

DEVELOPMENT OF RADIATION PROCESSING TO FUNCTIONALIZE CARBON NANOFIBER TO USE IN NANOCOMPOSITE FOR INDUSTRIAL APPLICATION

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ABSTRACT

Radiation can be used to modify and improve the properties of materials. Electron beam and gamma ray irradiation has potential application in modifying the structure of carbon fibers in order to produce useful defects in the graphite structure and create reactive sites. In this study was investigated a methodology for radiation grafting processing to modify carbon nanofiber surfaces by grafting acrylic acid. The samples were submitted to direct radiation process. Several parameters were changed such as acrylic acid concentration, radiation dose and percentage of inhibitor to achieve functionalization with higher percentage of oxygen functional groups on carbon nanofiber surface and better dispersion. The samples were characterized by X-ray Photoelectron Spectroscopy and the dispersion stability upon storage was visually investigated. Carbon nanofiber directed irradiated with electron beam and gamma ray in a solution of acrylic acid with 6% of inhibitor ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and irradiated at 100 kGy had an increase of 20% of oxygen content onto carbon nanofiber surface. The Auger D-parameter for the samples direct irradiated grafted ranged between 17.0-17.7 compared to 21.1-18.9 of the unirradiated ones. This indicated that these samples had less sp^2 and more sp^3 bonding characteristics than unirradiated samples. This can be an indication of C=C bond breaking leading to the formation of new sp^3 carbon atoms on carbon nanofiber surface with oxygen functional groups grafted. The samples grafted presented a good and stable dispersion.

1. INTRODUCTION

The complex morphology of carbon nanofibers (CNFs) requires careful control of the surface to promote properties required for end use because CNFs are not highly compatible with most polymers. Therefore, it is necessary to modify, or “functionalize”, the surfaces through chemical or physical techniques to produce optimized polymer composites. The most commonly used approach is oxidation. Oxidizing the nanocarbon surface creates active sites (polar sites) which may prepare the nanocarbon surface for further chemical reaction or “grafting” with additional organic groups. Carboxylic acid groups are often considered the most desirable oxygen functional groups because of the variety of chemical reactions that can

be conducted with these groups. For example, carboxylic acid groups have the ability to initiate cationic polymerization of vinyl monomers, and they can facilitate the chemical grafting of amine or epoxy groups to carbon nanotube surfaces [1]. Polymers with amino side groups can be grafted onto the oxidized nanotubes through amide formation, leading to high solubility in most organic solvents and water. Alkyl chains with amine groups can be covalently attached onto the oxidized nanotubes using a carboxylate-ammonium salt that also improves the solubility of the nanotubes. For application of carbon nanofiber as a catalyst support, carboxylic acid plays an important role because it confers an acidic character to the carbon surface and they can be used as catalyst anchoring sites during ion exchange preparation [2].

In polymer composites reinforced with carbon nanofillers, interface plays a major role in materials in general because it will determine the mechanical and physical properties of the resulting composite materials. The large differences between the elastic properties of the matrix and the fiber are transmitted to the fiber through the interface. Functionalization process of covalent functional groups bonding on carbon nanofillers surface are intended to improve the efficiency of load transfer from the nanocarbon particle to the polymer matrix. However, the presence of these bonding alters the otherwise perfect structure of the basal plane and therefore lowers the strength of the nanoparticle [3].

There are several methods to functionalize carbon fiber and these modifications promote changes in composite properties [4-19]. It is believed that functionalization increases reactivity on the fiber surface allowing them to better disperse into the matrix resulting in more uniform properties [20]. Existing surface treatment methods include wet chemical, electrochemical, gas or plasma phase and polymer coating processes [21]. Many of these functionalization processes depend on having an oxidized nanocarbon surface as a starting point because oxidation is used as purification method as well as to create polar sites to allow a specific functional group to graft to the carbon nanofiber surface. Hydroxyl, carbonyl, ester, quinone, and carboxyl groups are typically found on a CNF surface after an oxidizing process. In general, oxidation processes are time consuming, energy inefficient, and may generate toxic residues. Acid oxidation is the most common process used to oxidize CNFs, but delivers a high amount of chemical waste to the environment. For example, to oxidize 4.5 mg carbon nanofiber oxidation with nitric acid (70% v/v) generated around 6 liters of chemical contaminated water used to wash the oxidized nanofiber. Grafting functional groups on CNFs surface by radiation process may be an environment friendly way to functionalize CNFs. Evora et al. explored the use of a high energy electron beam as the only available technique for selective area surface modification of CNFs through controlled parameters such as radiation dose, sample temperature, and environment [22-23].

