Thermal stability and chemical analysis of hybrid materials reinforced with graphene oxide

A F Betancur¹, A García², and F R Pérez¹
¹ Grupo de Óptica y Espectroscopía, Universidad Pontificia Bolivariana, Medellín, Colombia
² Laboratorio de Síntesis y Modificación de Nanoestructuras y Materiales Bidimensionales, Centro de Investigación en Materiales Avanzados S.C., Apodaca, México

E-mail: andresfebelo@gmail.com, fredy.perez@upb.edu.co

Abstract. Thermal stability and chemical analysis were done on a hybrid material (HM) reinforced with graphene oxide (GO). The base of hybrid system was bisphenol A diglycidyl ether (DGEBA) and tetraethyl orthosilicate (TEOS). Fourier-Transform Infrared (FTIR) and Raman spectroscopies measurements were performed. For the reinforced material (HM+GO), the features of its FTIR spectra indicated changes in the CH₂ groups into the epoxy ring within the GO plane structure in comparison to the spectrum of HM. The Raman spectra suggest the formation of C-O-C bonds into the HM+GO structure. From TGA and DSC measurements, an increasing in thermal stability of HM and HM+GO with respect to that of DGEBA was found, being HM+GO more stable. It could be explained for the presence of GO. The addition of GO increases the transition temperature of hybrid material in 10 °C in relation to the non-reinforced hybrid materials.

1. Introduction
Graphene oxide (GO) is a graphene sheet with functional groups such as hydroxyl, epoxide, carbonyl and carboxyl groups forming different hybrid orbitals sp³ and sp². It has been shown that GO increases the impermeability capacity of hybrid material. The modification of its electronic structure by controlling the oxidation degree, facilitates application as semiconductor material [1], but also this properties can be used to modified the interchange electronic and thermal stability of different materials like hybrid composites. The organic/inorganic hybrid systems have gained considerable interest of scientific community due to its unique molecular structure and interesting physicochemical properties. In the fields of material science and technology, the sol gel process is a low-temperature synthesis route starting from organo-metallic precursors such as silicates. Additionally, by a synergistic effect in the epoxy resin, it could be obtained different materials for diverse applications [2]. The organic/inorganic hybrid system is bound by covalent bonds that generate a positive effect on their properties like stiffness and thermal resistance. The latter is characteristics of inorganic phase, which is combined with the properties of the organic phase as adhesion and elasticity [3]. The combination of properties increases the efficiency of hybrid material extending its applications in fields as surface coatings, printed circuit boards, as well as anti-scratch and anticorrosive materials [4]. It has been reported that GO produces decreasing in the porosity of materials. Hence, osmosis to oxygen, aggressive ions and water through the coating can be less efficient and the mechanical properties like hardness and the strength values have...
been improved considerably [5]. In this work, a hybrid matrix was obtained, and the chemical and thermal resistances were evaluated before and after the addition of GO. The reinforced composite was synthesized from an inorganic reagent (Tetraethoxysilane or TEOS), organic resin (bisphenol A diglycidyl ether or DGEBA) and graphene oxide. Vibrational spectroscopy measurements for chemical analysis as well as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for the thermal characterization, were carried out.

2. Materials and methods
In order to obtain the hybrid matrix, different tests were carried out by using different concentrations of DGEBA and TEOS. Measurements of adhesion and microhardness were carried out to determine the best relation between organic and inorganic material concentrations. Subsequently, the GO was synthesized by chemical exfoliation [6]. After GO synthesis, tetrahydrofuran (THF) is added in order to solubilize and incorporate the OG into the hybrid matrix. THF helped to decrease the viscosity and increased the gelation time of the hybrid compound in order to increase the GO dispersion. 0.01%wt of GO was added to the HM. Later, a curing agent was added to the mix in order to accelerate the polymerization processes [7,8].

