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MULTI-SCALE EXPERIMENTAL ANALYSIS OF HYBRID CARBON/CNT+GRAPHENE COMPOSITES

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Abstract. *The addition of carbon based nanostructures as nanofillers in composite materials has been reported to improve its mechanical properties. However, these structures have the tendency to agglomerate due to the van der Waals forces between nanotubes and graphene sheets. Some studies have reported the use of surfactants to overcome this problem. This research goal is to analyze the surfactant effect on the overall behavior of carbon/epoxy composites nano-modified by graphene and carbon nanotubes. Multi-layered graphene and multiwall carbon nanotubes were dispersed with two different surfactants, i.e. Sodium dodecyl benzenesulfonate (SDBS) and Polyoxyethylenenonylphenyl ether (IGEPAL® CO-890). The morphological analysis was performed using scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy, while the macroscopic behavior follows the mechanical characterization by tensile tests (ASTM D 3039) and three point bending test (ASTM D 790). The stiffness seems to be insensible to functionalized nanostructures, in both tensile and bending tests. Nevertheless, an improvement on the ultimate strength of 23.5% for tensile tests and of 11.4% for bending tests was observed when the non-ionic CO890 surfactant was employed.*

Keywords: *Carbon nanotubes, Graphene, Nanocomposites, Surfactants.*

1. INTRODUCTION

According to Hirsch (2010), carbon provides the basis for life on Earth and it is also an important element for many technological applications. Due to carbon high reactivity, it could originate many molecular compounds and crystalline solids. Its four valence electrons tend to interact with each other, producing different kinds of allotrope (Wong & Akinwande, 2011). Among these allotropes, carbon nanotubes (CNT) and graphene have been receiving great attention because of their unique properties and a wide range of applications.

Carbon nanotubes are defined by Breuer and Sundararaj (2004) as a hexagonal network of carbon atoms rolled up into a hollow cylinder, with each end capped with half of a fullerene molecule. As pointed by Kong (2013), CNTs present different structures, differing in length, thickness, types of helicity and number of layers. Its large aspect ratio (length/diameter) is appointed as one of the reasons for the special electrical, mechanical, thermal and optical properties, unique to CNTs (Ávila, *et al.*, 2015; Kong, 2013). Owing to the combination of the outstanding Young's modulus and tensile strength, the small size and the low density, CNT is a great promising material for use in development of new composite materials with superior mechanical and physical properties (Georgantzinos *et al*., 2014; Godara *et al*., 2009). As discussed by Ashrafi *et al*. (2011), CNT have the potential to improve fiber/matrix adhesion and to address some weaknesses of conventional laminated composites, such as delamination problems and low impact damage resistance.

Recently, graphene is emerging as an option to CNTs, with the advantage of their good relation benefit/cost. Presenting approximately the same stiffness of single walled carbon nanotubes (SWNT), graphene cost is much lower than CNT (Koo, 2006; Oliveira *et al*., 2015). Polschikov *et al.* (2013) defined graphene as a single layer of carbon atoms, bonded by sp^2 orbital into hexagonal two-dimensional crystal lattice. As pointed out by Kuilla *et al*. (2010), it is considered the "thinnest material in the universe", presenting huge application potential and remarkable properties. As discussed by Yang *et al*. (2012), graphene is also regarded as one of the strongest materials ever tested, with a breaking strength 200 times higher than steel, a tensile strength of 130 GPa and a Young modulus of about 1TPa. Avila *et al*. (2015) commented that this high stiffness and elevated strength can be attributed to the high specific surface area ($\approx$ 2600 m^2/g) and the strong carbon-carbon covalent bonds. According to Zaman *et al*. (2011) its elevated specific

surface area carries higher levels of transferring stress across interface and provides higher reinforcement than CNT. The hybrid nanocomposites obtained by the dispersion of graphene into polymeric matrix show significant improvement in physicochemical and mechanical properties of these materials (Kuila *et al.*, 2012).