2. MATERIALS AND METHODS

2.1- Direct radiation grafting process

The samples that were submitted to direct radiation grafting process are shown in Table 1.

Table 1: Samples prepared with acrylic acid submitted to direct radiation grafting process

Samples Name	Samples PR-25-PS-XT	Dose (kGy)		AA (%)	FeSO ₄ 7H ₂ O (%)	Condition of grafting solution after grafting reaction
GA1	prestine as received	0		None	None	Bad dispersion
GA2	prestine/acetona	0		20%	1 %	Bad dispersion
GA3	1000 kGy	0			0	Not performed
GA4	1000 kGy	175 kGy	gamma		0	Not performed
GA5	prestine/acetona	100 kGy	gamma	20%	3%	Gel
GA6	prestine/acetona	100 kGy	gamma	20%	1%	Gel
GA7	prestine/acetona	150 kGy	gamma	20%	1%	Gel
GA8	prestine/acetona	175 kGy	gamma	20%	1%	Gel
GA 8.1	prestine/acetona	175 kGy	gamma	8%	1%	Gel
GA 8.2	prestine/acetona	175 kGy	gamma	15%	1%	Gel
GA 8.3	prestine/acetona	175 kGy	gamma	30%	1%	Gel
GA9	prestine	10 kGy	gamma*	33%	1%	Gel
GA10	prestine	0	gamma	33%		Blank
GA11	prestine/acetona	50 kGy	ebeam			Good dispersion and no issue to filter
GA 11.1	prestine/acetona	100 kGy	ebeam	8%	6%	Very good dispersion and hard to filter (more than 12 hours filter process).
GA 11.2	prestine/acetona	150 kGy	ebeam			Gel
GA 11.3	prestine/acetona	0	ebeam			
GA 12	prestine	175 kGy	gamma	30%	1%	Gel
GA 13	prestine/acetona	100 kGy	gamma	10%	6%	Excelent dispersion
GA 14	prestine/acetona	100 kGy	gamma	10%	10%	Good dispersion but not stable

* Source of Institute of Advanced Studies.

Figure 1 shows the sample is GA5, GA 13 and GA14. All samples were irradiated at 100 kGy with different percentage of inhibitor (FeSO₄7H₂O). The GA5 sample has lower addition of FeSO₄7H₂O than in GA 13 and GA 14 samples allowing the homopolymerization to occur. GA 13 presented an excellent dispersion after radiation grafting process. GA 14 had a good dispersion however not very stable. Addition of inhibitor to the acrylic acid solution is needed to minimize homopolymerization. At the same time, hindering of the grafting reaction

cannot be excluded, the minor consequence being lowering of grafting yield. Clochard et al. used Mohr's salt as an inhibitor and concluded that with increasing inhibitor concentration, the grafting yield of PVDF films falls from 130% to 70 %. As the inhibitor is able to diffuse in the film, it speeds up the termination reaction of the grafting polymerization thus leading to lower grafting yields [12].