Two complementary vibrational techniques, Infrared and Raman spectroscopy, were used to observe the chemistry changes and different functional groups present in the hybrid material. The Fourier transform infrared spectrophotometer (FTIR) used for this analysis was a SHIMADZU IR Affinity-1S. All infrared measurements were done using attenuated total reflection (ATR) which enables the samples to be examined directly in the solid or liquid state without further preparation. The Raman measurements were carried out by using an inVia Renishaw confocal Raman spectrometer system utilizing a laser line of 814 nm. To measure of microhardness and adhesion, an Ubi1 Hysitron USA nanomechanical test equipment with Berkovich triangular pyramid diamond tip, and a manual equipment Elcometer 106, respectively, were used. The thermal stability studies were carried out by using both, a thermogravimetric (TGA) equipment and a Differential Scanning Calorimetry analysis DCS-SDT model Q600 from TA Instruments.

3. Results and discussions

3.1. Synthesis of hybrid composite
The concentrations of epoxy resin (DGEBA) and alkoxysilane (TEOS) were varied from 10% to 90% (wt/wt). The optimal values of these concentrations obtained, in which the highest adhesion (4.9 MPa) and the highest micro-hardness (0.272 GPa) were obtained, are show in Table 1. The ideal concentration was established when the microhardness and adhesion start to decrease. Those concentrations were 70%wt and 30%wt of DGEBA and TEOS, respectively. It was observed that values of the inorganic phase concentration higher than 40%wt significantly modifies the color, structure and superficial properties of HM. Thus, the adhesion and hardness decreased up to the value in which these properties are reduced to around zero. When the concentration of inorganic phase reaches the 90%wt, the material becomes a powder, losing completely its hardness and adhesive behavior. This is an indicative that from these concentrations the phases begin to change the properties completely and could be use in other applications.

| DGEBA (%wt) | TEOS (%wt) | Micro-Hardness (GPa) | Adhesion (MPa) |
|------------|------------|---------------------|---------------|
| 65         | 35         | 0.217               | 3.5           |
| 70         | 30         | 0.272               | 4.9           |
| 75         | 25         | 0.223               | 5             |
Under ideal phase concentrations conditions, the hybrid material show a synergetic effect of both phases (Organic-Inorganic), such as stiffness and thermal resistance which could be attributed to the inorganic phase. In contrast, the toughness, adhesion and elasticity could be obtained from the organic phase [7]. It has been reported that the inorganic phase form “nanofillers” into the hybrid material structure which could help to increase the dispersion of the nanoparticles in a polymer [9]. In this way, it could be an ideal scenario in which a dispersion of GO can be favored.

3.2. Raman and infrared spectroscopy

The Raman and FTIR analyses are used to understand the bonding interactions between the DGEBA, TEOS and the GO. Raman spectra of epoxy resin (DGEBA), hybrid material (HM) and hybrid+GO (HM+GO) is presented in Figure 1. The spectra of Figure 1 showed a decreasing in the intensity associated to some vibration modes as a result of the addition of each phase in the hybrid and reinforced-hybrid synthesis processes. This behavior is significantly evident in the HM+GO spectrum, specially in the spectral region between 2100 cm\(^{-1}\) and 3100 cm\(^{-1}\) [10]. Hence, the light scattering decreases with the addition of each component, especially with GO addition. The modification of epoxy groups due to polymerization reaction can produce changes in the 1304 cm\(^{-1}\) and 891 cm\(^{-1}\) modes which are related with C-O-C bonds (Figure 1). The deformations and vibrations of the CH\(_2\) group around 830 cm\(^{-1}\) and 1025.5 cm\(^{-1}\) from benzene ring of epoxy may be an indicative of the formation of bonds with inorganic phase and the GO [11]. Furthermore, the Si-O-Si groups formed during hybrid reaction can be detected around to 816 cm\(^{-1}\) and 1120 cm\(^{-1}\). The vibrational modes from organic phase overlap other bands from GO and inorganic phase due to the concentration of organic phase (70% wt) predominates over others.