The use of graphene and CNT as nanofillers is undoubted a very good option to improve the composite materials properties. However the dispersion process and the cluster formation are problems to be overcome. According to Kuila *et al*. (2012) and Bystrzejewski *et al*. (2010) the noncovalent functionalization is a technique to modify the surface of carbon based nanomaterials, without disturbs their structures, and it could be achieved by polymer wrapping and adsorption of surfactants or small aromatic molecules. Some researchers have suggested the use of surfactants to improve the dispersion process and avoid cluster formation. Wang (2009) and Tang *et al*. (2010) pointed out that the use of surfactants is an approach capable of debundle CNTs and/or graphene and form a stable solution. As discussed by Tkalya *et al*. (2012) and Pu *et al*. (2012), from a variety of surfactants, Sodium dodecyl benzenesulfonate (SDBS) and Polyoxyethylenenonylphenyl ether (IGEPAL® CO-890) can be considered the most promising ones.

The purpose of this research is to investigate the effect of surfactant addition on carbon/epoxy composites nano-modified by carbon nanotubes and graphene. The morphological investigation was performed by SEM, AFM, FTIR and Raman spectroscopy analyses, while the overall macroscopic behavior evaluated tensile and three point bending test.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

The multi-layered graphene (MLG) used in this research was obtained from expandable graphite using the technique developed by Avila *et al*. (2012) and the multiwall carbon nanotubes MWNT was grown by CVD as described by Lacerda *et al*. (2004). Based on Tkalya *et al*. (2012) and Pu *et al*. (2012) results, the surfactants Polyoxyethylene (40) nonylphenyl ether - IGEPAL® CO-890 and Sodium dodecyl benzenesulfonate – SDBS were selected. The fibers used to produce the laminates are plain weave carbon woven fabric with 200 g/m^2 areal density supplied by Texiglass Inc. and the resin is a DGBA epoxy system AR300/AH30-150 provided by Barracuda Inc., with a get time of 30 minutes and average viscosity (resin+hardner) of 1000 cps.

2.2 Non-covalent funcionalization of MLG and MWNT

Aqueous solutions of 200 ppm and 300 ppm for SDBS and CO-890, respectively, were prepared and a concentration of 0.01% of MLG or MWNT was added. These are the optimum concentrations according to Tkalya *et al*. (2012). A bath sonication system at 42 KHz was employed for 30 minutes and after the completely dispersion of MLG/MWNT, the aqueous solution was dried in an oven at 100ºC for 30 hours.

2.3 Carbon/epoxy laminates production

It was reported by previous studies (Silva Neto *et al*., 2013; Carley *et al*., 2013) that the optimum concentration for MWNT dispersion into epoxy systems seems to be around 0.30% wt. and for MLG, there is a saturation limit close to 2% wt. Therefore, the amount of MLG and MWNT analyzed in this research were 0.15% wt. and 0.30% wt.

The functionalized MLG/MWNTs were dispersed into the epoxy system by sonication at 42 KHz for 30 minutes. The laminate was prepared by hand lay-up and it is a four layer symmetric and balanced composite. The laminate was cure on air at room temperature, for 24 hours followed by a post-cure with a uniform pressure of 1.0 ton, at 80ºC, for 6 hours. The thirty three plates prepared, with fiber/resin weight fraction of 50/50, are listed on Tab. 1.

2.4 Carbon/epoxy composite characterization

The morphological investigation was performed using a FEG Quanta 200 FEI scanning electron microscopy (SEM), a Nicolet 380 FT-IR from Thermo Electron Corporation and the Raman Spectra were obtained on a Horiba Jobin Yvon LABRAM-HR 800 spectrograph, while the overall macroscopic behavior evaluated was tensile and three point bending tests. The tensile test follows the ASTM D3039 standard, while the three point bending test followed the ASTM D790 standard, which was performed using an aspect ratio L/d (support spam/specimen depth) of 16:1, close to the ASTM recommendation for high performance composites. Finally, an atomic force microscopy (Asylum MFP-3A-SA) was employed to observe the carbon based nanostructures dispersion inside the polymeric system.

3. EXPERIMENTAL DATA AND ANALYSIS

In order to investigate the influence of the addition of carbon based nanostructures on the mechanical properties of carbon/epoxy laminates the macroscopic analysis were made based on bending and tensile tests. Stiffness and strength were the two key parameters evaluated.

