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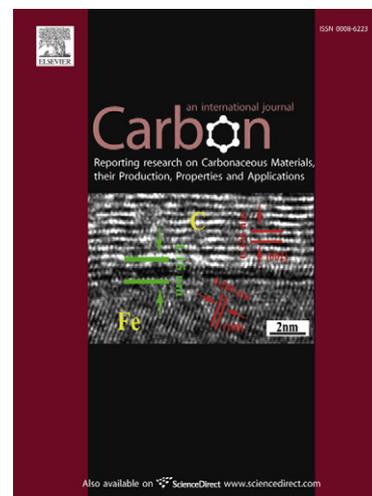
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Improvement of Mechanical Properties of Graphene Oxide / Poly(allylamine) Composites by Chemical Crosslinking

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Abstract

Graphite oxide was prepared by oxidation of graphite using the Hummers method, and its ultrasonication in water yielded dispersed graphene oxide (GO) sheets. These sheets were then crosslinked with a water soluble polymer, namely poly (allylamine) hydrochloride (PAH), by carbodiimide coupling. Free standing composite films were obtained by filtration. These crosslinked composites showed better mechanical properties than unmodified GO films and those of composites that were made by simple mixing of GO and PAH. The filtration process was optimized to produce strong GO films which were subsequently crosslinked with PAH *in-situ* to produce very strong composites with tensile strengths up to 146 MPa.

1. Introduction

Theoretical and experimental studies of graphene predicted that graphene and graphene based materials may possess superior mechanical and electrical properties [1-5]. Hence graphene-based materials may be used in a wide range of application, such as hydrogen storage [6], displays [7] and solar cells [8]. Graphene sheets are expected to have tensile modulus and ultimate strength values similar to those of SWCNTs [9]. However, obtaining single graphene layers from graphite is a major obstacle. There are reported methods on the production of graphene such as graphitization of SiC [10] micromechanical cleavage [11] and solution exfoliation of graphite in organic solvents [12]. However, these methods produce a poor yield of graphene layers. Another method is the oxidation of graphite to graphite oxide which can be easily exfoliated into graphene oxide (GO) layers in solution [13-15] and readily converted back to graphene by chemical reduction [15-20]. Unfortunately the reduction does not completely restore the graphitic structure. Oxidation is achieved by treating graphite flakes or powder in strong acid and oxidizing agents. This process introduces oxygen containing functional groups to the surface of graphite including carboxylic acid and epoxy groups [21]. This functionality makes the graphite hydrophilic and allows further modification of the resulting graphite oxide structure for further

applications [22, 23]. It has been shown before the preparation GO composites with various materials including GO/polyelectrolyte layered nanostructure [24, 25]. Such structures were made conductive after subsequent reduction of GO. Moreover, Dekany and co-workers have shown the nature of interaction between aliphatic amines and GO in various solvents and how they intercalate between the GO sheets [26, 27]. GO papers made by filtration have shown to have excellent mechanical properties [28]. Ruoff and co-workers have shown a way of crosslinking pre-made GO paper using divalent ions to increase the mechanical properties of such films [29]. Recently the same group showed a solution based approach where GO was crosslinked to poly (allylamine) in solution to produce strong composites [30]. Here we report the preparation of GO/poly (allylamine) composites by chemical crosslinking using carbodiimide coupling. Free standing films were then prepared by filtration and characterized using several techniques. The mechanical properties of the free standing films were investigated

2. Experimental

All chemicals were purchased from Aldrich unless otherwise stated. Field emission scanning electron microscopy (SEM) studies were performed using a Hitachi S-4300, which was operated at 5.0 kV, on gold coated fracture surfaces. Fourier transform infrared (FT-IR) measurements were performed in transmission and reflectance mode using a Digilab FTS-6000 spectrometer using Perkin-Elmer micro-sampling attachment. Thermogravimetric analysis (TGA) measurements were carried out in air for all the samples using a Perkin-Elmer Pyris 1 TGA with a temperature scan rate of 10 °C per min. The ultrasonic bath used was a Grant XB6 at 50-60 Hz. The ultrasonic processor used was Model GEX-750 ultrasonic processor operated at 20 %. Mechanical tests were performed using a Zwick tensile tester Z100 using a 100 N load cell with a cross-head speed of 0.5 mm/min. Centrifugations were performed on a Hettich Zentrifugen, Universal 32. X-ray diffraction (XRD) was performed on Bruker D8 X-ray diffractometer.