![Figure 1. Raman spectra of DGEBA, Hybrid material (HM) and Hybrid material reinforced with GO (HM+GO).](image1)

![Figure 2. FTIR spectra of DGEBA, Hybrid material (HM) and Hybrid material reinforced with GO (HM+GO).](image2)

The FTIR spectra (see Figure 2) show characteristic bands at 833 cm\(^{-1}\), 1042.5 cm\(^{-1}\) and 1231 cm\(^{-1}\) attributed to the epoxy groups which were reduced during the polymerization reaction [12]. Furthermore, in the HM spectrum, the range of 1000 cm\(^{-1}\) to 1150 cm\(^{-1}\) are associate to the Si-O-Si bonds [13]. This vibrational modes suggest the interaction of both phases (DGEBA-TEOS) through the condensation reactions during hybrid material formation [2]. The absorption bands for DGEBA around at 3389 cm\(^{-1}\) correspond to stretching vibration of hydroxyl groups. The bands of 3034 cm\(^{-1}\), 1580 cm\(^{-1}\), and 733 cm\(^{-1}\) are attributed to a stretching of aromatic rings. In 1602 cm\(^{-1}\), 1580 cm\(^{-1}\), 1504 cm\(^{-1}\) and 826 cm\(^{-1}\) correspond to a benzene ring of epoxy structure from DGEBA. The band at 3060 cm\(^{-1}\) is associated to N-H stretching associate to amine groups from hardener (KCA-4303 modified cycloaliphatic amine) added to accelerate de polymerization reaction in the epoxy resin. The bands
associated with the epoxy groups decreased their intensities in the spectra of HM and HM+GO materials, due to a polymerization reaction in the material and chemistry integration between compounds.

3.3. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

TGA analyses were performed in order to observe the thermal decomposition of the composites, specifically in relation to the effect of the GO incorporated into the HM. A temperature range between 50 °C and 600 °C and a heating rate of 10 °C/min for all the samples, were used. In principle, the more important contributions of GO to the hybrid material is to increase its chemical and thermal stability modes [13]. The results from the TGA (Figure 3(a)) and DSC (Figure 3(b)) measurements, show that it is true. As it can be seen in Figure 3a, the initial 2% weight loss found for all materials up to 100 °C was associated with the thermal desorption of some water molecules and mostly alkanols onto the materials. Followed for another significant weight loss around 3% at 250 °C, which can be associated with loss of oxygen containing groups, before the complete oxidative decomposition between 350 °C and 490 °C [2,14]. The Figure 3(a) shows the thermal degradation temperature of each sample. The lowest weight lost found was for MH+GO sample which is an indicative of the highest thermal stability. The degradation temperatures measured of DGEBA, HM and HM+GO were 360.58 °C, 361.77°C, respectively and 363.53 °C, respectively, indicating an increasing in the thermal stability while each component is added. Thus, it can be observed that the GO contributes to increase the thermal stability of hybrid material, which could be explained because the functional group of graphene oxide (carbonyl, hydroxide an epoxy) reacting with the other phases (DGEBA/TEOS) promoting the formation of covalent bonds between them. This was confirmed by the DSC measurements.

![Figure 3](image)