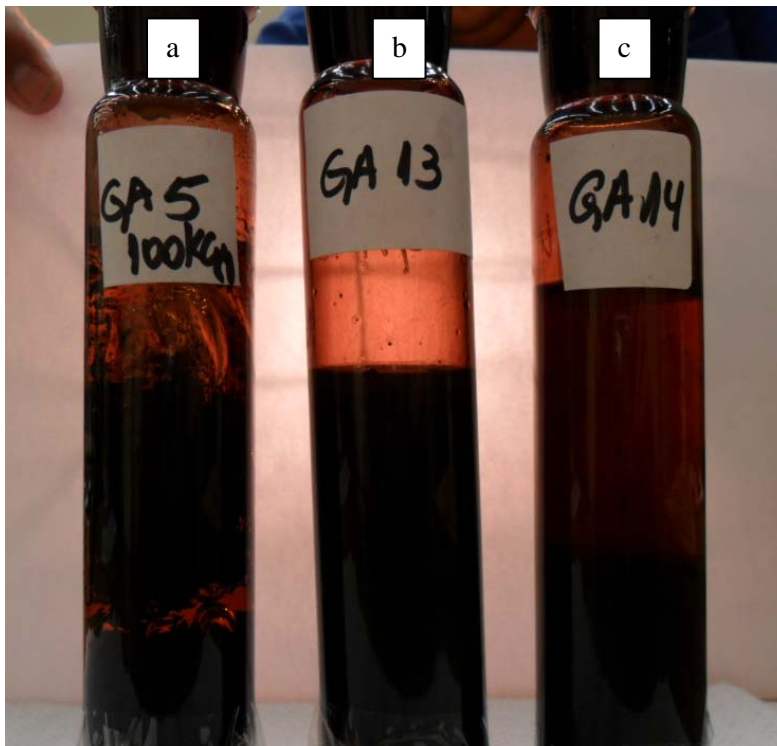


Figure1: Illustration of some samples presented in Table 2. a) PR-25-PS-XT cleaned with acetone mixed with acrylic acid + 3% $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and irradiated at 100 kGy dose, b) PR-25-PS-XT cleaned with acetone mixed with acrylic acid + 6% $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and irradiated at 100 kGy dose (estable and excelente dispersion) PR-25-PS-XT cleaned with acetone mixed with acrylic acid + 10% $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and irradiated at 100 kGy dose.

2.1.1 -Samples description summary for direct radiation grafting process :

Gamma radiation

1. In GA2 (Blank), GA6, GA7 and GA8- CNFs were add to same percentage of acrylic acid and percentage of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$.
2. GA5 and GA6- CNFs were add to same percentage of acrylic acid but different percentage of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and irradiated at same dose (100 kGy).
3. GA 3 and GA 4- This experiment was not performed. The objective of this experiment is to take advantage of polar sites available on the CNFs that was irradiated in previous experiments whose results have already been presented when the project was proposed.

4. GA 8, GA 8.1, GA 8.2 and GA 8.3- CNFs were added to different percentage of acrylic acid, same percentage of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ and irradiated at same dose (175 kGy).
5. GA 9 and GA 10- Sample irradiated at Institute of Advanced Studies.
6. GA13 and GA14- CNFs were add to same percentage of acrylic acid, irradiated at same dose (100 kGy), but different percentage of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$.

Electron Beam radiation

1. GA11, GA11.1 and GA11.2- CNFs were add to same percentage of acrylic acid and percentage of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, but irradiated at different doses.
2. GA11.3 (Blank) - CNFs were add to same percentage of acrylic acid and percentage of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, but irradiated at different doses.

2.2. Development of grafting process using electron beam

As-received PR-25-PS-XT samples were washed with acetone, dried in a vacuum oven at 60°C for 24 hour. Carbon nanofibers were weighed, and then immersed in solutions of acrylic acid with 6% of inhibitor metal salt ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$). The acrylic acid was purchased from MERK and it is stabilized with 200 ppm of hydroquinone. The samples were poured into petri dish and irradiated with a direct accelerator operated by the Instituto de Pesquisas Energéticas e Nucleares (IPEN- São Paulo/Brazil). The samples were irradiated with an industrial electron accelerator Dynamitron, from Radiation Dynamics Inc., model DC 1500/25-JOB 188 that was operated with the following parameters: beam energy 1.5 MeV, pulse current 5.62 mA, 5 kGy/pass with dose rate of 22.42 kGy/sec. The samples were irradiated with 50, 100 and 150 kGy (see Figure 2).



Figure 2: Samples GA11, GA11.1 and GA11.2 poured into the petri dishes to start the electron beam radiation process in a industrial electron accelerator Dynamitron model DC 1500/25-JOB 188.

2.3. Development of grafting process using Gamma rays

The graft copolymerization was carried out using the direct radiation technique. The reaction was conducted in an inert atmosphere in the presence of N_2 gas. Dried pristine PR-25-PS samples were dispersed in solution of acrylic acid in presence of inhibitor metal salt ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) in glass ampoule. The mixtures were purged with dry nitrogen for 7 min to

Therefore, seven not gelled samples were investigated by X-ray Photoelectron Spectroscopy (XPS). All analysis were conducted in a K- Alpha XPS equipment from ThermoFisher Scientific with a 400 μm X-ray spot size and with the low energy electron/argon ion charge neutralization system turned on. XPS survey spectra (0-1350 eV) were collected for all samples to provide qualitative and quantitative surface analysis information. The technique is sensitive only to surface atoms and the results are reported in terms of atom % oxygen (O), % nitrogen (N) and % Ferro (Fe).

