Study on the Nanoparticles Influence on the Properties of Epoxy Systems

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The aim of the present paper was to obtain epoxy nanocomposites reinforced with layered clays type nanofiller. Nanocomposites materials have been obtained through mechanical mixing of resins based on diglycidyl ether of bisphenol A (DGEBA) chemically modified with low molecular glycols filled with Cloisit type layered clays and crosslinked using 4,4 'diaminodiphenyl metane (DDM)as curing agent. Epoxy nanocomposites have been obtained and characterized as compared to standard epoxy nanocomposites not only by conventional methods-physical-mechanical properties, but also by DMA tests in order to establish the degree of dispersion of the nanocaly in the epoxy matrix. Flexural strength and impact tests have shown that the reinforcement of composite materials with laminated clays leads to an improvement in their properties as compared to unmodified epoxy systems.

Keywords: epoxy nanocomposite, glass transition, dynamical properties, mechanical properties

Diglycidyl ether of bisphenol A (DGEBA)-based epoxy resins of belong to one of the most important thermosetting polymers class exhibiting good heat, moisture, corrosion and chemical resistance, electrical and mechanical strength and remarkable adhesion to many substrates. The coatings industry is the biggest consumer of epoxy resins mostly as chemical and special purpose coatings and is considered as the first line defense in chemical corrosion and harsh environment. But the epoxy coatings are the common victim of surface abrasion and low resistance to the initiation and propagation of cracks resulting in its localized corrosion [1].

The incorporation of various mineral fillers such as metal oxides, carbon nanotubes, graphene, nanosilica etc. to the epoxy resins leads to the obtaining of epoxy composites which have superior properties in terms of the most of the characteristics.The commonly used techniques for processing epoxy clay nanocomposite are: direct mixing and solution mixing [2-7].

Generally, to obtain layered clay-based nanocomposites, it is neccessary to incorporate a low concentration of clay into the matrix polymer, this being enough to significantly modify the desired properties. On the other hand, large amounts of clay can significantly change the viscosity of the system and can result in a significant increase in it, which will decrease the processability [8-13].

Also the structures based of layered silicate nanocomposites /polymer are classified according to the delamination level of clay. Various parameters such as the nature of organic modifier of the clay, polymer matrix influence the intercalation /exfoliation degree of the composites.

Therefore, it is possible to obtain different microcomposite structures depending on the nature and properties of clays, of polymeric matrix and on the elaboration of methodology for obtaining nanocomposites. The Cloisite type modified clays are layered clays consisting of treated natural montmorillonite(MMT)with alkyl quaternary ammonium salts. Depending on their structure, these modifiers allow to organofilize the clay, namely making it compatible with organic compounds. It was chosen Cloisit 30B [14] as reinforcing agent at a ratio of 2.5% to the polymer matrix, being known from literature that it leads to a high degree of exfoliation and at low concentrations (<5%) superior mechanical properties are obtained for the modified epoxy resins[15-19].

Epoxy resin was modified by synthesis at 150^{0}C with low molecular weight glycols. Thus, there were obtained epoxy resins modified with excess glycols, which were reinforced with layered organofillled Cloisit 30 B type clay. The proper selection of nanolayed clay is essential for effective penetration of polymer or of precursors in the galleries or clay (interlayer spacing) and therefore to obtain products with high degree of exfoliation.

Experimental part

Cloisite ® 30B is a natural montmorillonite modified with cuaternatre ammonium salts from Southern Clay Products which acts as reinforciment agent of the polymeric matrix. The main physical properties are: white color, 2.17 g/cm^3 density; 6 μm particle size, distance between the basal layers of clay (d_{001}) of 18.5 Å, the particle surface area 750 m^2/g. The matrix material is the DGEBA,

ROPOXID 501 comercial product available from Policolor. Physico-chemical characteristics of the resins are: dynamic viscosity -14600mPa. s (250 C), epoxy equivalent - 189 g/eq.

Low molecular weight glycols: ethylene glycol (EG), diethylene glycol (DEG), thetraetylene glycol (TTEG) from Merck were used as such.

The catalyst for the synthesis of epoxy resin modified, LiCl ,available from Merck, was used as 50% solution in distilled water.