**Figure 3.** (a) TGA and (b) DSC from DGEBA, hybrid material (HM) and Hybrid material reinforced with GO (HM+GO).

In the Figure 3(b) there are in some peaks like a temperature value shift around 10 °C. The shoulder observed at 140-210 °C for all the sample, which can be attributed to condensation reactions in the siloxane domains [14]. Thus, is possible that GO stabilized thermally and chemically the HM structure [2]. Like GO, the Si–OH groups accelerated the curing reaction improving the thermal stability of HM [13]. This interaction between silica nanodomain and the matrix leads to the formation of an interfacial polymer layer with a constrained chain mobility resulting in an increase in the glass transition temperature of the hybrid [3,15] Therefore, the GO dispersed homogeneous in a HM coating facilitates the synthesis reaction improving the thermal and chemical stability.
4. Conclusions
A new material was developed employing DGEBA, TEOS and GO. Optimal concentrations established were founded follow the measured of adhesion and microhardness. The optimal phase concentration was 70% of DGEBA and 30% of TEOS. The HM had an improvement in its chemical and thermal properties when graphene oxide was added. The degradation temperature was improved in 10 °C using GO. Therefore, the GO can be a good active principle to improve or modified different composites properties. More experimental studies are needed in order to improve the thermal and mechanical properties of the reinforced hybrid material and in the direction of new applications.

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References
[1] Hernández Rosas J J, Ramírez Gutiérrez R E, Escobedo-Morales A and Chigo Anota E 2011 First principles calculations of the electronic and chemical properties of graphene, graphane, and graphene oxide J. Mol. Model. 17 1133
[2] Xue Y, Liu Y, Lu F, Qu J, Chen H and Dai L 2012 Functionalization of graphene oxide with polyhedral oligomeric silsesquioxane (POSS) for multifunctional applications J. Phys. Chem. Lett. 3 1607
[3] Chruściel J J and Leśniak E 2014 Modification of epoxy resins with functional silanes, polysiloxanes, silsesquioxanes, silica and silicates Prog. Polym. Sci. 41 67
[4] Ponyrko S, Kobera L, Brus J and Matějka L 2013 Epoxy-silica hybrids by nonaqueous sol-gel process Polymer 54(23) 6271
[5] Dasari B L, Morshed M, Nouri J M, Brabazon D and Naher S 2018 Mechanical properties of graphene oxide reinforced aluminium matrix composites Compos. Part B Eng. 145 136
[6] Betancur A F, Ornelas-Soto N, Garay-Tapia A M, Pérez F R, Salazar Á and García A G 2018 A general strategy for direct synthesis of reduced graphene oxide by chemical exfoliation of graphite Mater. Chem. Phys. 218 51
[7] Merhari L 2009 Hybrid Nanocomposites for Nanotechnology (New York: Springer)
[8] Córdova Osorio P L, García García A, Betancur Lopera A F 2016 Modificación química de nanoestructuras de carbono”: Optimización del proceso de síntesis de materiales híbridos (orgánico-inorgánico) XXXVII Encuentro Nacional de la AMIDIQ "Nuevas Tecnologías y Tendencias en la Ingeniería Química (Puerto Vallarta) (México: La Academia Mexicana de Investigación y Docencia en Ingeniería Química) pp MAT 205-208
[9] Serra A, Ramis X and Fernández-Francos X 2016 Epoxy Sol-Gel Hybrid Thermosets Coatings 6(1) 8
[10] Tucureanu V, Matei A and Avram A M 2016 FTIR spectroscopy for carbon family study crit. Rev. Anal. Chem. 46 502
[11] Lyon R E, Chike K E and Angel S M 1994 In situ cure monitoring of epoxy resins using fiber-optic raman spectroscopy J. Appl. Polym. Sci. 53 1805
[12] Kevrekidis P G 2001 Multipulses in discrete Hamiltonian nonlinear systems Phys. Rev. E 64(2) 026611
[13] Devaraju S, Vengatesan M R, Selvi M, Song J K and Alagar M 2013 Hyperbranched polysiloxane-based diglycidyl ether of bisphenol an epoxy composite for low k dielectric application Polym. Compos. 34 904
[14] Lionetto F, Mascia L and Frigione M 2013 Evolution of transient states and properties of an epoxy-silica hybrid cured at ambient temperature Eur. Polym. J. 49 1298
[15] Pascault J P and Williams R J J 2010 Epoxy polymers: new materials and innovations ed R J J W Jean-Pierre Pascault (Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA)