LA-UR-18-25996 (Accepted Manuscript)

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Vinod, Soumya
Tiwary, Chandra Sekhar
Samanta, Atanu
Ozden, Sehmus
Narayanan, Tharangattu N.
vajtai, Robert
Agarwal, Vipin
Singh, Abhishek K.
John, George
Ajayan, Pulickel M.

Provided by the author(s) and the Los Alamos National Laboratory (2019-06-28).

To be published in: Advanced Materials Interfaces

DOI to publisher's version: 10.1002/admi.201700657

Permalink to record: http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-18-25996

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Graphene Oxide Epoxy (GO-xy): GO as Epoxy Adhesive by Interfacial Reaction of Functionalities

Soumya Vinod [1,2], Chandra Sekhar Tiwary [1], Atanu Samanta [3], Sehmus Ozden [1,4], Tharangattu.N. Narayanan [5], Robert Vajtai [1], Vipin Agarwal [5], Abhishek.K.Singh [3], George John [6*], Pulickel M. Ajayan [1*]*

[1] Department of Materials Science and Nanoengineering, Rice University, Houston, TX-77005

[2] Clarkson Aerospace Corporation, Houston, TX-77004

[3] Materials Research Centre, Indian Institute of Science(IISc), Bangalore - 560012, India

[4]Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos NM, 87545, USA

[5] Tata Institute of Fundamental Research - Center for Interdisciplinary Sciences, Hyderabad-500075, India

[6] Department of Chemistry and Biochemistry,, The City College of New York, New York, NY- 10031

Correspondence to: Pulickel M. Ajayan (ajayan@rice.edu), George John (gjohn@ccny.cuny.edu), Soumya Vinod (sv7@rice.edu)

ABSTRACT

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/admi.201700657.

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The unique combination of layered structure and chemical moieties grant very interesting physio-chemical properties to graphene oxide (GO). Functional groups such as epoxide, hydroxyl and carboxyl are abundantly distributed along the hexagonal lattice of carbon atoms. The superior properties of GO and increased interfacial interaction with other compounds make them excellent filler materials in polymers such as epoxies for creating multifunctional composites. Alternatively, the presence of epoxide group on GO opens up the possibility of using it as the major epoxy matrix constituent rather than just as a filler material. In this work, we report the formation of GO-xy (cross-linked GO via the epoxide functionality) resin by reaction of GO with polymercaptan based hardener by completely eliminating the need for conventional epoxy component. Substituting epoxy with GO marks notable advance in preparing adhesive materials with high temperature stability.

Keywords: Graphene Oxide, epoxy, functionalities, polymercaptan, crosslinking

The growth in graphene research lead to popularity of graphene oxide (GO) as an efficient precursor for the preparation of chemically derived graphene. Although initial prominence of GO was attributed to its use as an effective source for mass production of graphene, further studies on structural and chemical properties unfolded interesting features of GO. The fascinating properties arising from the two-dimensional layers of carbon atoms inhabited by oxygenated species endow uniqueness to GO in its inherent form. The functional groups aid GO dispersion in most solvents and has increased interaction with various organic and inorganic compounds[1–4]. This has led to GO being used as precursor for various solution processed nanostructures[5–7]. The properties of GO also show marked variation from pristine graphene. Since the presence of oxygen functional groups introduces sp^3 hybridization into the sp^2 hybridized graphene lattice, distortion of bandgap is observed in GO. Selected removal of functional groups allows tai-

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loring the electrical, optical and chemical properties of the material[8]. Mechanical behavior of GO is also dominated by the functionalities as their interactions causes brittle to ductile transition[9].

The high surface area, excellent thermal/electrical conductivities and mechanical toughness of graphene and other carbon nanomaterials have resulted in it being highly sought nanofiller for polymer composites[10–22]. Nevertheless, the composite properties suffer from poor interface between the filler and the matrix. Using GO eliminates this issue to a large extent as the functional groups in GO can create strong interface with the matrix and also lead to more homogenous dispersion[23–26]. The chemical moieties in GO have been utilized in epoxy composites for improving the physical properties [27–29]. It is well documented in Lerf and Klinowsky models and other models that GO is decorated with hydroxyl and epoxy groups on basal planes and edges[1]. Although the epoxy groups have been used previously for creating better bonding with epoxy matrix, the possibility of substituting epoxy with GO has not been explored before to the best of our knowledge. Epoxy ring groups in GO are formed by oxygen atoms covalently bonded to carbon atoms in graphene sheet. The low density of epoxy groups could be one reason why GO has not been used as epoxy; but when reacted with strong epoxy curing agents, it could crosslink the epoxy groups and form a thermosetting resin. It has been demonstrated that carbon, nitrogen, oxygen or sulfur nucleophiles reacts with epoxides in GO[30–32]. Mixing epoxy hardener with GO allows the possibility of opening the ring and forming resin in the process. Polymercaptan based curing agent has highly nucleophilic thiol (-SH) groups that can open the epoxide functional groups and was selected for investigating the potential of crosslinking GO to form epoxy resin. Eliminating the need for epoxy matrix can considerably reduce the polymeric content in adhesives

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which can be beneficial for applications requiring high thermal stability and conductivity. Moreover, various combinations of GO and hardener system can be used based on specific application.