Table 1. Testing Group Characteristics

Group ID	MLG + SDBS (%)	MLG + CO890 (%)	CNT + SDBS (%)	CNT + CO890 (%)	MLG (%)	CNT (%)
1	-	-	-	-	-	-
2	-	-	-	-	-	0,15
3	-	-	-	-	-	0,30
4	-	-	-	-	0,15	-
5	-	-	-	-	0,30	-
6	-	-	-	-	0,15	0,15
7	-	-	-	-	0,15	0,30
8	-	-	-	-	0,30	0,15
9	-	-	-	-	0,30	0,30
10	-	-	0,15	-	-	-
11	-	-	0,30	-	-	-
12	0,15	-	-	-	-	-
13	0,30	-	-	-	-	-
14	0,15	-	-	-	-	0,15
15	0,30	-	-	-	-	0,15
16	0,15	-	-	-	-	0,30
17	0,30	-	-	-	-	0,30
18	-	0,15	-	-	-	-
19	-	0,30	-	-	-	-
20	-	-	-	0,15	-	-
21	-	-	-	0,30	-	-
22	-	0,15	-	-	-	0,15
23	-	0,30	-	-	-	0,15
24	-	0,15	-	-	-	0,30
25	-	0,30	-	-	-	0,30
26	-	0,15	0,15	-	-	-
27	-	0,15	0,30	-	-	-
28	-	0,30	0,15	-	-	-
29	-	0,30	0,30	-	-	-
30	0,15	-	-	0,15	-	-
31	0,15	-	-	0,30	-	-
32	0,30	-	-	0,15	-	-
33	0,30	-	-	0,30	-	-

The results obtained in these tests and a statistical analysis served as basis for analyzing the influence of carbon based nanostructures influence into overall macroscopic behavior. Based on ANOVA analysis of tensile stiffness, the only statistically different groups, with a level of significance of 0.05, were the samples 11, 16, 25 and 27. As can be noticed in Fig 1A, the tensile stiffness is practically insensible to the carbon nanostructure addition. However, in terms of strength (Fig. 1B) an increase of 23.49% was achieved in group 25, which contain 0.30% wt. of MLG functionalized by CO890 and 0.30% wt. of non-functionalized MWNT. The second best result in terms of strength was achieved in sample 24, that differ from group 25 only by the amount of MLG which was 0.15% wt.

The stress-strain curve for groups 1 (blank), 11, 16, 19, 24, 25 and 27 are shown in Fig. 2. As it can be seen in Fig. 2, the initial stiffness seems to be no affected but after a deformation around 1.025 mm/mm changes are observed. It seems that due to internal damage, the stress-strain slope is decreasing. The group 25 was the only sample where the stiffness increases. It seems that graphene and CO890 nanostructures associated to pristine carbon nanotubes are effective into energy release. Notice that for the group 27, an observation on failure region (see Fig. 3A and 3B) shows the failure mode as fiber failure. It means that somehow the hybrid nanostructure MLG+CO890+MWNT was able to change the matrix behavior and effective transfer the load to the fibers.

After the 3 point bending tests, again all data based on flexural stiffness and strength were analyzed based on ANOVA. Figures 4A-B describes the bending stiffness and strength. Moreover, only the ones with statistically significant differences are plotted. The bending stiffness seems not be significantly affected by the usage or not of surfactants. Notice that ionic (SDBS) or non-ionic (CO890) surfactants do not influenced the bending stiffness. This phenomenon may be due to a different mechanism, i.e. the load transfer through the thickness between layers. Avila *et al*. (2012), however, reported different load transfer due to the presence of un-functionalized graphene into the epoxy

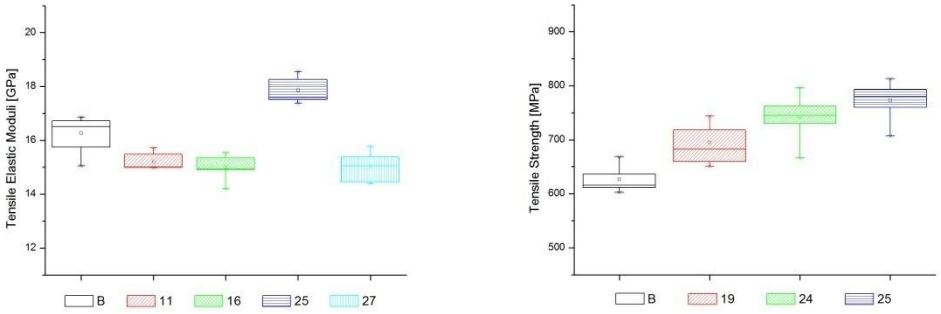


Figure 1. Tensile test summary after ANOVA. (a) Stiffness; (b) Strength.