The 4,4 ' diaminodiphenyl methane (DDM) 97%, from ACROS ORGANICS, with the following features: M = 198,

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Samples	Storage Modulus - E', MPa		Tan δ	
	Tg,°C	E'_{30^oC}(MPa)	Tan δ	T_g,°C
R_{501}/ Cloisit 30B	**126.49**	**2502**	**1.233**	**144.89**
60R_{mEG} -40R_{501}/Cloisit30 B	61.74	2515	0.8491	80.56
50R_{mEG} -50R_{501}/Cloisit 30B	108.40	2353	1.082	119.08
40R_{mEG} -60R_{501}/Cloisit 30B	117.15	2407	1.005	127.75
60R_{mDEG} -40R_{501}/Cloisit 30B	57.08	2526	0.8711	76.99
50R_{mDEG} -50R_{501}/Cloisit 30B	62.04	2242	0.7371	85.12
40R_{mDEG} -60R_{501}/Cloisit 30B	105.72	2483	0.8636	118.23
60R_{mTTEG}-40R_{501}/Cloisit 30B	-	1996	1.267	46.97
50R_{mTTEG} -50R_{501}/Cloisit 30B	51.19	1523	0.851	65.86
40Rm_{TTEG}-60R_{501}/Cloisit 30B	59.13	1377	0.824	77.15

Table 1
THE INFLUENCE OF MODIFIED EPOXY RESINE/ STANDARD EPOXY RESINE CONTENT ON Tg VALUES FOR EPOXY CLAY NANOCOMPOSITE

p.t. = 89^{0}C-91^{0}C, p.f. = 398^{0}C, was used for curing of epoxy resin matrix.

In order to reinforce epoxy nanocomposites with layered clays it is necessary to carry out the dispersion of clay platelets in modified epoxy resin with flexibilizers glycol type. For this reason, it was used a 750 Watt ULTRASONIC type ultrasonication device with VCX processor, CV33 end model to a set maximum amplitude of 50%. Epoxy resins-nanoclays mixtures were kept in sonication for 20 min. The sonication of clay particles induces viscosity, besides the resin viscose nature. The viscose force favours the separation of nanoclay platelets favouring thereby the intercalation/exfoliation in the matrix.

Fourier Transform Infrared (FT-IR) Spectrometra were recorded on a JASCO FT/IR 6300, equipped with a Specac Golden Gate attenuated total reflectance (ATR) device (30 scans, resolution 4 cm^{-1}) at room temperature (25^{o}C) on samples taken periodically up to the complete synthesis of modified resin.

Dynamical mechanical analyses (DMA) were performed on a "TA Q800-Instruments" machine using specimens having size 60 mm x 12 mm x 3 mm. Tests were performed in air atmosphere using temperature ramp method. Each sample was heated from 100 to 160 ^{0}C at a heating rate of 30^o C/min and a frequency of 1 Hz and an amplitude of oscillation of 20 μm.

Mechanical testing (tensile strength, elongation and flexural strength) were performed on a TINUS OLSEN universal machine for the testing of materials in static class.

Mechanical bending determinations were carried out on a TINIUS OLSEN test machine, static 0-10 kN, class I, v = 2 mm/min respectively v = 5 mm/min and for determination of the resistance to the shock it was used a CEAST and 4KJ pendulum.

The samples prepared by cutting the material were characterized in terms of mechanic – physical properties using sets of three identical samples.

The synthesis of epoxy resin modified took place in a steel reactor equipped with a heating mantle, a stirrer, coupled with a thermostat in which 1 mol standard epoxy (Ropoxid 501) and 2 moles of glycols (EG, DEG, TTEG) were introduced under stirring. The reaction catalyst is a 50% aqueous solution of LiCl in quantities of 50 ppm which is added under continuous stirring. Polyaddition reaction takes place at 150^{0}C, temperature kept constant throughout the reaction.

To determine the degree of advancement of the reaction of epoxy resin and glycol samples were taken periodically. The samples were characterized by chemical analysis and by spectrophotometric determinations (FT-IR). The reaction was stopped at an index value 0.117 epoxy eq/ 100 g resin in order to avoid side reactions.

Since the resin so obtained does not have the epoxy groups , it cannot be cross-linked with specific epoxy hardener, therefore it was mixed with standard Ropoxid 501 resin in the ratio 40, 50 and 60%.

The 2,5 % to the resin gravimetrical content Cloisit 30 B clay is then gently added in bath and mixed using ultrasonication technique until uniform disperion of clay takes place in the matrix.

Epoxy nanocomposites have undergone hot hardening using an aminic hardener type DDM in stochiometric quantities based on number of epoxy groups.

During the hot conditions , the epoxy matrix is initially heated to 100^0 C for 1 h with DDM hardener. The mixtures thus obtained were cast in teflon moulds of dimensions 10 mm x 100 mm x 3 mm and were cured after the following thermal regime: 24h/ 25 ^{0}C , 7 h/60° C and 7 h/120°C. The nanocomposite specimens procesed by the above mentioned process are tested for characterization and property studies.

Results and discussions

Polymer matrix mixing with clay particles was carried out by sonication in order to ensure an uniform distribution of the layered clay. At the same time, sonication promotes the delamination of clay platelets, phenomenon that leads to a high degree of exfoliation/ interacalation of silicate in the epoxy matrix. During sonication, it occurs an increase in the mixture viscosity due to the delamination of clay layers. The final product was mixed with the hardener and cured for characterization.

The dependence of physical and mechanical properties of epoxy nanocomposites sample on the modification degree with various glycols are presented in fig. (1-3).For this study the following glycols were investigated: **R_mEG; R_mDEG; R_mTTEG** - modified resin with glycols (ethyleneglycol diethyleneglycol; tetraetilenglycol) and reinforced by Cloisit B30.

For modified epoxy nanocomposites with glycols (EG, DEG, TTEG) and reinforced with 2.5% Cloisit 30B, the dependency graphs were drawn for elongation and bending strength depending on the content of the modified epoxy resin .

An increase in the content of modified resine leads to an enhancement in the elongation at break and in the impact resistance, but to a decrease in the tensile strenght and D Shore hardness. Specific gravity is a physical property which is not significantly modified by an increase in the content of modified epoxy resine.

DMA tests confirm, also, that the improvement properties depends on the ratio between modified epoxy resine/standard epoxy resine. DMA tests express the energy absorption capacity in wide temperature ranges by glass transition temperature values (Tg), loss factor (tanδ) and energy storage modulus (E') ,are shown in table 1.

The E' value, as expression of elasticity module can provide information on mechanical properties of nanocomposites. They, also, show that, an increase in the mobility of glycolic molecular chain leads to a decrease in the T_g value.

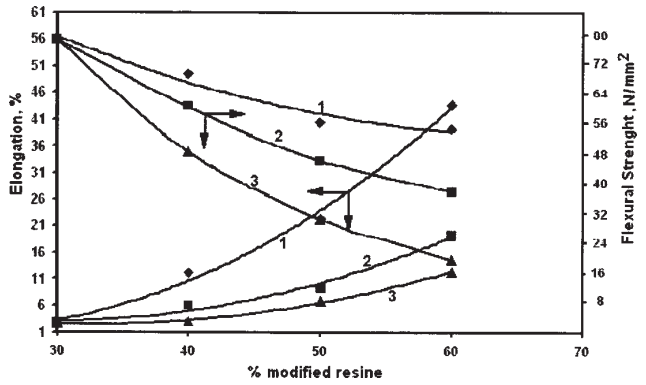

Fig. 1 – Elongation and flexural strenght versus modified epoxy resine content for clay nanocomposites: 1.R_{mEG} ; 2.R_{mDEG} ; 3. R_{mTTEG}

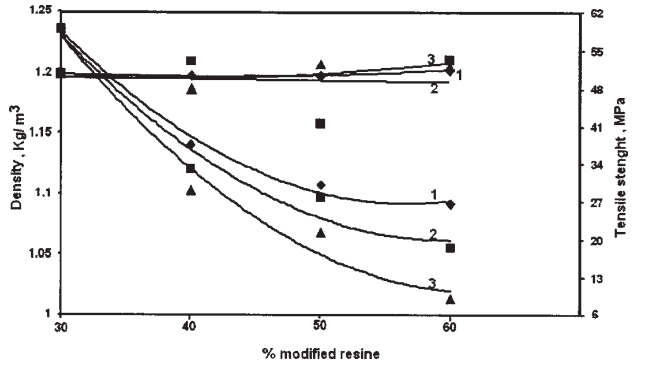

Fig. 2 -Density and tensile strenght versus modified epoxy resine content for clay nanocomposites:1. R_{mEG} ; 2. R_{mDEG} ; 3. R_{mTTEG}

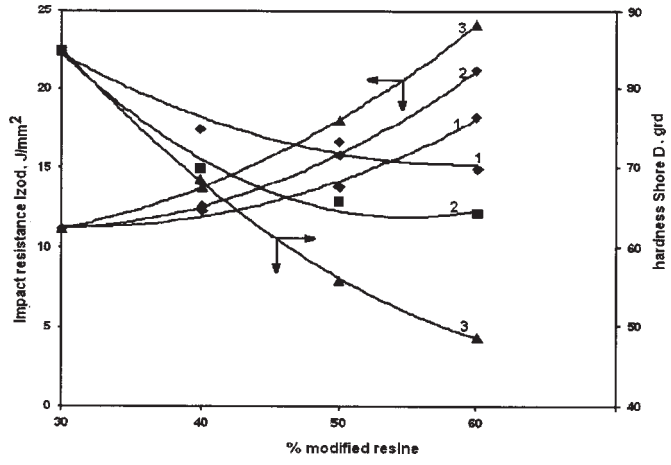

Fig. 3- Izod impact strenght and Shore D hardness versus modified epoxy resine content for clay nanocomposite: 1.R_{mEG} ; 2.$R_{m\ DEG}$; 3.R_{mTTEG}

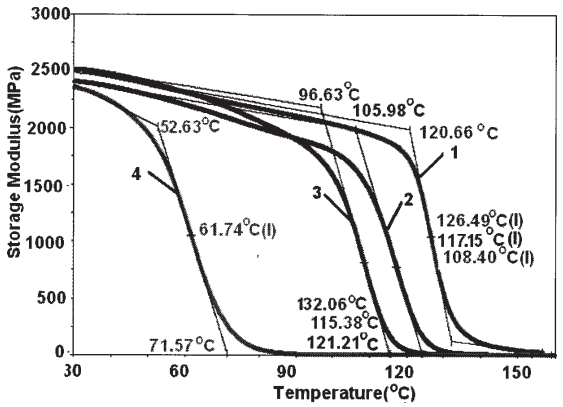

Fig. 4. Storage modulus versus temperature plot for all sample epoxy clay nanocomposites system : 1-Standard epoxy clay nanocomposite; 2- Epoxy clay nanocomposite with 40R_{mEG}-60 Rstandard; 3- Epoxy clay nanocomposite with 50R_{mEG}-50Rstandard B30; 4 - Epoxy clay nanocomposite 60R_{mEG}-40Rstandard.

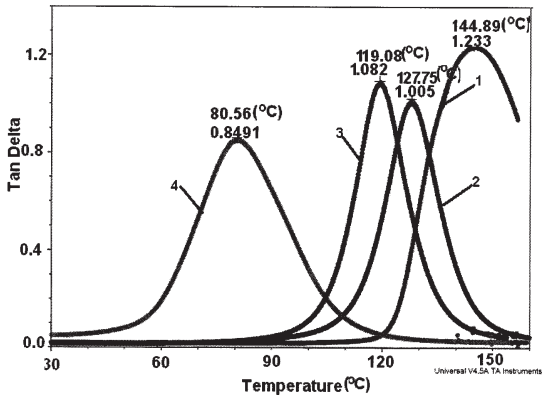

Fig.5. Tan δ versus temperature for all sample epoxy clay nanocomposites system: 1- Standard epoxy clay nanocomposite; 2- Epoxy clay nanocomposite with 40R_{mEG}-60Rstandard; 3- Epoxy clay nanocomposite with 50R_{mEG}-50Rstandard; 4 – Epoxy clay nanocomposite with 60R_{mEG}/40Rstandard

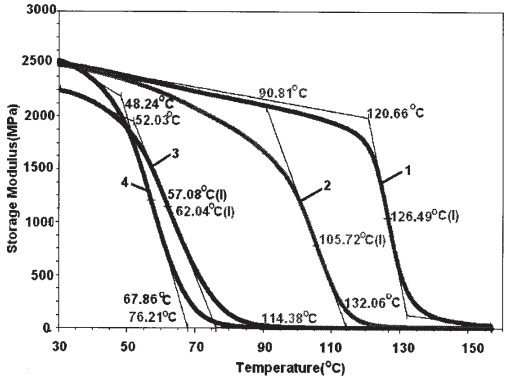

Fig.6. Storage modulus versus temperature plot for all sample epoxy clay nanocomposites system : 1-Standard epoxy clay nanocomposite; 2-Epoxy clay nanocomposite with 40R_{mDEG}-60Rstandard; 3-Epoxy clay nanocomposite with 50R_{mDEG}-50Rstandard; 4-Epoxy clay nanocomposite with 60R_{mDEG}-40Rstandard.