The C1s spectra obtained for the seven samples (see Figure 5 and 6) indicated the presence of various amount of C-O, C=O and O=C-O surface functional groups on the seven samples however samples GA11, GA 11.1, GA13, GA14 (irradiated) had the highest intensity peaks for O=C-O bonding (~ 289.7 eV).

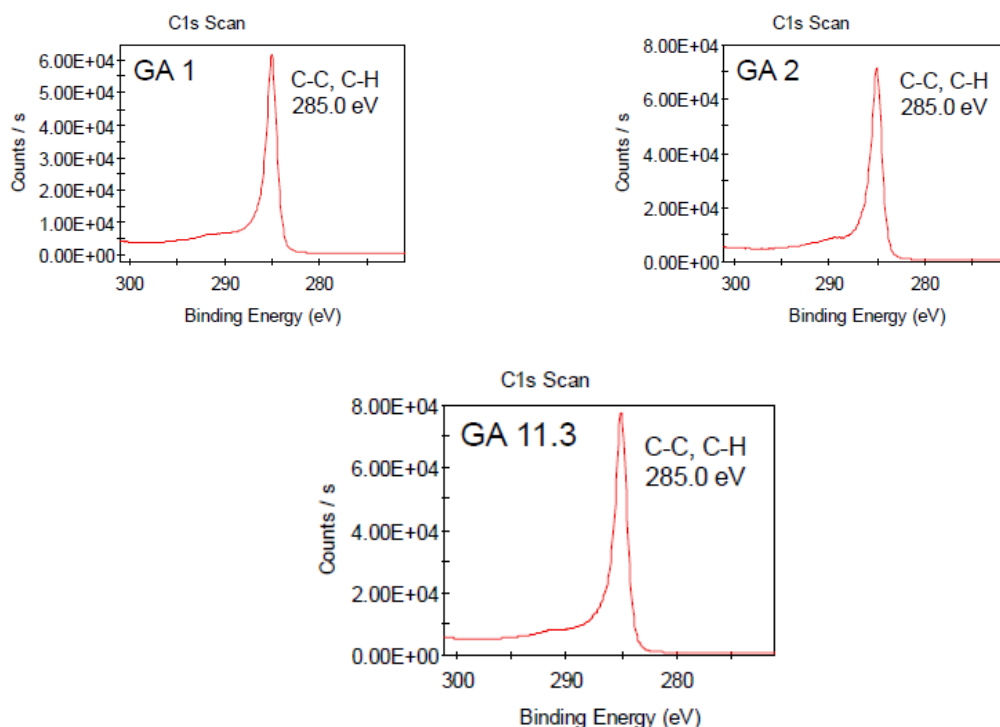
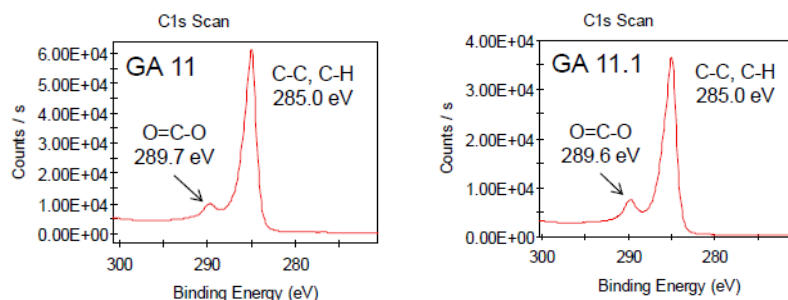


Figure 5: High Resolution C 1s XPS spectra for unirradiated samples.



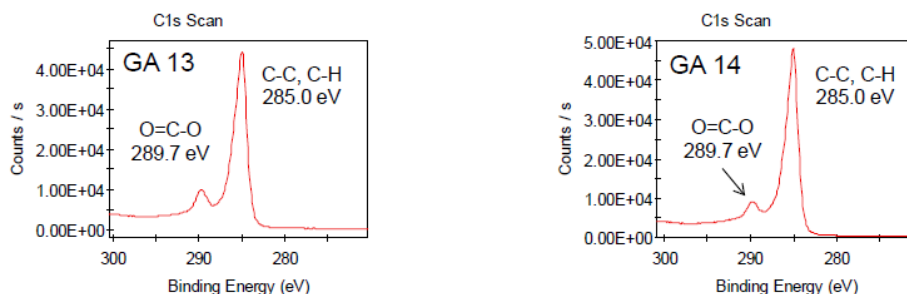


Figure 6: High Resolution C 1s XPS spectra for irradiated samples.