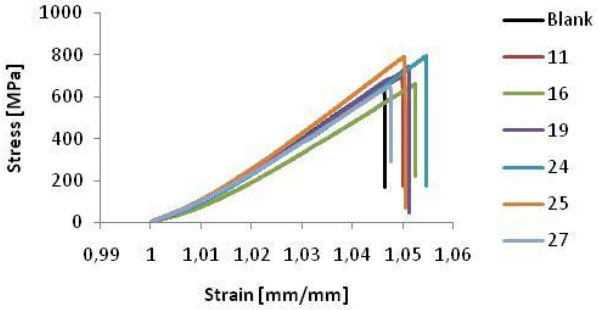
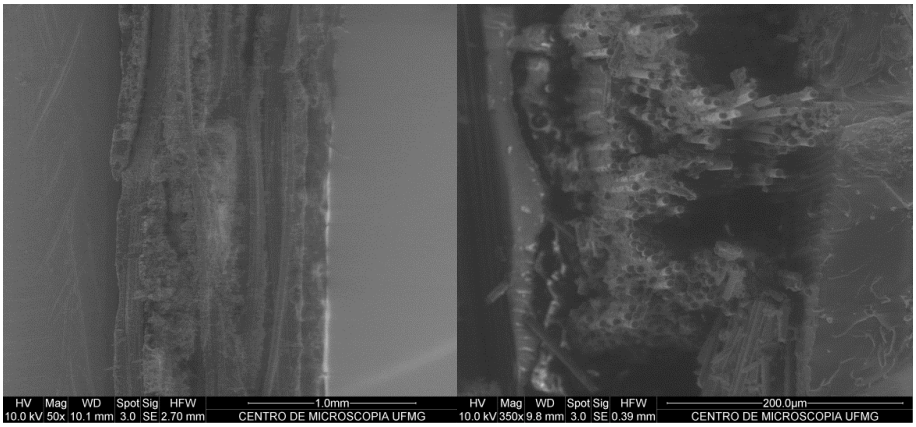


Figure 2. Tensile stress-strain curves



(a) (b)

Figure 3. Tensile test failure region for the group 27. (a) Overall view; (b) failure zoom

system. A different mechanism can be described in the present case, as the samples thickness is lower (the present work deals with 4 layers), the stress gradient is larger and the fracture is fiber dominated. The flexural strength mechanism, however, can be affected by the non-covalent linkage between surfactant and graphene (groups 7 and 19).

Figure 5 describes the bending stress-strain curve for groups 1 (blank), 7, 9, 11, 16, 19, 22 and 27. When the carbon/epoxy nano-modified composite macro mechanical behavior is analyzed some comments can be drawn. First, when considering bending stiffness (see Fig. 5), the usage of ionic surfactants (SDBS), which is commonly used to disperse carbon nanotubes, has no significant effect into the CNT-epoxy system interaction. On the other hand, the non-ionic surfactant (CO890) seems to be effective to the graphene-epoxy and/or the graphene-CNT-epoxy systems. Based on tensile tests an increase on stiffness around 9.45% was observed due to the usage of CO890 and MLG in addition to the pristine MWNT. A much higher increase was detected on ultimate strength, i.e. 23.49%. For the bending analysis, no significant change on flexural stiffness was observed; in fact for some groups (27 and 33) a decrease was detected. An average increase on bending ultimate strength of approximately 11.44% was notice for the specimens with MLG+CO890 and pristine MWNT (group 19). One hypothesis is that CO890 tail preferably “attached” to graphene leaving the head to link to the polymer chain. As Smith *et al*. (2010) pointed out; the CO890 tail is the part where the interactions with non-polar objects, e.g. graphene layers, occur by forming van der Waals bonds.

