Photochemical Thiolation of Carbon Particles with Mercaptoproyltrimethoxysilane

Photochemical Thiolation of Carbon Particles with Mercaptopropyltrimethoxysilane

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ABSTRACT:

Surface modification of carbon black (CB) is an important tool to refashion its properties in view of preparing composites. CB surface modification is usually practiced through thermal procedures. However, environmental concerns have provided the base to rethink for alternate methods, particularly photochemical methods that are considered comparatively eco-friendly due to reduced chemical waste and thermal consumption. Present investigation is based on a photochemical method for CB surface modification decorating the particle surface with alkoxysilane. Effectiveness of the photochemical modification method to alter the surface of CB has been confirmed through different instrumental techniques including XPS, TGA, FTIR, Raman and SEM.

Keywords:
Carbon Black; Surface Modification; Photochemical Reaction; XPS analysis; Dispersability; Mercaptopropyltrimethoxysilane;

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1. INTRODUCTION:

CB particles interact with each other as well as with external media (solvent or polymer) depending on the surface chemistry [1,2].

CB Surface chemistry can be amended through physisorption[3] or chemisorption[4], either thermally or photochemically. Grafting functional molecules on the surface of CB has been explored, introducing interesting functionalities on CB surface [8,9,10]. It is evident that desired properties of material can be obtained by CB surface modification through specific reactions [11].

Plentiful data on thermal modification have grown up in years [5], contrary to photochemical methods for surface modification of filler particles. Whereas the photochemical approach has quite large benefits, including the high rate of the reaction and the low energy consumption. Although photochemical modification of fillers is a documented approach [6], yet has several limitations for colored particles. The foremost one is that colored filler particles, within reaction mixture, compete for incoming photons with reactants, namely a photoinitiator, and reduce the activity.

This research has utilized a photochemical approach to implant alkoxysilane functionality onto CB surface and demonstrates that a better dispersion of the particles and prevention of agglomeration in solvents and epoxy resin can be obtained.

2. EXPERIMENTAL:

2.1. Materials:

Charcoal activated (glassy carbon, spherical powder from Sigma Aldrich) with average particle size 20 µm, relative density 0.25-0.60 g/cm^3, specific surface area (BET) >100 m^2/g, resistivity 1375 µΩ-cm 20°C. Commercial Glassy CB (2-12µ diameter) has been used for surface modification.

Mercaptopropyltrimethoxysilane (MPTS) has been used as CB surface modifier (Figure 1 top), Benzophenone has been used as photoinitiator (Figure 1 bottom). Tetrahydrofuran (THF) analytical grade has been used as solvent. All chemicals were purchased from Sigma Aldrich and were used as received.

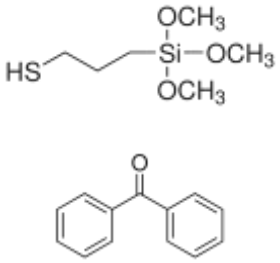


Figure 1: Alkoxysilane and Photo-initiator

2.2. Sample Preparation

Pristine-Glassy CB, MPTS (1:2 molar ratios) and PI (1:150 molar ratios with MPTS) were taken in glass flask. The contents of flask were mixed for 30 minutes, by using mechanical stirrer, and irradiated for 60 seconds, with UV radiation of intensity 33 mW/cm^2. The temperature of the mixture was controlled at 20^0C. Final product (MPTS-Glassy CB) after filtration was washed with Tetrahydrofuran (THF) and dried at 60^oC for 30 minutes.

In an alternative procedure, the reaction mixture while irradiation was heated at 50^0C.

2.3. Samples Analysis:

Modified CB particles along with unmodified ones have been characterized by using below mentioned techniques.

X-ray Photoelectron Spectroscopy (XPS) analysis was done in ultra high vacuum (10-8 Pascal) with Versa Probe PHI 5000 instrument. CB samples were outgassed for 12 hours in pre-chamber of XPS. 100µm diameter monochromatic X-ray beam source with Al (1486.6 eV) at 25.6W were used to analyze 500µm x 500µm sample area. Electron and Argon ion guns have been used to neutralize the sample charge.