The surface composition (atomic %) is presented in Table 2 and 3. The results given by XPS analysis showed a significant increase of oxygen content for the samples irradiated. The sample with 6% of FeSO₄H₂O and irradiated at dose of 100 kGy had higher percentage oxygen therefore offering excellent and very stable dispersion.

Table 2: XPS results of unirradiated PR-25-PS, a blank and PR-25-PS grafted with acrylic acid using an industrial electron accelerator Dynamitron, from Radiation Dynamics Inc., model DC 1500/25-JOB 188 at doses of 50, 100 and 150 kGy

Carbon nanofiber	Surface oxygen (atom%)		
	O	N	Fe
GA1	2.5	3.6	< 0.1
GA11.3	4.9	1.8	< 0.1
GA 11	14.6	1.4	0.1
GA 11.1	18.4	0.9	0.1

Table 3: XPS results of unirradiated PR-25-PS, a blank and PR-25-PS grafted with acrylic acid using ⁶⁰CO γ - rays at doses of 100 kGy.

Carbon nanofiber	Surface oxygen (atom%)		
	O	N	Fe
GA1	2.5	3.6	< 0.1
GA2	7.0	1.6	0.1
GA 13	20.3	0.9	0.1
GA 14	16.8	0.9	0.2

It has been shown in the published literature that, after differentiation, c KLL Alger spectra can give important information regarding the relative amount of sp^2 and sp^3 bonding in carbon materials by the so called Auger "D-parameter" [24]. The D-parameter value gives an indirect measure of the % sp^2 character of the material (see figure 7).

The measured Auger D-parameter for samples GA1, GA 2 and GA 11.3 (see Figure 8) is higher and similar to the literature reference for graphite and indicates a significant amount of sp^2 bonding on the surface. These three samples also had the lowest oxygen concentrations among the samples.

The Auger D-parameter for the other four samples (see Figure 9) ranged between 17.0-17.7 indicated that these samples had less sp^2 and more sp^3 bonding characteristics compared to samples GA1, GA2 and GA 11.3. This can be an indication of C=C bond breaking leading to the formation of new sp^3 carbon atoms on CNT surface with oxygen functional groups.

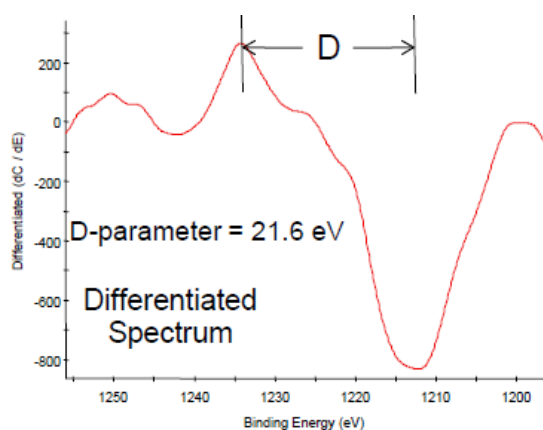
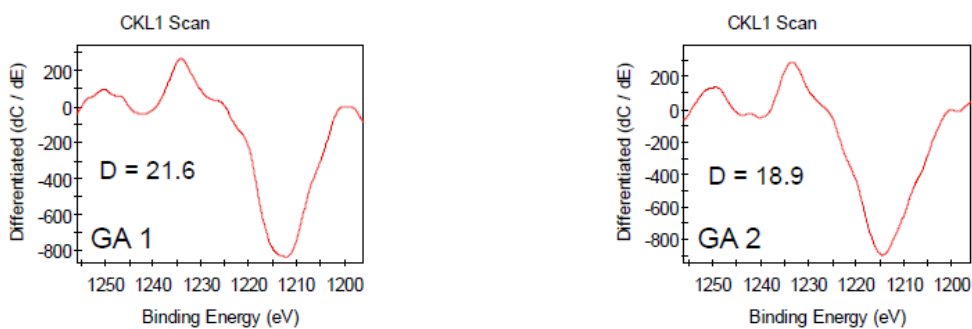


Figure 7: Illustration of Auger D-parameter for sample GA1.