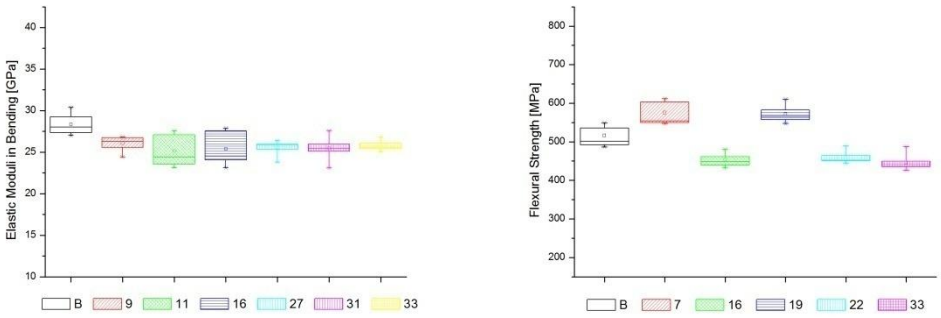


Figure 4. Three point bending test summary after ANOVA. (a) Stiffness; (b) Strength.

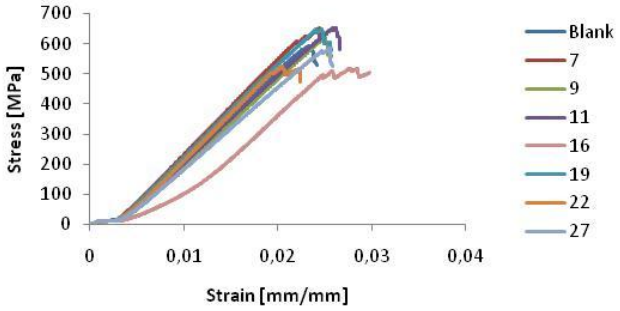


Figure 5. Bending stress-strain curves

The next step is the nanoscale morphological analysis based on AFM observations. To be able to illustrate the concept of "extra grip" provided by the non-covalent functionalized nanostructures an AFM analysis was performed. Figures 6A and 6B describe two different conditions, i.e. groups 24 and 16. As it can noticed for group 24 (CO890) the nanostructure density is much larger than for group 16 (SDBS). This can be explained by the surfactant effectiveness to successfully link to MLG and/or MWNT.

(a) (b)

Figure 6.AFM observations. (a) sample with CO890; (b) sample with SDBS.

Analyzing the FTIR results (Fig.7) it is possible to observe the characteristic bands (2922 cm^{-1} and 2853 cm^{-1}) for the SDBS in both carbon structures functionalized by this surfactant, indicating the existence of an interaction between MLG and MWNT with SDBS. On the other hand, for CO890 it is possible to observe its characteristic bands (2883 cm^{-1}, 947 cm^{-1} and 841 cm^{-1}) in functionalized MLG, but there is none of these bands in CNT functionalized with this surfactant. This fact indicates that there is an interaction between CO890 with MLG and that MWNT did not interact with CO890.

The Raman spectroscopy signature can suggest which surfactant is more reactive with specific carbon based nanostructures, either MWNT or MLG. Observing the Raman spectra (Fig. 8) it is possible to see that for CNT, the intensity of both G and G' bands increase with the addition of SDBS and decrease with the addition of CO890. In the case of MLG, the intensity of G and G' bands increase when it is functionalized by CO890 and decrease with the functionalization with SDBS. It seems that CNT have more affinity with SDBS and MLG is more reactive with CO890.