2.1 Preparation of graphite oxide and graphene oxide/PAH composites

Graphite oxide was prepared according to the Hummers method [31]. Powdered graphite (0.50g) and Sodium nitrite (0.25 g, 3.6×10^{-3} mol) were mixed together in Sulfuric acid (16.5 mL). After 10 min of stirring, KMnO_4 (1.5 g, 9.5×10^{-3} mol) was slowly added over 30 min to the solution at 0 °C in an ice bath. The mixture was then allowed to stir for 30 min at 35 °C in an oil bath. Millipore water (23 mL) was added slowly which increased the temperature to 98 °C followed by more Millipore water (70 mL). Next H_2O_2 (1.75 mL) was added to the stirring solution. The resulting dark solution was then divided into 4 plastic centrifuge tubes for centrifugation (10 min, 3000 t/min). Black Graphite oxide which deposited on the bottom of the tubes was then washed 3 times with HCl solution (10 %) followed with ethanol. Each washing was followed by centrifugation and removal of the supernatant using a Pasteur pipette. The powder was left drying overnight (30 °C in oven) and graphite oxide was collected as a dark black solid.

Graphite oxide (10 mg) was dispersed in Millipore water (20 mL) using tip sonication (2 min) leading to dispersed graphene oxide sheets in solution. N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride, EDAC, (50 mg, 2.6×10^{-4} mol) was added to the dispersion and allowed to stir for 10 min. PAH (20 mg, ~56,000 Mwt) was then added to the mixture as well as excess dimethylamino pyridine (DMAP). The dispersion was stirred overnight. It was then sonicated in a sonic bath for 10 min and filtered through an Alumina membrane (Whatman, 0.2 μm pore size). After washing with Millipore water (2x150 mL) and drying (in oven, 30 °C), graphene oxide/PAH (GO/PAH) composite paper was peeled off the membrane. Characterization techniques were performed on all the composites collected. Control experiments were performed where the composites were prepared as above but without the use of EDC. For optimized preparation of strong GO composites via slow filtration, all composites were made filtered on Alumina membrane (Whatman, 0.02 μm pore size).

2.2 *In-Situ* preparation of GO/PAH composites

In-situ crosslinking was prepared by slow filtration of GO suspension in water (0.5 mg/mL) on an alumina membrane (Whatman, 0.02 μm pore size). Next an aqueous solution of EDAC (50 mg, 2.6×10^{-4} mol) was deposited on the prepared film and left to stand for 10 min before filtering slowly through. 20 mL of an aqueous solution of PAH (1 mg/mL) was deposited on the GO film and slowly filtered over 30 min. The GO/PAH film was washed with copious amount of water to remove excess PAH and side products. The films were dried and peeled off the membrane and the mechanical properties were measured as before.

3. Results and Discussion

The proposed mechanism for this reaction is that an amide linkage is formed between the amine groups of the polymer and the carboxylic acid groups which are predominantly at the edges of the GO sheets. Fourier transform infrared (FT-IR) spectra was recorded for the composites as well as unmodified GO (Figure 1). IR of the crosslinked composites showed characteristic stretch at $\sim 1650 \text{ cm}^{-1}$ assigned for the amide C=O stretch. For the crosslinked composites, a sharp peak appears at $\sim 1460 \text{ cm}^{-1}$ indicating the formation of the amide bond. Moreover, the broad O-H stretch at $\sim 3300 \text{ cm}^{-1}$ is not as broad or possibly indicates N-H stretch of the polymer and the success of the crosslinking reaction.

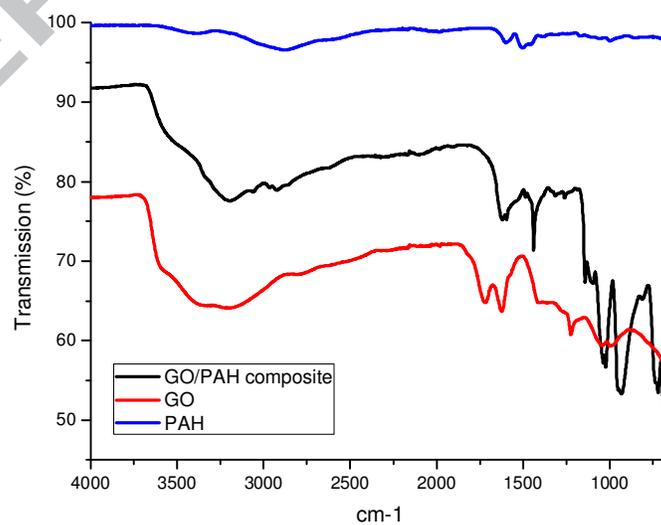


Fig. 1. FT-IR spectra of crosslinked GO/PAH composites, GO and PAH.

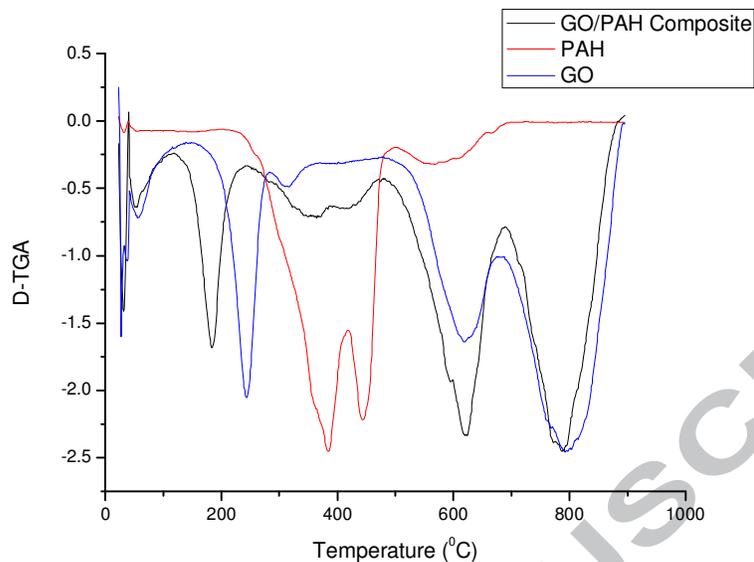


Fig. 2. D-TGA plot of GO, GO/PAH composite and PAH.

Figure 2 shows differential TGA (D-TGA) curves of unmodified GO, GO/PAH composite and pure PAH. GO/PAH composite shows the same decomposition peaks for unmodified GO representing decomposition of oxygen functionality at ~ 200 °C and sp^3 and sp^2 carbons at ~ 800 and 900 °C respectively. However, decomposition peaks for PAH were also present between ~ 380 - 430 °C which were shifted to lower temperatures by ~ 20 °C compared to the pure polymer. This may be explained by the fact that graphene oxide sheets may provide better heat transfer to the polymer in the composites causing it to decompose at lower temperatures.

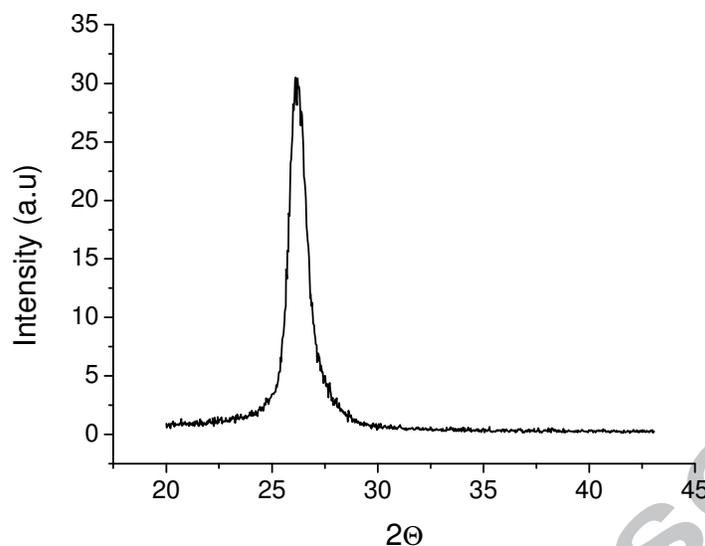


Fig. 3. XRD of GO/PAH composite

Figure 3 shows an XRD of GO/PAH crosslinked composite. The d -spacing was found to be $d_{002} = 0.667$ nm with crystal size of 8.6 nm.