For functional group analysis through IR, pellets made of CB in KBr (1 wt.%) were prepared, after grinding and drying the powders at 120^{o}C for 2 hours. IR Spectral data (4000-500 cm^{-1}) was gathered with Nicolet 5700 apparatus.

Thermal gravimetric analysis (TGA) was done by TGA/SDTA851^{e} METTLER TOLEDO apparatus. 15-20 mg CB sample in 70 µL Alumina crucible was analyzed at temperature ramp rate of 10^{o}C/min from ambient to 800^{o}C, keeping gas deliverance of 60 ml/min;

Raman analysis of pristine and modified CBs was carried out with Renishaw Ramascope, Ar+ laser 514.5 nm excitation, to determine average size of CB Particles through comparison of position, width and intensity between D (1345 cm^{-1} **)** and G peaks(1575 cm^{-1}**)**. With an increase in particle size, peak width decreases with maxima elevation.

For pictorial evidences of surface modification Field Emission Scanning Electron Microscopy (FE-SEM) analysis was carried out through Model Zeiss Supra 40.

Dynamic Light Scattering (DLS, Nanosizer ZS90, Malvern) quantified Zeta potential values of 1 w/v % suspensions of Pristine and modified samples.

3. RESULT & DISCUSSION:

Figure 2 represents the FTIR spectra of unmodified carbon black (Pristine-Glassy CB), the carbon black subjected to irradiation in the presence od mercaptoalkoxysilane MPTS (MPTS-Glassy CB) and MPTS as a reference.

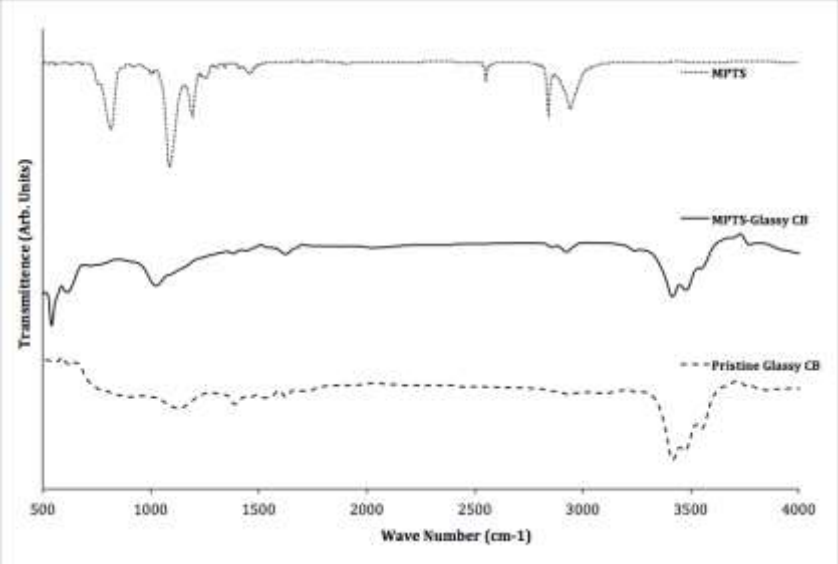


Figure 2: IR of Pristine-Glassy CB, MPTS and MPTS-Glassy CB

The spectrum of MPTS displays main peaks at 2920 cm^{-1} (anti-symmetric stretching of methylene), 2850 cm^{-1} (symmetric stretching of the methylene), 2550 cm^{-1} (Thiol), 1191 cm^{-1} (Si-OCH_3 bending), 1089 cm^{-1} (Si-O stretching), 820 cm^{-1} (rocking of methyl in Si-OCH_3). While the spectrum of pristine carbon particles, before modification, displays peaks at about 1400-1700 cm^{-1} and 3400-3600 cm^{-1} for oxygen functionalities (carbonyl and hydroxyl) [12].