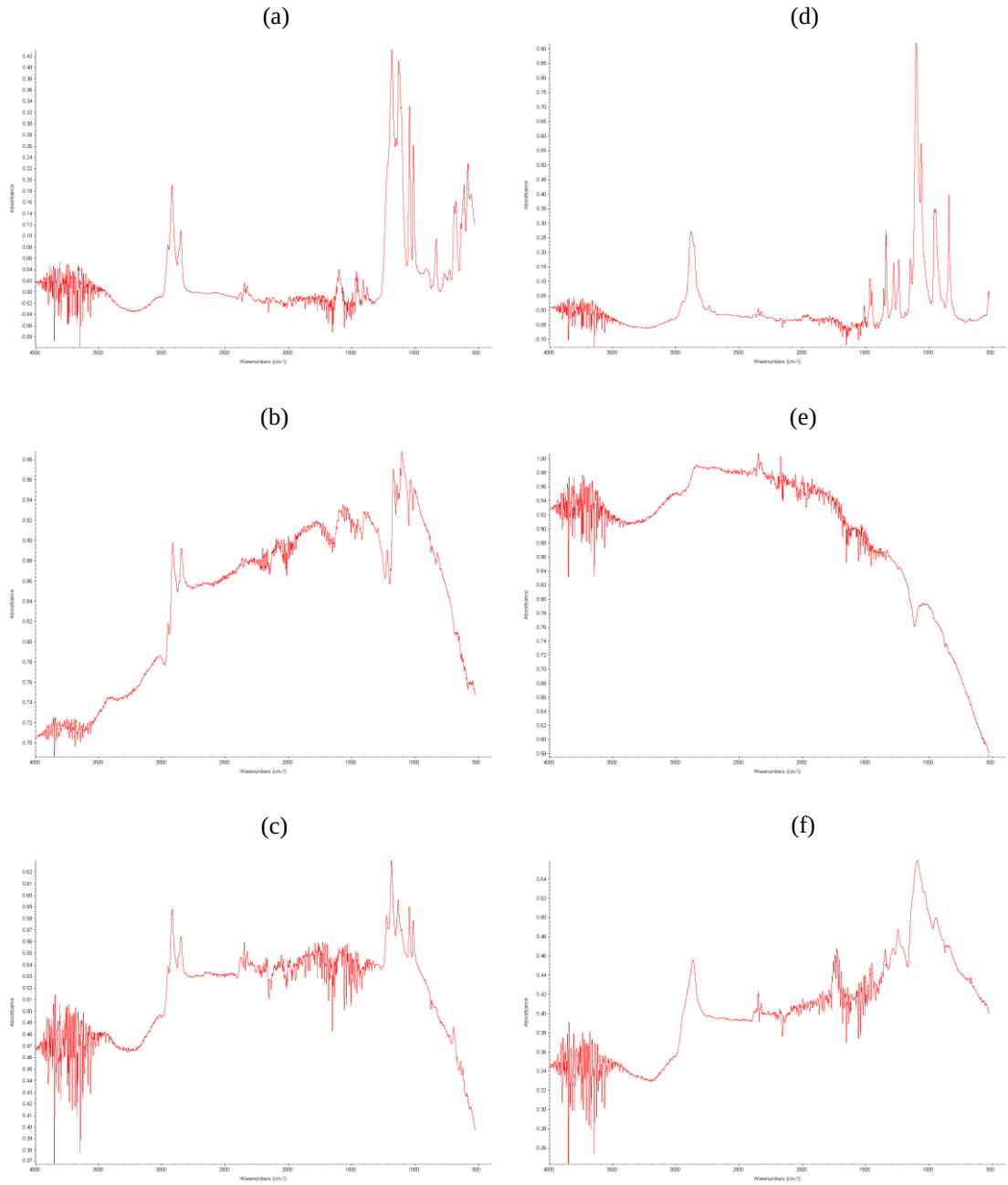


Figure 7. FTIR spectra (a) SDBS; (b) CNT+SDBS; (c) MLG+SDBS; (d) CO890; (e) CNT+CO890; (f) MLG+CO890

4. CONCLUSION

The non-functionalization of MLG and MWNT seems to be a viable option to improve the bonds between these carbon nanostructures and polymeric chains. Although the stiffness seems to be insensible to non-functionalization, in both tensile and bending tests, the ultimate strength was affected by the usage of surfactants. When the non-ionic CO890 was used with MLG and pristine MWNT, an increase close to 23.5% for tensile tests and an improvement of 11.4% for bending tests was observed. The non-ionic CO890 surfactant seems to be more effective with MLG and pristine MWNT. The morphological analysis suggests that MLG is more reactive with CO890 and, in the case of MWNT it has more affinity with SDBS and did not interact with CO890.