In this work, a resin was created solely from GO and curing agent without using a separate epoxy component. Theoretical calculations (Figure 1) predicted possible reaction between -SH and functional groups in GO and the experiments were carried out by combining GO with polymercaptan based curing agents at 120^0C. The schematic of the proposed reaction is given in Figure 2a.

Results and Discussion

To investigate the interaction between graphene and functional groups (-OH, -O-, and –COOH), we have employed the first-principles density functional theory (DFT) (Details are given in theoretical methods section). The enthalpy of formation of a functional group is determined as , where , , and are the total energy of the functionalized graphene, pristine graphene and isolated functional group, respectively[33]. The calculated value of E_f indicates that oxygen can form C-O (top of the carbon) and C-O-C (bridge between two carbon atoms known as epoxy) bonds with graphene as shown in Figure 1 (I and II). The bridge formation is much more preferable compared to the top of the carbon atoms of graphene due to more negative value of E_f. Due to bond formation between carbon atoms of graphene and functional groups (>O and –OH), the carbon atoms near the attached functional groups deflected from their original position (Figure 1 (I-III)). This indicates that the carbon atoms near the functional groups have sp^2-sp^3 hybridization. To study the addition –SH functional group to functionalized (<O,-OH, and -COOH) graphene, we have calculated E_f at different positions of –SH on graphene sheet

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as shown in Figure 1 (V-VIII). The calculations indicate that –SH interacts strongly with oxygen of the functional groups <O and –OH compare to the graphene sheet. The interaction between functional groups and –SH breaks the C-O, C-O-C and C-OH bond and formed X-SH (where, X= >O and -OH) molecules as shown in Figure 1. This molecule can be physically absorbed on graphene sheet. However, different configuration calculations indicate that there will be barrier to flow –SH group over the graphene surface and interact with the functional groups. The interaction with the C-O-C group was found to be high in all the configurations indicating a favorable reaction between -SH and the epoxy group if the barrier energy is crossed. The possible reaction between -SH group and GO predicted using DFT calculation was applied to experimental studies using GO and polymercaptan hardener. A schematic for the proposed reaction is presented in Figure 2a. For this, first the GO synthesized using improved Hummer's method is finely powdered to ensure fine mixing with epoxy curing agent (ECA). GO flakes prepared using the improved Hummer's method have a lateral size of few microns. Detailed characterization of GO has been provided in our previous work[7]. The digital and scanning electron microscope (SEM) images for GO powder is shown in Figures 2b and 2c respectively. GO was first finely powdered with mortar and pestle before mixing with ECA. It is important to have GO as very fine powder to disperse it homogeneously in ECA which is a viscous medium. Once powdered, the brown colored GO and transparent ECA is combined in 1:10 weight ratio using mortar and pestle to form a highly viscous brown gel. Other weight ratios of GO and ECA were tried but lower amount of GO resulted in no solidification and higher amount resulted in formation of very dry and brittle solid that breaks into powder. The heating of the gel at 120^{0}C results in a completely cured solid as shown in Figure 2d and has been named GO-xy. GO and ECA are completely mixed and form a relatively homogeneous mixture as seen in the SEM image (Figure 2e). Con-

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trol experiments were conducted using pure ECA and ECA – Graphite mixture under same physical conditions. While pure ECA resulted in a pale yellow low viscous flowy gel that spread out, ECA- Graphite showed poor mixing and showed similar consistency as the pure ECA sample. This indicates that it not the thermal curing of ECA alone or presence of filler material that leads to the formation of the resin but the chemical interaction between GO and ECA that causes it. For bonding two surfaces, small amount of GO-xy was applied to the area to be covered and kept in oven at 120^0C for few hours (Supplementary Figure 1).

