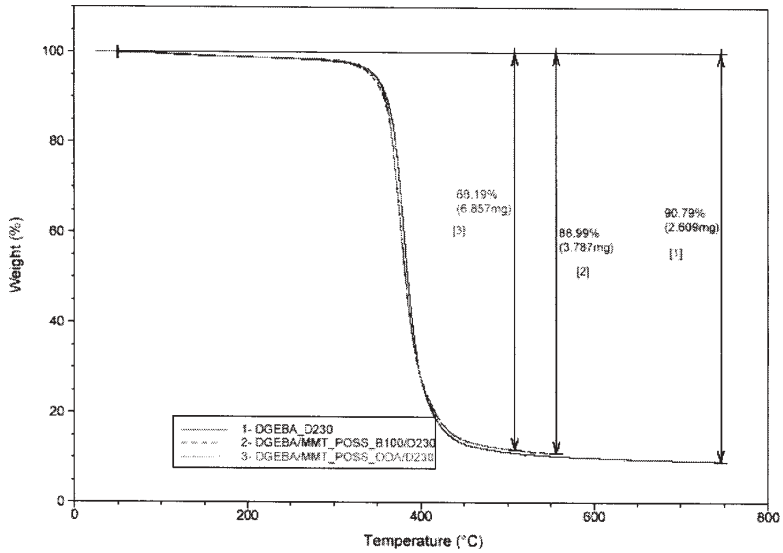


Fig. 9. TGA curves of epoxy system reinforced with modified MMT with POSS-amines

was noticed at 630°C. It is very important to know the weight loss of unmodified MMT in order to evaluate the organic compounds content which exists into the silicate layers after the cationic exchange process. In the case of modified montmorillonites with different amines and modified POSS one may observe that the weight loss increased to 30-50 % due to the existence of organic fraction into the silicate layers (table 1).

The most important argument for the silicate layers intercalation with different agents was revealed by the XRD analysis which gives the value of the basal distance between silicate layers (fig. 5).

From figure 5 one may notice that the modified montmorillonites exhibit higher basal distances values than for unmodified montmorillonite. A small increase of basal distance was recorded for modified MMT with protonated benzylamine (MMT-BA). The modified montmorillonites with B100 and ODA exhibit a significant increase of basal distance due to the longer molecular chains in comparison with the short benzylamine chain.

The modified MMT with POSS-amines exhibit even a higher basal distance than for the modified MMT with amines which is a strong evidence of POSS-amine intercalation between the silicate layers.

The influence of the modified montmorillonite on the epoxy resin reactivity

The DSC analyses proved that the modifier agent of MMT exhibits an influence on the epoxy resin curing process. In all the systems which included modified montmorillonite it could be observed a shift of exothermal peaks assigned to the crosslinking process to lower temperatures. This fact may be explained by the catalytic activity of modifier agent which included amino group.

Figure 7 and Figure 8 show the TGA and DTG curves of hybrids systems which contain modified MMT with different agents.

From these figures one may notice that the introduction of modified MMT with protonated amines (BA and ODA) into the epoxy systems does not significantly influence the final product thermostability. The DTG curves show a low decrease of T_{max} with aproximatively 5-6 °C in comparison with the reference (DGEBA-D230).

Also for the epoxy systems which contain modified MMT with POSS-amines as reinforcing agents the thermostability of the final hybrid system was not affected (fig. 9-10).

The effect of modified MMT type on the glass transition temperature of the final hybrid was investigated using DMA tests (fig. 11, table 3).

DMA results show that for hybrids including modified montmorillonite with amines the T_g value decreases with

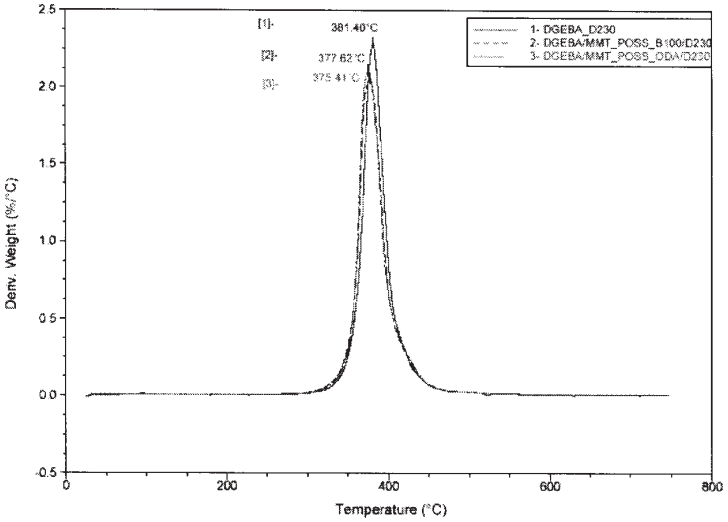


Fig. 10. DTG curves of epoxy systems reinforced with modified MMT with different POSS-amines

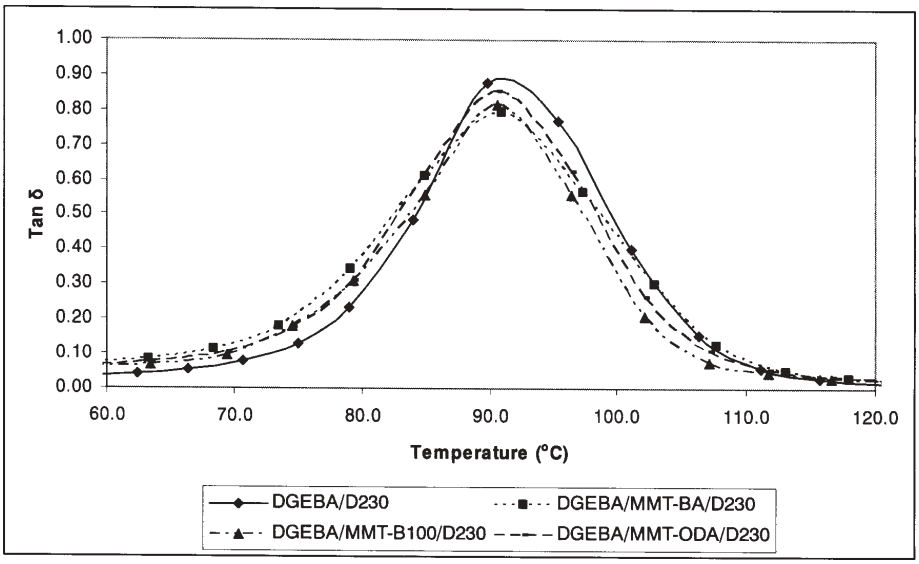


Fig. 11. The dependence of Tan δ against temperature for hybrid systems which contain different modified MMT

Hybrid system	Glass transition temperature (°C)
DGEBA/D230	95
DGEBA/MMT-B100/D230	89
DGEBA/MMT-ODA/D230	90
DGEBA/MMT-BA/D230	90

Table 3
THE GLASS TRANSITION TEMPERATURES OF HYBRIDS WITH DIFFERENT MMT DETERMINED FROM DMA TESTS

approximatively 5 °C in comparison with the reference. The lowest T_g value was achieved by the system reinforced with MMT-B100.

Conclusions

New nanocomposites based on epoxy resin and modified montmorillonite with various types of POSS-amine compounds were synthesized.

The intercalation of POSS-amine molecules between the MMT layers was proved by the increase of the basal distance from XRD analysis.

The thermostability of the final hybrid systems was not affected by the introduction of the modified MMT.

The modifier agents of MMT exhibit a catalytic activity on the epoxy crosslinking process. In all hybrids which contain modified MMT a shift of exothermal peaks to lower temperature was observed.

The T_g value of the hybrid systems was influnced by the presence of modified MMT.

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