5. ACKNOWLEDGEMENTS

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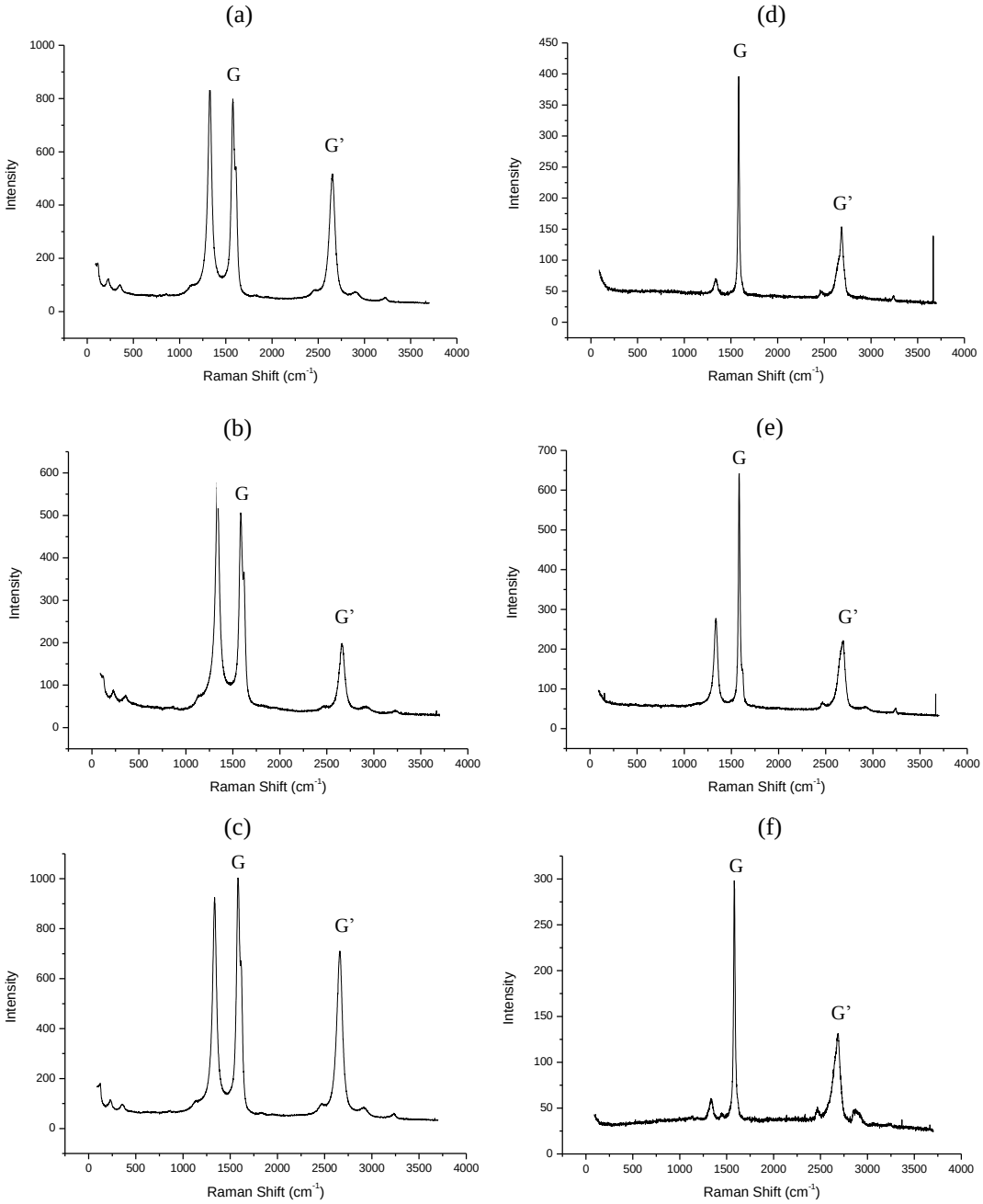

Figure 8. Raman spectra (a) CNT; (b) CNT+CO890; (c) CNT+SDBS; (d) MLG; (e) MLG+CO890; (f) MLG+SDBS.

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