GO-xy characterization

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are very effective tools in studying the curing kinetics of polymer based samples. GO and ECA were mixed well together and was immediately placed in TGA alumina pan and the temperature was increased from room temperature to 200^0C at a rate of 5^0C per minute under Ar atmosphere. Similar experiment was done on GO and ECA control samples to identify the weight loss and heat flow of individual samples. After initial gradual weight decrease till 150^0C, a sharp decrease is observed that is associated with the removal of functional groups. The TGA curve for GO-ECA shows decreased weight loss compared to ECA possibly due to the onset of crosslinking reaction (Supplementary Figure 2). Also in the presence of ECA there is no sharp weight loss indicating complete reduction of GO functional groups. This is possibly due to the reaction of the functionalities with ECA. The exothermic peak for ECA at low temperature may be from the initial reactions. In the DSC curve (Figure 3a) a new exothermic peak which is not observed in GO or ECA samples is found in GO-ECA at 150^0C (the sample for TGA is named GO-ECA instead of GO-xy as during the process they are not crosslinked). This is believed to be from the

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reaction between GO and ECA that is instigated by thermal energy. Although curing temperature is at 120^0C the fast heating rate may have led to the peak appearing at a higher temperature. For gaining insight to the changes occurring in the mixture that lead to the formation of the resin, a freshly mixed sample was heated and the evolution of the blend was dynamically monitored using optical microscope. As the temperature was increased slowly, GO and ECA starts to coalesce after few minutes, indicating some chemical interaction between the two materials instigated by thermal energy. The schematic showing the coalescing of GO and ECA as the temperature rises in shown in Figure 3b panel. GO-xy at different stages was observed under optical microscope (Figure 3b). At room temperature, GO is randomly distributed in ECA. As the temperature is increased GO sheets starts joining together and at a temperature of 120^0C, GO is rather homogeneously distributed. The scanning electron microscope (SEM) images in Figure 3b show interconnected structure of GO and ECA with some agglomerates that could have been generated from non-homogeneous mixing. The blending of GO with ECA happens only when annealed as SEM of the mixture at lower temperatures show islands of GO separated from ECA (Figure 3b). X-ray Photoelectron Spectroscopy (XPS) analysis was conducted on the ECA (Supplementary Figure 3) and GO-xy samples (Figure 3c). The C1s core level of peak position of carbon atom is approximately at 285 eV. In high-resolution XPS analysis of ECA, the C=C and C=O bonds are at 286.84 and 286.20eV. The C-S peak is present at 285.11eV. The atomic percentage of carbon, oxygen and sulfur are 67.03, 27.66 and 2.30 respectively. The GO-xy sample also shows similar C=C, C=O and C-S peaks. The atomic percentage of carbon, oxygen and sulfur is 62.38, 35.38 and 2.24 respectively. The C1s XPS spectra of GO usually has C=C bonds, C=O bonds from carbonyl groups and C-O from epoxy groups. However, In GO-xy there is no evident C-O

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peak from epoxy groups in GO which indicates the epoxy ring opening for reaction with ECA.

Solid state NMR (ssNMR) is a very effective tool for studying amorphous material or materials lacking long-range order[34]. It can be used to monitor changes in chemical moieties and changes in atomic level structural changes in a range of molecules. For insoluble samples like GO, solid-state NMR has been used to identify the presence of different functional groups and their relative distribution in graphene layers. A comparative analysis of ^{13}C NMR of GO and GO with hardener was conducted to study the proposed mechanism in the formation of resin that involves opening of epoxy groups in GO to react with the mercaptan groups in the hardener. The NMR spectra for GO and GO-hardener cured samples are shown in Figure 3d. Previous literature reports on ^{13}C spectrum for GO indicate the resonance peaks observed in at ~ 60 ppm and 70 ppm corresponds to the carbon atoms connected to the epoxy and hydroxyl functional groups. The peak at ~ 130 ppm arises from the sp^2 carbon atoms. The GO-hardener spectrum shows complete disappearance of the C-O-C epoxy peak in GO and a shift of 6ppm to low field for the C-OH peak. The absence of C-O-C peak in the GO- hardener sample is in good agreement with the hypothesis that the epoxy rings in GO are reacting with –SH groups in the hardener. An excess of hardener seems to be present in the sample as observed from the lower intensity sp^2 carbon peak. However, the absence of C-O-C peak is not expected from the predominant effect of hardener. This is due to the high intensity of the peak observed in GO sample and the absolute disappearance in the GO-hardener cured sample.

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Mechanical Characterization

It is important to understand the mechanical characteristics of GO-xy for them to be applied in thermal applications. It is necessary for the sample to maintain the mechanical stability at higher temperature and for testing this, *insitu* temperature controlled experiments were carried out in DMA where the GO-xy cured sample was subjected to stiffness measurements when the temperature was increased from room temperature to 150^0C (Figure 4a). Increased temperature had no adverse effect on stiffness that emphasizes the temperature stability of the material. GO-xy is a resin that exhibits flexibility and its response to varying the forces were monitored using controlled force experiment (inlay of Figure 4a). The force was first increased to 2N and held for 30 minutes followed by at 4N and 8N for the same duration. No deterioration in the stiffness response was monitored for GO-xy. Load/unload experiments also showed good resilience of the sample (Supplementary Figure 4). To examine whether any evidence of curing can be obtained from the mechanical characteristics, partially cured GO-ECA was placed inside the temperature control chamber of DMA and when the temperature reached 120^0C a small rise in stiffness was observed which could be from the crosslinking process in the sample (Supplementary Figure 5). The adhesive strength of the GO-xy on two glass surfaces was evaluated by performing a lap shear test. For preparing samples, two glass slides were cleaned and GO mixed with ECA was applied to the bond area of overlap length 25mm and annealed at 120^0C overnight. Control sample prepared using ECA was also annealed in similar conditions. Although GO-xy bonds the glass slides within an hour or two, ECA takes longer time and hence to keep the parameters constant the curing period was extended to 12 hours. The amounts of GO-xy and pure ECA applied for preparing the samples were same (~100 mg). The test was conducted using Instron Universal Test Machine. An improvement in the adhesion strength