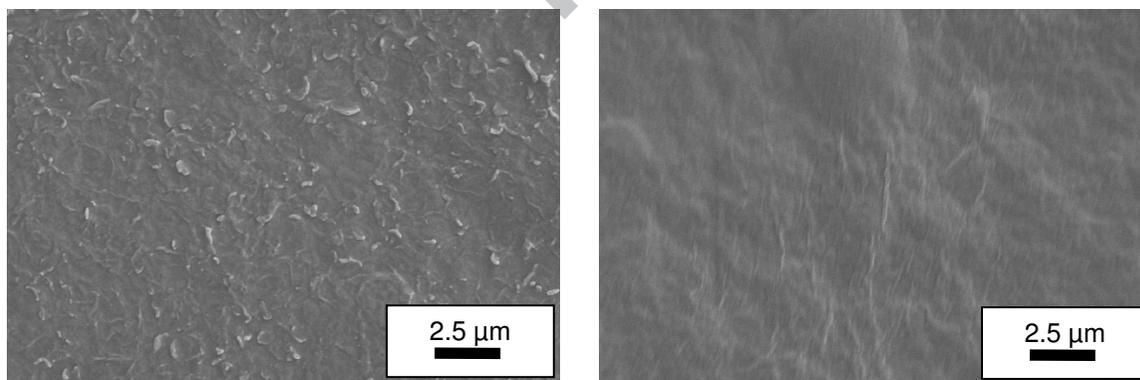


Fig. 4. SEM images of crosslinked (*left*) and non-crosslinked (*right*) composites. The polymer is visible at the surface of the crosslinked composites where it is washed away in the non-crosslinked one.

Figure 4 presents SEM images of the surface morphology of the composites. In the case of crosslinked composites the polymer is visible on the surface of the graphene oxide surface. On the other hand the non-crosslinked composites seem to have a smoother surface with no evidence of polymer presence very similar to that of pure graphene oxide films. This is further evidence that the polymer is chemically linked to the graphene oxide sheets in the crosslinked composites and is not affected by the washing step

during film preparation, where the polymer is washed away in the non-crosslinked composites. This however does not rule out that some polymer may be still be present in between the sheets of the non-crosslinked composites. In fact TGA analysis of the non-crosslinked composites showed presence of PAH in the composite. It is worth mentioning here that GO loses some of its solubility in water after the crosslinking reaction. This may be due to the reduction of hydrophilic groups on the GO sheets. This reduction in solubility makes it difficult to exfoliate the composites in water after free standing films have been formed.