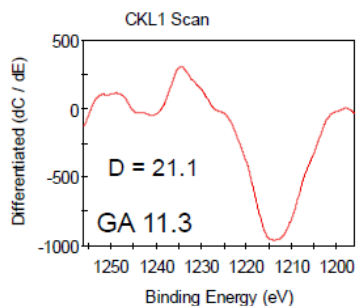


Figure 8: Auger D- parameter for non irradiated PR-25-PS and blank samples.

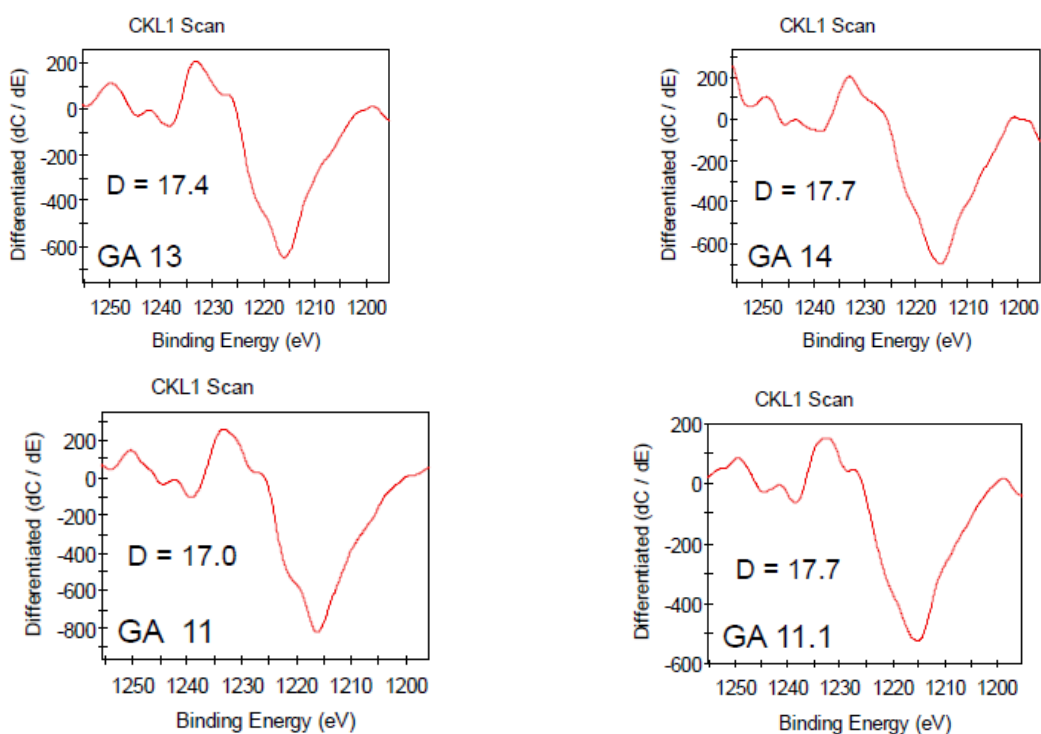


Figure 9: Auger D- parameter for PR-25-PS grafted with acrylic acid ^{60}Co γ -rays and industrial electron accelerator.

3. CONCLUSIONS

Radiation induced graft copolymerization is a method to modify materials with many advantages. The goal of the present study was to establish a methodology for radiation induced grafting via radiation for functionalizing CNFs. The experiments were set up in order to determine the optimum radiation dose and inhibitor content required for this process to take place using the existing irradiators.

Characterization of the physical properties of the nanomaterials is still a challenge. The small size and complexity of nanoscale structure make the use of characterization technique more challenging than ever and require extremely sensitive instrumentation and this has been an issue during the process of this investigation.

In this study, the samples that were added to a solution of acrylic acid with 6% of inhibitor and were direct irradiated with electron beam and gamma source at 100 kGy dose presented higher oxygen content and better dispersion. The Auger D-parameter for these samples ranged between 17.0-17.7 which indicate that these samples had less sp^2 and more sp^3 bonding characteristics compared to unirradiated samples. This can be an indication that grafting process took place and C=C bond breaking leading to the formation of new sp^3 carbon atoms on CNF surface with oxygen functional groups.

As an immediate next step we intend to manufacture nanostructured composites with this modified carbon nanofiber to assess the impact of these modifications on macroscopic properties and evaluate the adhesion between these modified nanofibers and polymeric matrix.

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