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and critical load is observed in glass slides bonded using GO-xy sample compared to ECA (Figure 4b). The failure strain from the adhesion test of ECA and GO-xy are given in Figure 4c. For the test, two ends of the glass specimen are held by the tensile grasps as shown in Figure 4d. Force was applied at a controlled rate until the bonding between the surfaces break. The samples were examined after the failure and while ECA allows sliding of the glass slides with minimal force, the GO flakes in GO-xy shows a locking mechanism that protects the surfaces from sliding away easily (Figure 4d). Although not entirely the same mechanism, improvement in adhesion strength by interlocking mechanism have been observed in carbon nanotubes[35]. It is easier for nanomaterials to fill the voids on rough surfaces that leads to increased bonding. The filling of voids by GO present in GO-xy enhances the adhesion between the glass surfaces. It is expected that the bonding strength can be improved by ensuring homogeneous application of the GO-ECA mixture and preventing agglomerates that could have negative effects on the interfacial contact between the surfaces.

Discussion

In this work, GO was mixed with polymercaptan based hardener that resulted in the formation of a resin when thermal energy was provided. Control experiments with graphite powder and reduced GO did not form a resin which confirms it is the functional groups in GO that instigates the reaction. Since the curing only occurs at high temperature it can be mixed and stored which gives it a good shelf life and can effectively work as a one part epoxy[36]. The NMR and DSC results indicate reaction occurring between GO and ECA. A major application area for GO-xy is thermal interface materials (TIMs). High thermal conductivity, easy application, void free contact and temperature stability are the key requirements for TIMs. Conventional thermal greases, phase change materi-

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als and filled polymers fail to meet all the requirements. Here, GO acts as epoxy and simple mixing with hardener leads to the formation of a thermally and mechanically stable adhesive between two solid surfaces. The possibility of chemically crosslinking GO or other functionalized 2D materials with epoxy hardener matrix has not been previously explored. The chemical bonds between GO and the hardener allows easy blending and curing at higher temperature provides the option of storing the mixture at room temperature for long time before use which is again not an option in most conventional TIMs.

GO is considered an excellent filler material while preparing composites not just because of the physical properties but also due to the ease of interaction it can have with the matrix from the functional groups present in them. The abundance of epoxy groups provides an option of using it as alternative choice for epoxy in standard two-part epoxy system and essentially converting it to one-part epoxy. Improving synthesis methods where density of epoxy groups can be increased would provide more reactive sites and result in accelerated curing. The work proposes using GO as epoxy and provides case study that supports the idea. Further optimization in the mixing process, selection of hardener with higher density of thiol groups, increasing the density of epoxide functionalities in GO are expected to produce epoxy systems with enhanced adhesive and thermal properties. The thermal properties of GO, good adhesion strength between different surfaces, ease of preparation and application makes GO-xy a very attractive choice for high temperature stable thermally conducting epoxies.

Materials and Methods

Synthesis: GO powder was synthesized using improved Hummer's method. In the method, 3g of SP-1 graphite powder (Bay Carbon) with 18g of potassium permanganate

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is mixed in 360mL sulfuric acid along with 40 mL phosphoric acid. The mixture was left for stirring overnight and then poured to ice. 10-14 mL of hydrogen peroxide is poured to this very slowly as the reaction is highly exothermic. The solution turns color to yellow and the solid material is allowed to settle down. The solid material is then filtered and washed multiple times with water, 30% HCl and ethanol. The dried material obtained is GO which is then finely powdered using mortar and pestle. Polymercptan based epoxy hardener (Hardman Epoxy Double/Bubble obtained from Sanford Distributing Company) was mixed with GO powder in the weight ratio 10:1 and kept in oven at 120^0C for 12 hours. The gel mixture turns into a solidified flexible resin after heating.