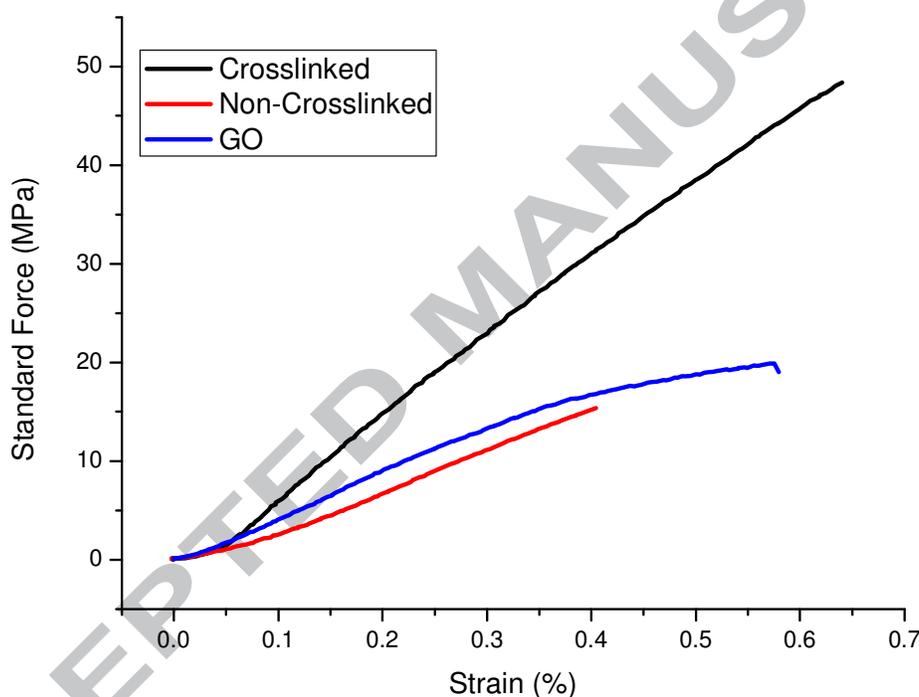


Fig. 5. Stress-strain curves of crosslinked and non-crosslinked GO/PAH composites and GO

The mechanical properties of all composites prepared were tested. The composite films obtained after filtration were cut into strips of 2.25 mm wide and several centimeters long. The strips thickness varied between 9 -12 μm . Pure graphene oxide films made by filtration were found to have an average tensile strength of 17.24 MPa and Young's modulus of 5.32 GPa. The mechanical properties of the crosslinked and non-crosslinked composites were compared. Figure 5 shows the tensile strength of crosslinked, non-

crosslinked and pure GO. Comparing the crosslinked and non-crosslinked composites it is clear that the crosslinked composites have better mechanical properties. An increase of 200% and 395% for tensile strength and Young's modulus respectively was observed. The non-crosslinked composites showed similar mechanical properties to pure graphene oxide films.

Increasing the amount of polymer added to the reaction, while keeping the amount of GO constant does not have an effect on the mechanical properties. This may be explained by the fact that the polymer has sufficiently crosslinked the GO sheets at low concentrations and therefore increasing the amount of polymer does not affect the mechanical properties of the composites. The amount of PAH bound to the GO in the crosslinked composites was calculated from the TGA graphs. At increasing mass percentage the amount of PAH was almost constant (~ 18 %) confirming that all the carboxylic acid groups on GO were consumed by PAH and no more were available for binding. The amount of PAH in the non-crosslinked composites was also calculated from TGA. It was found that there a residual PAH still present in the composites (~15 % wt.) even after washing. The fact that this residual PAH present in the non-crosslinked composites has no effect on the mechanical properties proves that the chemical crosslinking of between GO and PAH is the primary reason for the enhancement of the composite strength. Table 1 summarizes the mechanical properties data.

Table 1. Summary of the mechanical properties of the composites

<i>Composite</i>	<i>Strength (MPa)</i>	<i>Young's Modulus (GPa)</i>	<i>Strain (%)</i>
GO	17.24 ± 3.47	5.32 ± 0.61	0.58 ± 0.08
Crosslinked GO/PAH	49.04 ± 9.0	8.10 ± 0.54	0.64 ± 0.04
Non-crosslinked GO/PAH	16.15 ± 7.27	3.64 ± 0.99	0.47 ± 0.09

Controlling the rate at which the GO dispersions are filtered has a major effect on the strength of resulting papers. Slow filtration may allow the GO sheets to assemble and pack more efficiently therefore giving stronger films. In the case of our composites slow filtration doesn't seem to have an effect on their strength, however slow filtration of unmodified GO dispersions resulted in much stronger films (74 MPa, ~ 330 % increase in tensile strength compared to fast filtration of unmodified GO). Crosslinking and the presence of the polymer may affect the efficiency of packing of the GO sheets and hence give weaker films.

A different approach was used to produce stronger GO/PAH composite films where crosslinking was performed directly on dry strong GO films made by slow filtration (*in-situ crosslinking*). An aqueous solution of the coupling agent (EDC) followed by a solution of PAH (20 mL, 1 mg/mL) were deposited on the pre-made films and slowly filtered through to allow time for the reaction to take place. The films were subsequently washed with Millipore water to remove excess polymer and side products. These films showed the best mechanical properties of any composites made previously (see Fig. 6). They showed maximum values of ~146 MPa for tensile strength and ~19 GPa for Young's modulus. A control experiment was performed where GO film was made by slow filtration and PAH was subsequently filtered through, however no EDC was used. The mechanical properties of such films were similar to that of unmodified GO. We can conclude that no crosslinking reaction took place and hence no improvement of the mechanical properties.