In the FTIR spectrum of the modified CB, depletion of thiol peak at 2550 cm^{-1} and formation of thio-ether peak at 550 cm^{-1}, proves the CB thiolation with MPTS. On the other side, modified CB showed peak reduction near 3400 cm^{-1} (hydroxyl groups) indicating consumption of hydroxyl functionalities on the surface of CB, which advocates hydroxyl groups as reaction sites on the surface of CB for MPTS. Moreover a shift of FTIR peaks in modified CB, towards 3700 cm^{-1} (for Si-OH) [13] indicates conversion of MPTS methoxy into hydroxyl. Raman spectra of modified sample (Figure 7) supports the finding by presenting a peak at 3475 cm^{-1}(hydroxyl groups). On comparison of FTIR spectra, no appreciable change has been observed in carbonyl functionalities of unmodified and modified CBs. However, in modified CB broad peaks at around 1000 cm^{-1} hints for Si–O–Si and Si–O–C bond formation.

FTIR analyses suggests that CB particles react with MPTS. The reaction one can propose is the formation of radicals from benzophenone and the subsequent formation of thioradicals from MPTS, then the reaction with CB and the formation of thioether bonds.

XPS analysis confirms the findings. In Figure 3 the wide scan spectra of CB prior to and after functionalization, named respectively as Pristine-Glassy CB and MPTS-Glassy CB are reported. All the peaks are assigned positions with reference to peak at 978 eV. XPS spectrum of Pristine CB contains common peaks at 284.8 eV for C1s and at 532 eV for O1s; whereas in modified CB along with common peaks, some extra peaks are present at 100 eV and 150 eV respectively for Si2p and Si2s, and at 164 eV and 229 eV respectively for S2p and S2s. These peaks demonstrate clearly the efficiency of photochemical surface modification of CB.

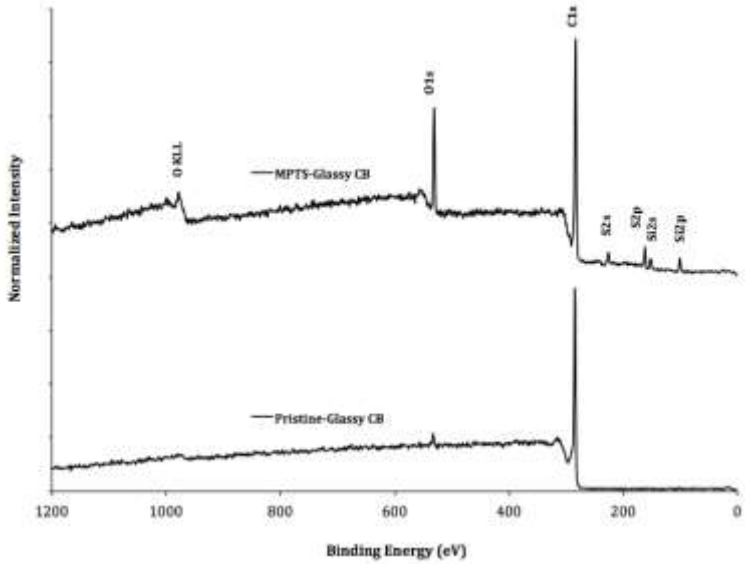


Figure 3: XPS spectra of Pristine-Glassy CB and MPTS-Glassy CB

To have a thorough analysis of atomic linkages in modified CB, deconvolution study of XPS peaks has been made.

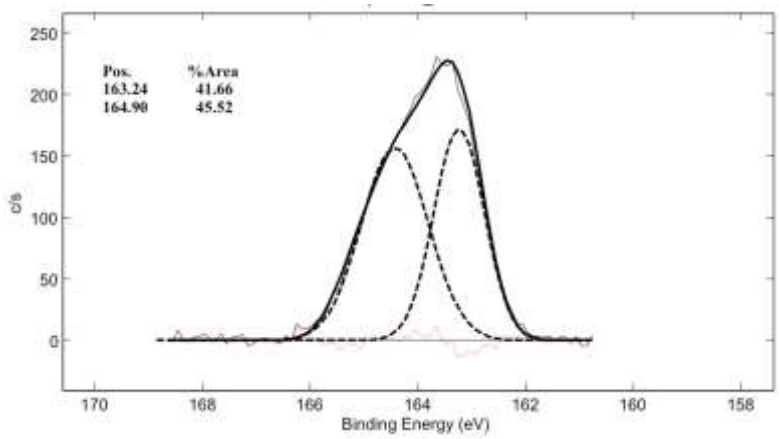


Figure 4: XPS spectra of MPTS-Glassy CB

Fig. 4 represents deconvoluted spectrum of S2p peak on modified CB, with two major peaks located. The peak at 163.2 ± 0.1 eV refers to covalent bond between sulfur and sp_3 hybridized C atom [14]. The peak at 164.9 ± 0.2 eV denotes thio-ethers [15]. Almost equal intensity of both segments in the XPS data suggests that quantity of sulfur attached to methylene group is almost same to that in the form of thioether. Hence it can be concluded that almost all thiol functionalities in MPTS converted into thioether. This is in conformity with FTIR data.

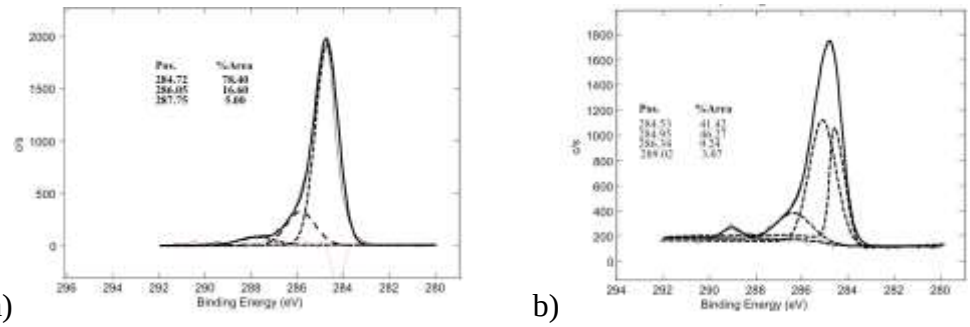
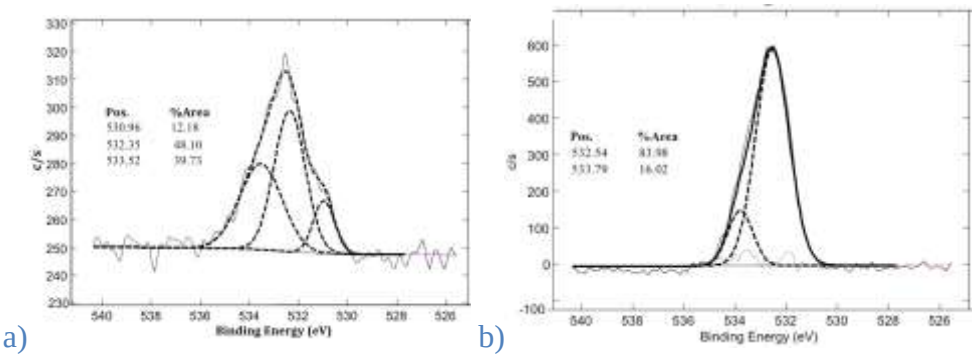


Figure 5: XPS spectra of Carbon a) Pristine-Glassy CB and b) MPTS-Glassy CB

Comparison of the C1s deconvoluted peaks (Fig. 5) of pristine and modified CBs has been made to expound the results of photochemical modification procedure. In pristine CB a segment at 284.81 ± 0.1 eV relates to sp2/sp3 non-functionalized carbon, which after modification (284.95 eV) has reduced to half, and besides that modified CB has shown a segment at 284.52 eV, which denotes to C-S linkage; this segment was absent in Pristine CB.