Characterization: The structural characterization was performed using FEI Quanta 400 Scanning Electron Microscope under high vacuum at 15kV. Q-600 Simultaneous TGA/ DSC was used for studying the thermal behavior and curing kinetics. Q800 Dynamic Mechanical Analysis (DMA) was used for the mechanical measurements on GO-xy free standing sample and adhesion testing of glass slides bonded using GO-xy. Solid state NMR experiments were carried out at 11.7 T (^{1}H Larmor frequency of 500 MHz) using Bruker AV NMR spectrometer. A 4-mm triple-resonance standard Bruker MAS probe was used for experiments at MAS frequencies of 7 kHz. Hahn echo spectra were recorded with an echo time of 10 microseconds and a recycle delay of more than 15 seconds. Approximately 4200 scans were recorded for each sample at room temperature.

Theoretical Methodology: All the calculations were performed using first-principles density functional theory (DFT) by considering plane-wave method as implemented in the Vienna ab-Initio Simulation Package (VASP)[37,38] . The interactions among the electron are represented by all-electron projector augmented wave potentials[39]. The exchange-correlation potential is approximated by the generalized gradient approxima-

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tion (GGA) of Perdew-Burke-Ernzerhof functional (PBE)[40]). The wave function of electron in the crystal structure is replaced by plane wave basis set with plane kinetic energy cut-off 400 eV. The van der Waals (Vdw) interaction is included in all the calculation within Tkatchenko and Scheffler (TS) model as implemented in VASP[41]. This model takes into account environment dependent Vdw interaction via electron density. The dispersion energy in TS is represented by considering lowest-order two-body dispersion energy ()[41,42] , where, , and are the dispersion coefficient, distance between i^{th} and j^{th} species and damping functions, respectively. To model the interaction between the isolated functional group and graphene, we have considered 5×5×1 supercell of graphene. To avoid artificial electrostatic interaction among the neighboring images a vacuum region of ~15 Å is used in the out-off-plane direction. The structures were optimized using the conjugate gradient scheme until the forces on every atom were ≤ 10^{-2}eV/Å . The Brillouin zone was sampled by 3×3×1 Monkhorst-Pack (MP)[43] **k**-mesh.

Acknowledgement

Authors acknowledge the funding support from U.S. Department of Defense: U.S. Air Force Office of Scientific Research for the Project MURI: "Synthesis and Characterization of 3-D Carbon Nanotube Solid Networks" Award No. etFA9550-12-1-0035.LDM and Supercomputing Education Research Centre (SERC) for providing computing facilities and Indo–US Science and Technology Forum (IUSSTF), Govt. of India for assisting the Indo–US Research Fellowship. S.O. acknowledges financial support from a LANL Director's Postdoctoral Fellowship.

Notes

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The authors declare no competing financial interest.

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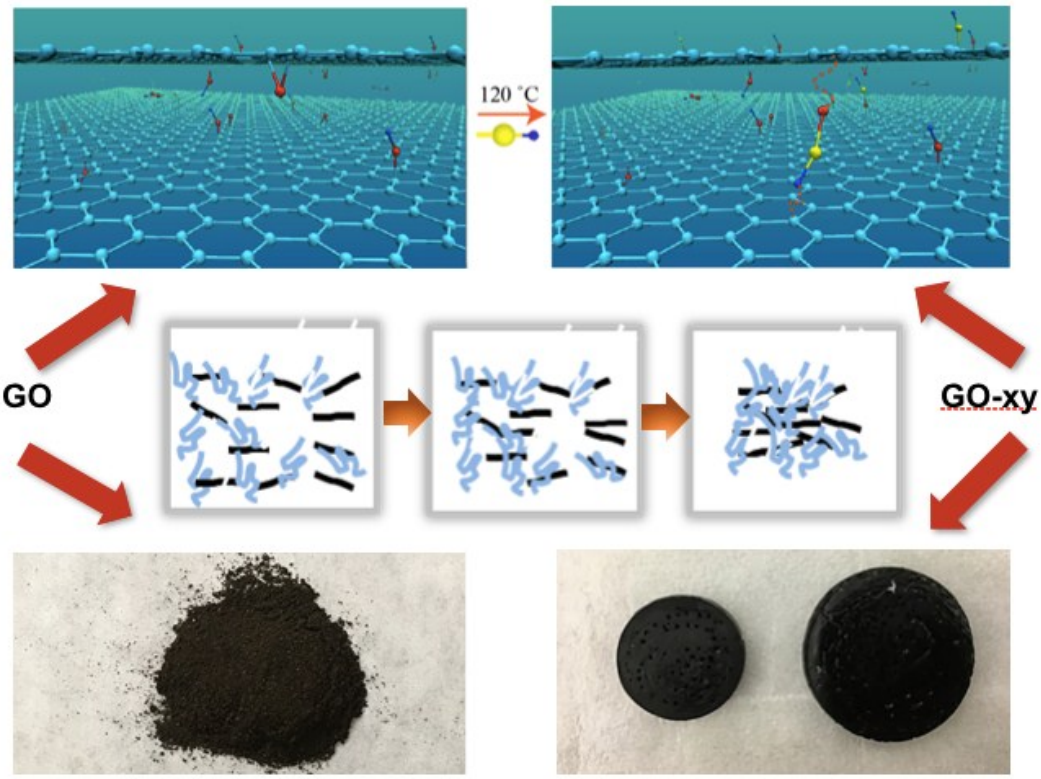
TOC Graphic



TOC Summary: Graphene Oxide has epoxide groups that can essentially act as epoxy component in two part epoxy system. The epoxide ring opens and crosslinks with the highly nucleophilic -SH group in polymercaptan based hardener. Powdered GO when mixed with polymercaptan based hardener and heated to 120^{0}C forms a resin that is named GO-xy.

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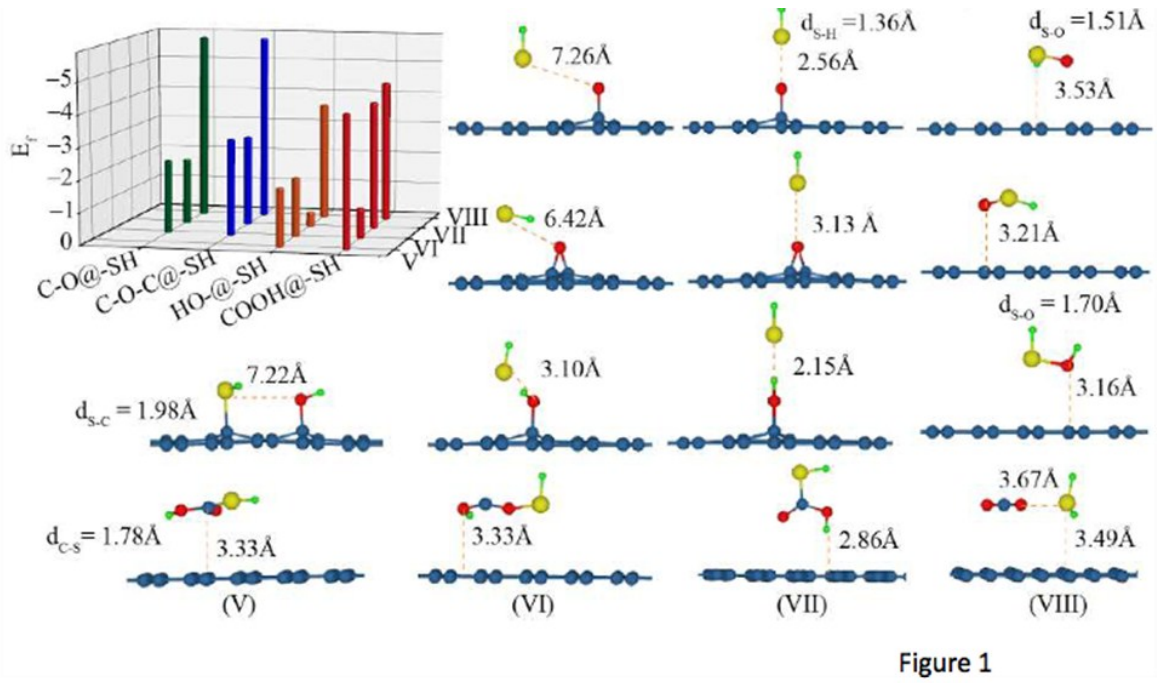

Figure 1: DFT calculations showing the enthalpy of formation of various functional groups in GO with mercaptan group (I), (II), (III), and (IV) enthalpy of formation (E_f) of =O, >O, –OH, and –COOH functional groups, respectively attached to the graphene sheet. The side view of the functionalized graphene sheet is shown here for clarity. (V)-(VIII) showing enthalpy of formation of different functionalities in the GO with mercaptan (-SH) group in different configurations. Green, sky-blue, red, and yellow color boll represents H, C, O, and S atom, respectively. Among the different functional groups the interaction of C-O-C (epoxide) group with -SH is found to be high in all configurations indicating a favorable reaction between the two provided the thermal barrier is overcome.

Author Mar

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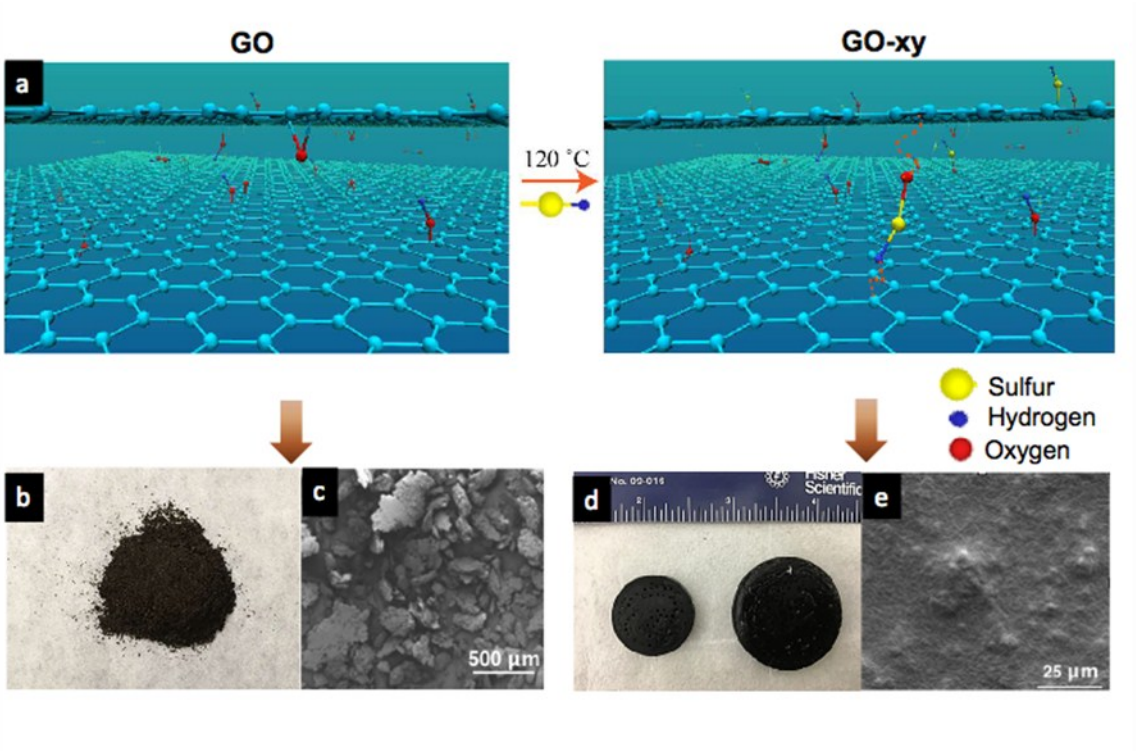

Figure 2: Schematic representation and digital images of GO-xy (a) Reaction schematic of GO with polymercaptan based hardener where the mercaptan groups (-SH) opens epoxy rings in GO when heated at 120^{0}C and crosslinks the GO sheets (b,c) Digital and SEM images of GO powder respectively where SEM shows the individual flakes agglomerated to form larger solids (d) Digital image of GO-xy showing a completely cured solid of definite shape after GO and ECA is mixed and cured at 120^{0}C (e) SEM image of GO-xy showing GO blended well with epoxy harderner .

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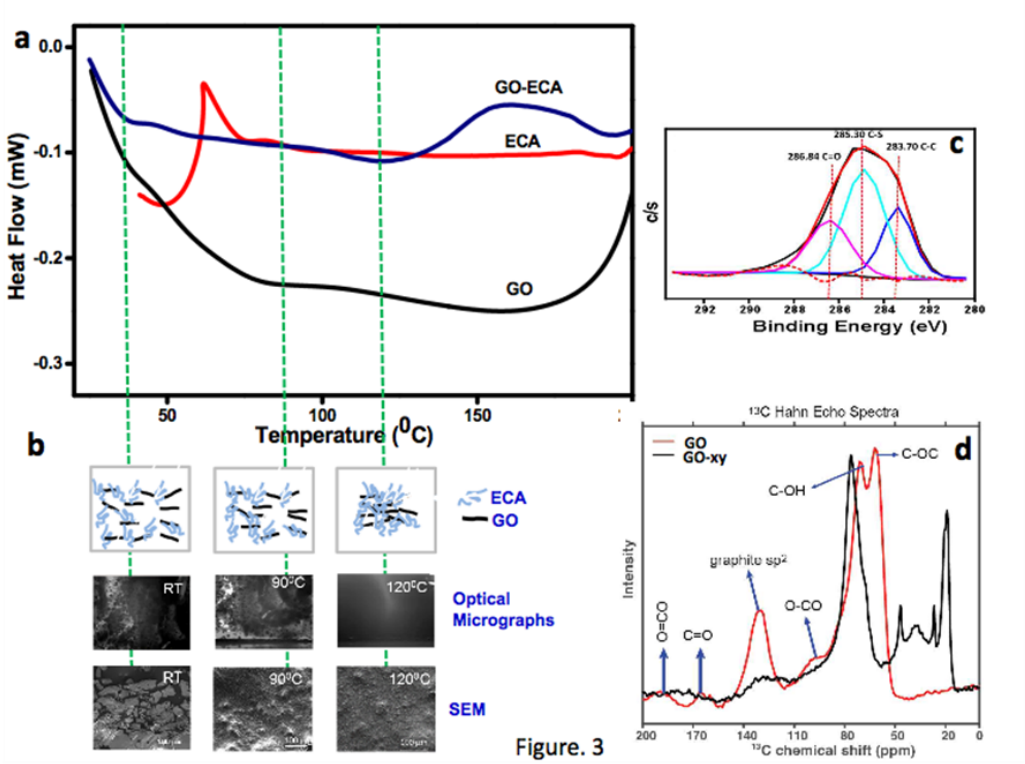

