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GRAPHENE OXIDE FUNCTIONALIZATION WITH SILANES FOR ADVANCED COMPATIBILITY IN EPOXY NANOCOMPOSITES

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The incorporation of graphene oxide (GO) functionalized with silanes in epoxy matrix is expected to greatly increase the properties of the final composites. Changes on the functionalized GO samples surface were proved by deconvolution of high resolution C1 s XPS spectra, showing the attachment of amino and glycidyl silane molecules through covalent linkage. Quantification of the functionalization reaction was given by TGA degradation curves. The nanocomposites showed increased cure reaction enthalpy compared with the epoxy matrix, caused by the functional groups from the silanes which could be involved in the curing process. Further investigation by SEM shows that functionalized GO are well dispersed in the epoxy matrix.

Keywords: graphene oxide, functionalization, thermostability, epoxy nanocomposites

1. Introduction

Polymer nanocomposites based on nanofillers like expanded graphite, carbon nanotubes, carbon nanofibers have been investigated in many studies due to their great thermal and mechanical properties [1]. Compared with conventional nanofillers, graphene has amazing thermal, electrical and mechanical properties, while the high surface area is an advantage for great interface between reinforcing agent and epoxy matrix in high performance nanocomposites [2].

Graphene oxide is obtained from graphite through a process which involves two main steps: the first step corresponding to the graphite oxidation to obtain graphite oxide and the second step consists in the exfoliation of graphite oxide by sonication [3].

A new perspective in surface treatment and functionalization of GO takes into account modification of their surface with different agents in order to increase compatibility between polymer and GO when it is used as reinforcing agent [4].

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The oxygen containing groups from the GO surface like hydroxyl, carboxyl and epoxy, are suitable anchoring points for further functionalization. Graphene oxide and its derivates have created a new class of polymer nanocomposites as reinforcing agents, due to their extraordinary physical properties and the ability to be dispersed in various polymer matrices [2].

Epoxy resins are one of the most important thermosetting polymer classes used in a wide range of applications like: matrices for composites, paints and adhesive industry, impregnating varnishes, corrosion protective coatings, in electrical and electronics industry. All this applications are feasible due to their remarkable performance, processability and low cost [5]. In such an application approach, Bin Yu and his team [6] dispersed MWCNT in silane and this solution was applied on carbon nanofibers. After that, the carbon nanofibers were compatibilized with epoxy resin to obtain nanocomposites. These nanocomposites showed improved interfacial bonding compared with the conventional carbon fiber-reinforced resins.

Silanization offers GO the possibility to diversify their surface depending the type of organosilane inserted to their surface [7]. The degree of GO surface functionalization through silanization is related to the functionality of the graphene specific surface area and silane concentration, but also the pH of the solution is important in order to obtain high yield [8]. Silanization of GO with 3-aminopropiltrietoxisilan (APTS) was presented in a recent study dealing with the formation of covalent bonds between the epoxy groups from the GO surface and the amine groups of the APTS chain by a S_N2 mechanism [9]. The similar work of Yang et al.[1] performed a functionalization of GO with APTS developing an interest in the dispersion of functionalized GO in different polar or non-polar solvents. Wan et al. [5] functionalized graphene using GPTS, showing improved dispersion and interfacial interaction between the functionalized graphene sheets and the epoxy matrix. This way increased tensile properties of epoxy/graphene nanocomposites were observed. In a recent study, the synthesis of reduced silanized graphene oxide and the reinforcement with this modified filler agent of a mixture epoxy-polyurethane is described. Thermogravimetric Analysis and Differential Scanning Calorimetry characterization showed that the thermal stability of the final composites was considerably increased [10].

This article focuses on the development of simple functionalization method of GO with two types of silanes through an activation method of carboxyl groups from the GO surface. A new approach is brought by the correlation between the functionalization degree and improved thermal properties of epoxy nanocomposites systems. The cure reaction study of epoxy type matrix in the presence of the functionalized GO highlights the importance of the efficient compatibilization between GO surface and the polymer matrix in terms of reaction enthalpy.

2. Materials and Experimental procedure

2.1. Materials

DGEBA type epoxy resin-(A506, EEW = 172-185 g/eq), (3-Aminopropyl) triethoxysilane (APTS, ≥98%), (3-Glycidyloxypropyl) trimethoxysilane (GPTS, ≥98%), hydrochloric acid, 37%, 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide, polymer-bound (EDC, Mw=10375 g/mol) and N-Hydroxysuccinimide (NHS, purum ≥97%) were supplied by Sigma-Aldrich. Sodium hydroxide was purchased from Chemreactiv (Romania). The chloroacetic acid (M=94.49 g/mol) was purchased from Merck and Jeffamine D230 was kindly supplied by Huntsman.

2.2. Experimental procedure

GO functionalization

i) The first stage consists in the enhancement of the number of carboxyl groups at the GO surface. Thus, in a round bottom flask a 1 mg/mL suspension of laboratory synthesized GO [11] in water was prepared, then chloroacetic acid and NaOH were added, followed by ultrasonation for 3h. The mixture was neutralized with HCl solution 37%, then it was centrifuged and washed with distilled water until neutral pH. The black powder representing GO-COOH was dried under vacuum.

ii) The second stage is a carbodiimide coupling between GO-COOH and APTS /GPTS. At this point, GO-COOH was suspended in water under sonication for 2h , then a solution of EDC in PBS buffer (pH=5.5) was added and the sonication was continued for another 30 minutes. The NHS coupling agent was introduced and the pH was adjusted to 7.2 with PBS for APTS and respectively to 1.5 with HCl solution 5% in case of GPTS. At this point, the silane was added and sonicated for 30 minutes. The resulted suspension was filtrated and washed with distilled water until neutral pH. The GO-APTS and GO-GPTS having the structures proposed in figure 1 were dried under vacuum for 24h.

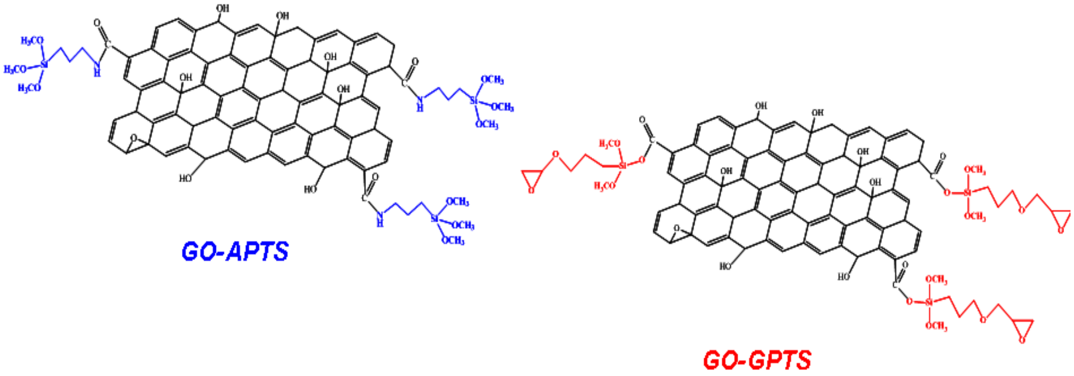

Fig. 1. Schematic structures proposed for the silane functionalized GO

Epoxy nanocomposites synthesis

Calculated amounts of unmodified and functionalized GO (1 wt.%) were mixed with a polymer matrix consisting of a mixture between diglycidylether of bisphenol A (A506) and fluorinated epoxy resin (REF) synthesized by our team [12]. The two epoxy resins were mixed in a 2:1 wt. ratio. The mixture was then sonicated using a tip sonicator for 2 h having 60% amplitude at room temperature. Then the D230 hardener was added to the mixture and vigorously stirred for 2 min. The mixture was then cast into a mold and cured at 50°C for 3 h followed by 1 h postcuring process at 100 °C.

2.3 Materials characterization

Thermogravimetric Analysis (TGA) curves were registered on a Q500 TA Instruments equipment, under nitrogen atmosphere using a heating rate of 10°C/min from room temperature to 800°C.

The surface structures for functionalized GO were studied by X-ray Photoelectron Spectroscopy (XPS) using a K-Alpha instrument from Thermo Scientific, with a monochromatic Al Kα source (1486.6 eV), at a bass pressure of 2×10^{-9} mbar. Charging effects were compensated by a flood gun and binding energies were calibrated by placing the C 1s peak at 284.8 eV as internal standard. The pass energy for the survey spectra was 200 eV and 20 eV for high resolution. Deconvolutions of the C 1s peaks were performed after Shirley's inelastic background subtraction and were normalized for the measured transmission function of the spectrometer.

Differential Scanning Calorimetry (DSC) curves were recorded on a Netzsch DSC 204 F1 Phoenix equipment. The sample was heated from RT to 250 °C using a heating rate of 10 °C/min under nitrogen (20 mL/min flow rate).

Glass transition temperatures (Tg) were measured on a Tritec 2000 dynamic mechanical analyzer (DMA) from 25°C to 180°C with a 5°C/min rate.