In pristine-CB the segment at 286.16 eV represents C–O–C, which after modification (286.34 eV) has reduced. The last segment of pristine CB at 287.71 eV denotes carboxylic group [16]. This segment is the least and almost same in pristine and modified CB, which confirms FTIR results.



a) b)

Figure 6: XPS spectra of Oxygen a) Pristine-Glassy CB and b) MPTS-Glassy CB

Upon comparison of the O1s deconvoluted peaks of pristine and modified CBs (Figure 6), stronger signal of modified CB has been observed than the pristine one. In pristine CB three major segments have been found:

(i) 530.96 eV for carbonyl oxygen [14],

(ii) 532.35 eV for hydroxy / methoxy (sigma bonded oxygen and sp3 carbon) [14]

(iii)533.32 eV for sigma bonded oxygen with sp2 carbon [15].

XPS spectra of modified CB showed only two segments: (i) 532.54 eV for sigma bonded oxygen and sp3 carbon [14] (ii) 533.79 eV for sigma bonded oxygen with sp2 carbon [15]. In modified CB, carboxyl group segment disappeared; oxygen linked to sp2 carbon decreased; however component of sigma bonded oxygen and sp3 carbon has increased, because of methylene and methoxyl in MPTS. Outcomes comply with the C1s analysis. With XPS analyses % atomic ratio of available elements have been made (Table 1).

Unmodified and modified CBs were also examined through Raman spectroscopy. Raman spectrum of modified sample “MPTS-Glassy CB” (Figure 7) displays a slight increase in G and G’ peaks with reference to D peak; indicating a disorder decrease

after functionalization. A new peak, at 3475 cm^{-1}, has appeared in the spectra of functionalized sample due to hydroxyl groups [16]. Diminutive signals of surface modifications are reasonable as per the size of glassy CB balls (10 μm diameter). Photochemical functionalization altered only surface, whereas Raman analysis is a bulk analysis technique.

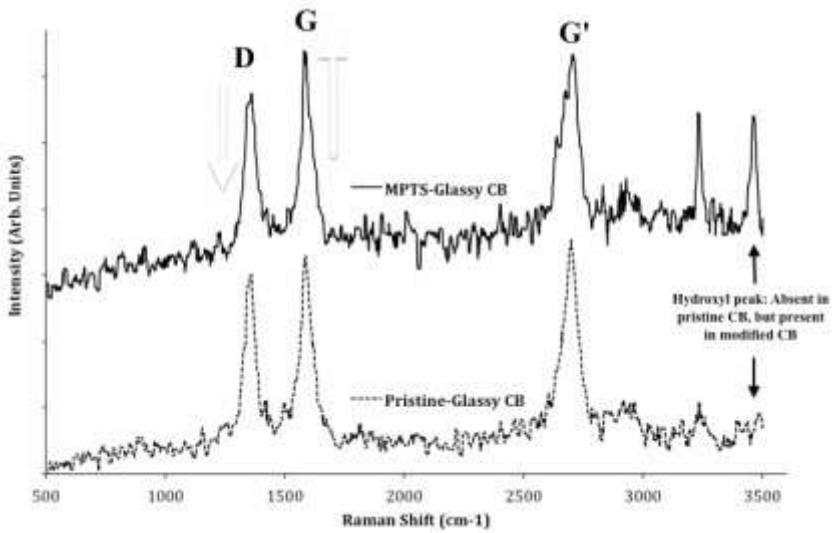


Figure 7: Raman spectra of Pristine-Glassy CB and MPTS-Glassy CB

FESEM images of Pristine-Glassy CB and MPTS-Glassy CB are presented in Figure 8. Images indicate that glassy CB have no large-scale alteration after functionalization treatment. Focusing on the brightness of CB surface, an increase in dark regions after functionalization can be noticed .