Figure 3: GO-xy thermal and spectroscopic characterization (a) DSC of the samples show sharp exothermic peak for the ECA due to some possible initial reaction, high intense peak for GO at 200⁰C corresponding to the removal of functional groups while a new exothermic peak at 150⁰C appears for GO-ECA which could be from the crosslinking reaction occurring at high temperature (b) The schematic, optical and scanning electron micrographs respectively, showing GO-ECA at different temperatures with poor mixing at lower temperature and coalescing to form a homogeneous material at higher temperature; in optical image the darker spots corresponds to GO and lighter regions correspond to ECA (d) High resolution XPS C1s spectra of GO-xy . C=C and C=O and C-S peaks are present at at 283.70, 285.30 and 286.84 (e) ^{13}C NMR spectra of GO and GO-xy. GO shows resonance peaks at 60 ppm, 70 ppm and 130 ppm corresponding to the

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epoxy, hydroxyl and sp^2 carbon atoms. In GO-xy the epoxy peak at 60 ppm disappears and C-OH shows a shift of 6 ppm to the low field.

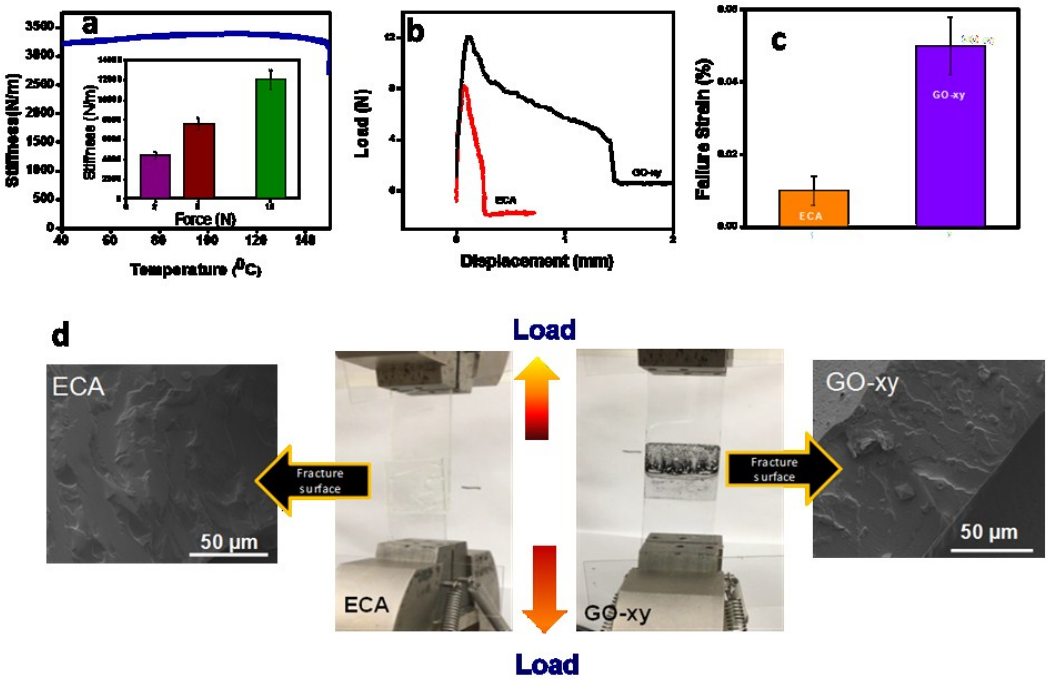

Figure 4: Mechanical characterization and adhesion test results (a) DMA results for GO-xy indicating stiffness of GO-xy stable when temperature is increased and inlay shows stiffness recorded in controlled force experiment where force first increased to 2N and held for 30 minutes followed by at 4N and 8N for the same duration (b) Load – Displacement curve from lap shear test using Instron for determining the adhesive strength on glass surfaces bonded using ECA and GO-xy respectively (c) Failure strain for glass surfaces bonded by ECA and GO-xy showing superior adhesion of GO-xy (d) test setup and fracture surfaces for adhesion test of ECA and GO-xy where glass slides bonded by ECA allows easy sliding due to tensile force while the ones bonded by GO-xy demonstrates a slow sliding and a locking mechanism. The error bars indicate standard deviation.

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