Scanning electron microscopy (SEM) was done on a Quanta Inspect F (FEI) instrument, with field emission electron gun, 1.2 nm resolution and X-ray energy dispersive spectrometer with 30 kV accelerating voltage. For a better contrast, the samples were first fractured in liquid nitrogen and covered with a thin gold layer.

3. Results and discussion

The compatibility between epoxy matrix and the surface of the reinforcing agent has a great influence on the thermo-physical properties of the designed nanocomposites, due to enhanced dispersion which will lead to good transfer of the mechanical stress within these materials. TGA was used to quantify the amount of silane functional groups which were attached to the GO surface (Fig. 2) in comparison with the laboratory synthesized GO and the carboxylated ones.

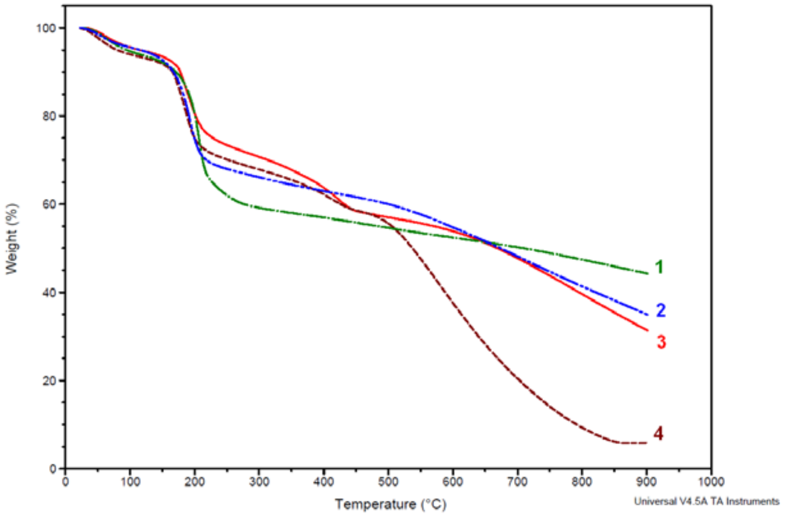

Fig. 2. TGA curves for the GO (1), GO-COOH (2), GO-GPTS (3) and GO-APTS (4).

It was noticed that the initial decomposition temperature was maintained at the same value when the GPTS was attached, but in case of APTS it was significantly lowered possibly because the newly formed structures are more sensitive than the initial oxygenated groups from the GO surface. Another explanation of this low value of decomposition temperature, was given by A.M. Shanmugharaj et al.[13] showing that in case of GO, oxygen containing groups are removed while in case of functionalized GO the physically adsorbed silane molecules are lost alond with residual water/solvent molecules. The silane functionalized samples show a four step degradation mechanism, compared with the degradation curves of GO and GO-COOH which presents only three steps. The supplementary degradation step between 300-500°C can be ascribed to the breakage of APTS and GPTS molecules attached to the GO surface. This fact is well pointed out in the literature by many studies conducted both on graphenes and carbon nanotubes [1, 13, 15]. These studies are considering a characteristic alkyl decomposition at 420°C as being the confirmation of silane attachment.

Another important parameter which can be calculated from the TGA curves is the mass loss of the samples (Table 1).

Table 1

Thermal properties of the GO and functionalized GO

Sample	$T_{d3\%}$, [°C]	Mass loss, [%] 25÷900°C
(1) GO	73	60.4
(2) GO-COOH	69	65.1
(3) GO-GPTS	75	69.7
(4) GO-APTS	57	94.1

The increase of the mass loss with almost 10% was attributed to the attachment of GPTS molecules to the GO surface through ester linkage as it was later observed in the deconvolution of high resolution XPS analysis (Table 2).

Table 2

Surface composition of the GO and silane functionalized GO

Sample	C At.%	O At.%	Si At.%	N At.%
GO-COOH	79.7	20.3	-	-
GO-GPTS	71.2	26.6	2.2	-
GO-APTS	72.8	23.0	2.7	1.5

In case of APTS attachment the mass loss is higher with 34%, which shows a higher yield of the coupling when amine groups are implied, because the EDC/NHS mechanism was developed for these type of functional groups.

The surface elemental analysis by XPS survey spectra showed the appearance of the Si2p species after functionalization, besides C 1s and O 1s compared with the GO and GO-COOH samples where only C 1s and O 1s were noticed. Even if the amount of Si 2p was aproximatively 2% (table 3) related to the total amount of atoms taken into account, these data are completing the TGA studies which showed higher functionalization degree for GO-APTS in case of this sample, it can also be noticed the N1s from APTS structure.

The deconvolutions of the C 1s peaks from the XPS spectra for the carboxylated and silane functionalized GO were realized. From figure 3, it can be noticed that mainly four peaks are appearing: the first one 284.8 eV attributed to the C-C bond from the GO structure (A), the second peak at proximately 286.5 eV assigned to the C-O bonds (B), the third one at 288.6 eV corresponding to C=O bonds (C) and 291.1 eV assigned to the π-π* transitions (D). Moreover for the GO-APTS sample, which gave a higher amount of Si content, it was noticed a new peak at 284.2 eV attributed to C-Si bond (E) from the silane molecules attached to the GO structure [16]. This tendency of lower binding energy for Si-C species was also observed for silane functionalization of carbon nanotubes [14]. However this last peak could not be observed in the GO-GPTS sample probably because of the lower of the functionalization reaction as it was noticed from TGA mass loss values .

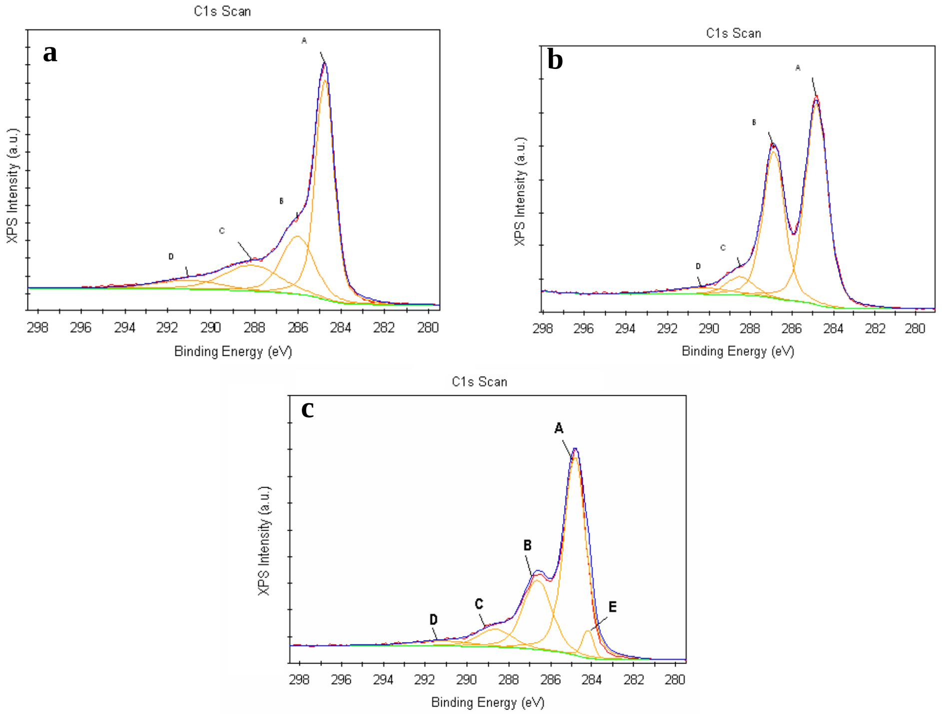

Fig. 3. High resolution C1s spectra for GO-COOH (a) and GO-GPTS (b) and GO-APTS (c)

The study of the cure reaction between epoxy matrix and the polyetheramine was realized by DSC analysis (figure 4). The epoxy reaction enthalpies were calculated from the exothermic peak area (Table 3) of the DSC curves and presented increased values when 1% of GO-GPTS/ GO-APTS was added. The difference between the two types of samples can be attributed to a higher amount of epoxy groups which reacts with the curing agent in case of GO-GPTS. Thus covalent bridges could be formed with the epoxy network because both the polymer matrix and the reinforcing agents could react with the same amine molecule. In case of GO-APTS, the C-N bonds could connect the reinforcing agent to the matrix because amine groups could act as curing agent of the epoxy matrix. In the same time, a slight shift of the maximum curing temperature (with 2°C and respectively 4°C) was noticed, which is caused by the steric hindrance exerted by the GO sheets in the nanocomposite system.

The values of the glass transition temperatures (Tg) are also higher for the epoxy nanocomposites when functionalized GO is used as reinforcing agent, which support the hypothesis of covalent bonds at the interface between GO-APTS/GO-GPTS and epoxy matrix. The higher functionalization degree of GO-APTS as it was observed from the TGA curves, is correlated in this case with the greater Tg value of the epoxy nanocomposites. This fact can be the indication of a higher corsslinking density [16, 17].

Table 3

Thermal properties of the epoxy matrix and nanocomposites

Sample	Area*, [J/g]	T_{max}*, [°C]	T_g**, [°C]
A506+REF+D230	301.1	114.7	69
A506+REF+GO-GPTS+D230	363.2	116.7	90.1
A506+REF+GO-APTS+D230	374.5	118.6	91.8

* data from DSC ; ** data from DMA

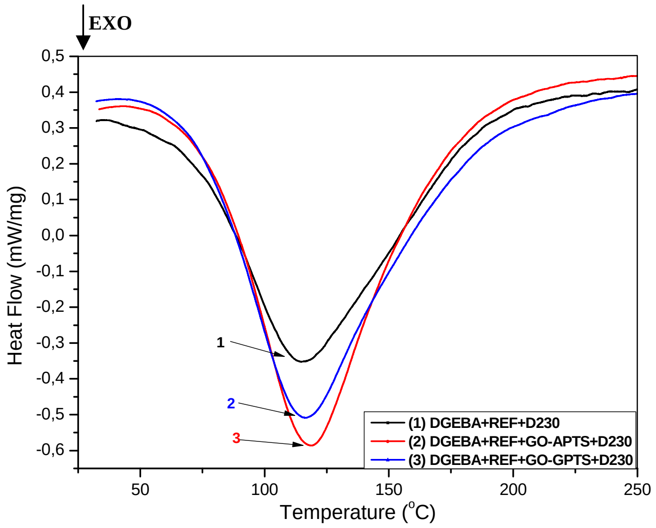

Fig. 4. The cure reaction curves from DSC measurements for epoxy nanocomposites

The morphology of the epoxy nanocomposites fracture surface was observed in the SEM images (Fig. 5). The difference between the cured matrix and the nanocomposites consist in a higher roughness which is caused by an advanced compatibility between the components, which led to a difficult extraction of GO during fracture process. It can be observed also that the fracture edges are linear in the nanocomposites samples due to a efficient dispersion of GO sheets which are orienting the fracture mechanism [18]. For the nanocomposites reinforced with GO-APTS it can be notice that some agglomerations are still present , due to the fact that not all the groups from the reinforcing agents could react with the epoxy matrix during the cure reaction, thus the interface formation in this case had lower efficiency than in case of glycidyl functional groups.

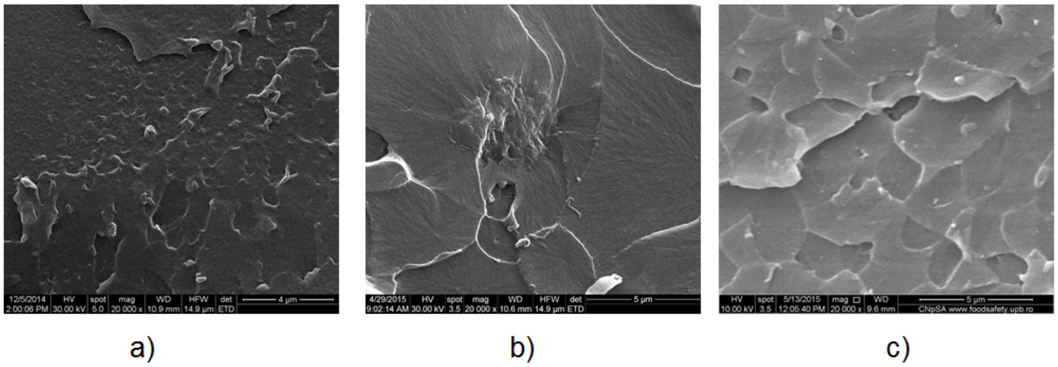

Fig. 5. SEM images for the epoxy matrix (a); the GO-APTS (b) and GO-GPTS (c) reinforced nanocomposites

4. Conclusions

Surface modification of GO with epoxy and amino silane was accomplished through an EDC-NHS coupling mechanism adopted from peptide chemistry. The surface composition was monitored using XPS and the presence of silane molecules was confirmed through Si 2p presence and also by the C1s peak deconvolution. Quantification of the elemental composition as resulted from the XPS survey spectra was correlated with the calculations of mass loss percent from the TGAcurves. Epoxy nanocomposites reinforced with the new nanomaterials were obtained with good dispersion as SEM images revealed, the supplementary curing sites given by the GPTS and APTS functional groups from the GO surface were translated in higher cure reaction enthalpy.

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