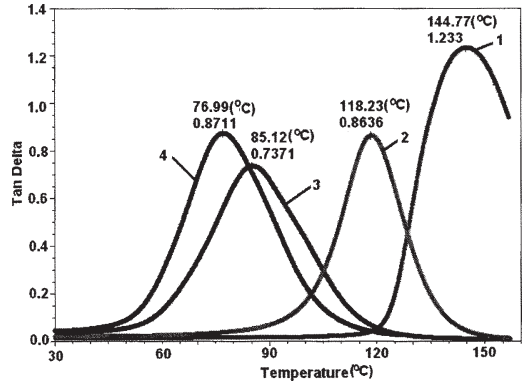

Fig.7 - Tanδ versus temperature for all sample epoxy clay nanocomposites system: 1-Standard epoxy clay nanocomposite; 2-Epoxy clay nanocomposite with 40R_{mDEG}-60Rstandard; 3-Epoxy clay nanocomposite with 50R_{mDEG}-50Rstandard; 4-Epoxy clay nanocomposite with 60R_{mDEG}-40Rstandard

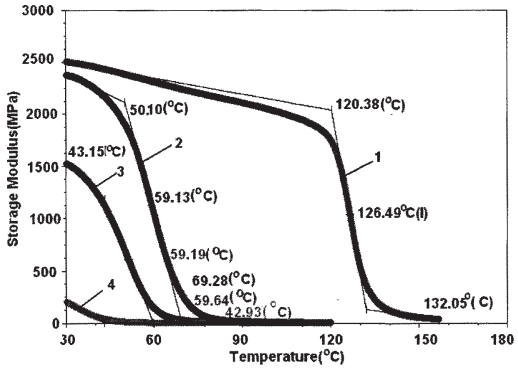

Fig.8. Storage modulus versus temperature plot for all sample epoxy clay nanocomposites system : 1-Standard epoxy clay nanocomposite; 2-Epoxy clay nanocomposite with 40R_{mTTEG}-60Rstandard; 3-Epoxy clay nanocomposite with 50R_{mTTEG}-50Rstandard'; 4-Epoxy clay nanocomposite with 60R_{mTTEG}-40Rstandard.

While the temperature is increasing, the storage modulus converges toward the value presented by the resin, indicating that at high temperatures the module composite is dominated by intrinsic properties of epoxy matrix.

The most frequent use of tests DMA is determination of the temperature of transition glassy T_g peak maximum on the curve of the loss factor (tanδ) and as a point of contact on how to store curves; in this region a drastic transformation takes place in the polymeric material what will be transmitted to glass transition to rubber state shown in figure 4-9.

Conclusions

Study on synthesis process of modified epoxy resin/ silica nanocomposites (Cloisit 30B) shown the following features.

Physical and mechanical properties of nanocomposites are determined by the weight ratio of modified resin / standard resin best results being obtained at ratios of 40/ 60;

Measurements made using DMA tests at a frequency of 1 hertz have shown that the value of T_g depends on the ratio of modified resin / resin standard and the nature of the glycol used to modify epoxy resin, which emphasizes that purpose to obtain resins with high flexibility has been achieved.

The ratio of modified epoxy resin /standard resin plays an important role on the T_g value of nanocomposites obtained at the highest values of the modified resins/ standard resin ratios (40/60).

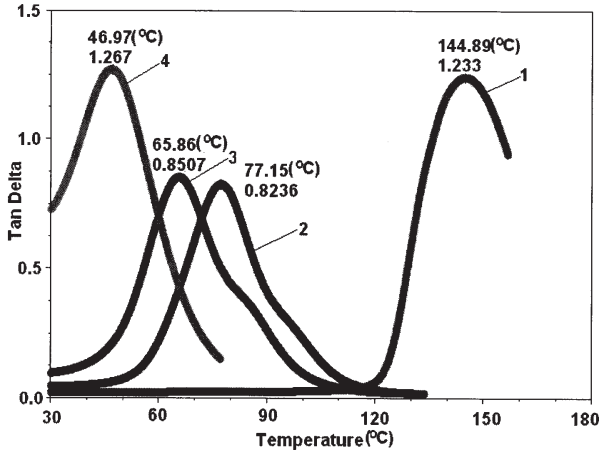

Fig.9- Tanδ versus temperature for all sample epoxy clay nanocomposites system: 1-Standard epoxy clay nanocomposite; 2-Epoxy clay nanocomposite with 40R_{mDEG}-60Rstandard; 3-Epoxy clay nanocomposite with 50R_{mDEG}-50Rstandard; 4-Epoxy clay nanocomposite with 60R_{mDEG}-40Rstandard.

Future research will consider the use analysis of electronic microscopy (SEM, TEM) to determine how it was built the clay in nanocomposite (exfoliated or intercalated).

The nanoparticle reinforcement (Cloisit30B) improves the mechanical properties epoxy system and this epoxy nanocomposite will be advantageous to be used in a large-scale commercial applications, in coating industry due to a high capacity to absorb the impact energy as a result of high flexibility.

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