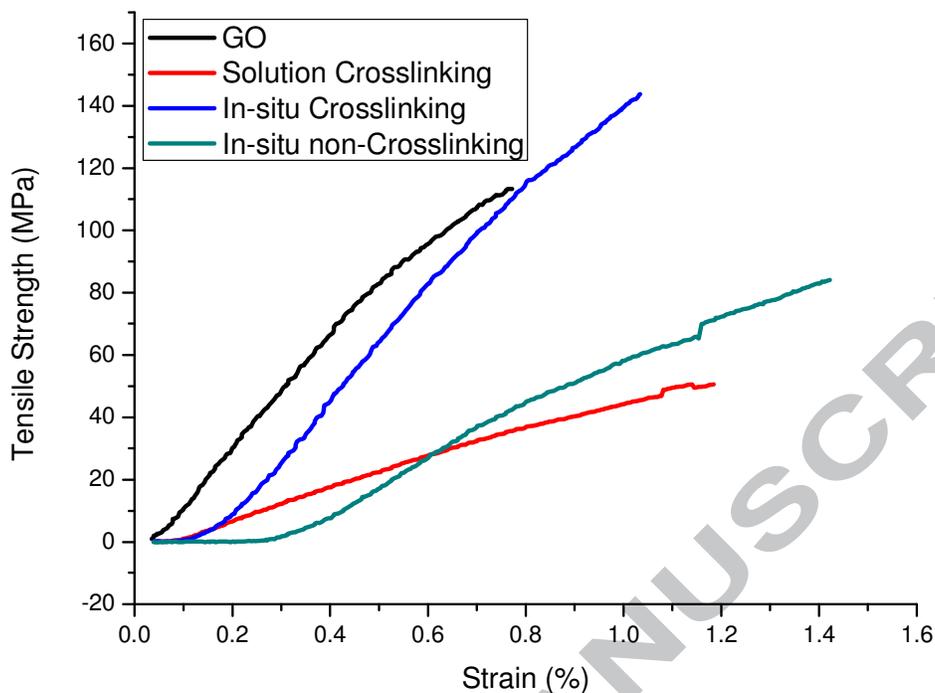


Fig. 6. Stress-strain curves of slow-filtered GO and composites

Comparing our result with previous work on GO/PAH composites [24], our way of making the composites is different in the sense that we use carbodiimide coupling to the $-\text{COOH}$ groups of the GO where the other method the linking is through the epoxy groups by sonication. Our composites are 28 % stronger in tensile strength. However the modulus is ~ 45 % less for our composites. Our composites show similar mechanical properties of reported GO paper modified with Ca ions [25]. Table 2 summarizes the mechanical properties data.

Table 2. Mechanical properties of slow filtered composites

<i>Composite</i>	<i>Tensile Strength (MPa)</i>	<i>Young's Modulus (GPa)</i>	<i>Strain (%)</i>
GO	74.20 ± 19.79	15.30 ± 1.42	0.95 ± 0.33
Solution crosslinking	43.40 ± 8.9	5.26 ± 0.21	1.05 ± 0.37
In-situ crosslinking	128.22 ± 19.15	18.31 ± 1.27	1.13 ± 0.26
In-situ non-crosslinking	62.69 ± 14.01	8.64 ± 2.31	1.09 ± 0.20

4. Conclusions

We have demonstrated a new way of making graphene oxide-polymer composites by covalent chemical bonding. The crosslinking of GO with the polymer enhances the mechanical properties of the composites compared to unmodified GO films made by filtration. Slow filtration of the unmodified GO dispersions allows efficient packing of the GO sheets resulting in mechanically stronger films. However, slow filtration of GO/PAH dispersions has no influence on the strength of the resulting paper due to inefficient packing. In-situ crosslinking reaction produced GO/PAH composites with enhanced mechanical properties to produce the strongest composites. Further work on these composites is on going to produce conductive strong composites by reduction of the GO or incorporation of metallic nanoparticles or both.

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Fig. 2. D-TGA plot of unmodified graphene oxide GO/PAH and PAH

Fig. 3. XRD of GO/PAH composite

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Fig. 6. Stress-strain curves of slow-filtered GO and composites

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Table 2. Mechanical properties of slow filtered composites