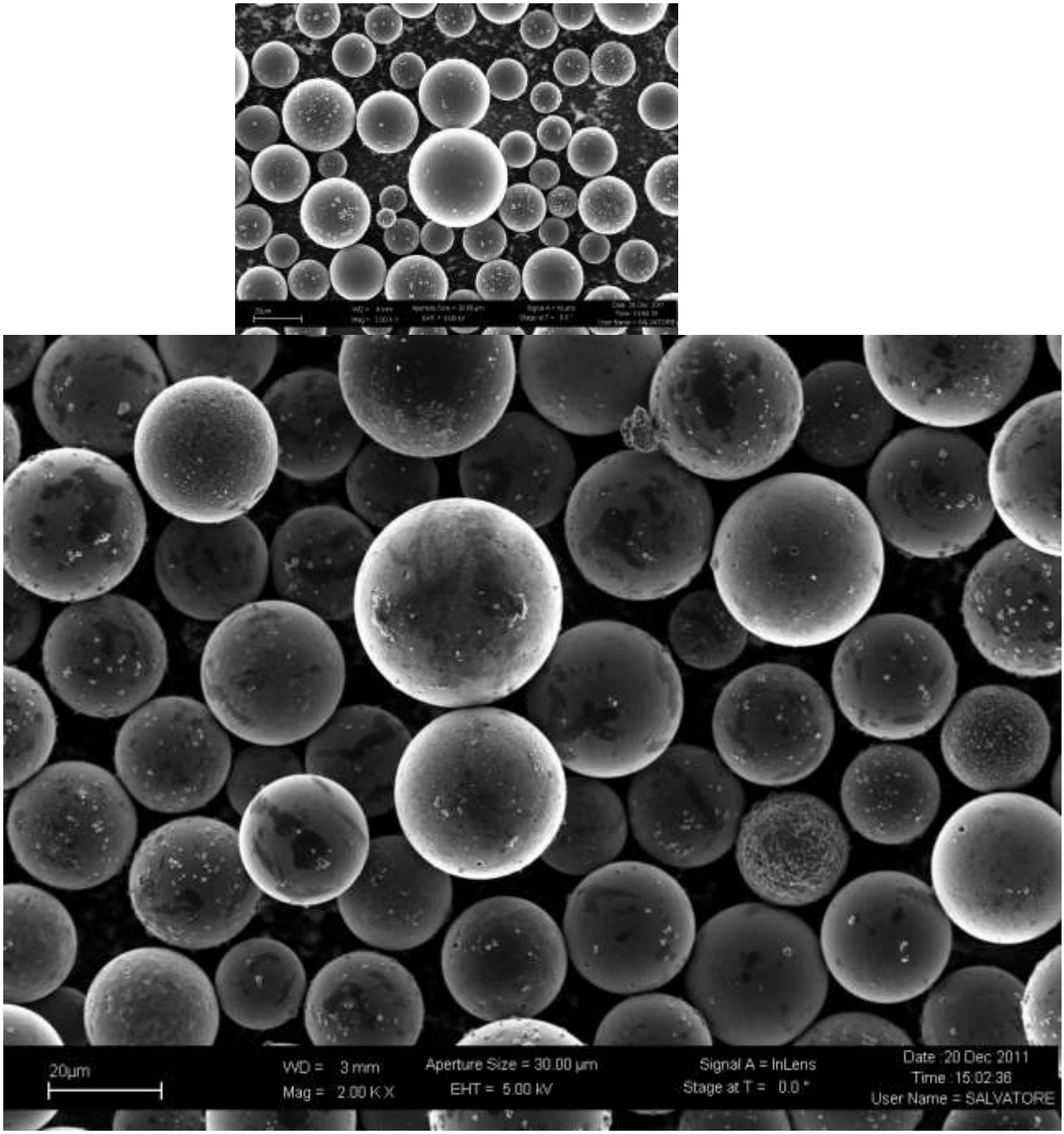


Figure 8: FESEM images of Pristine-Glassy CB (left) and MPTS-Glassy CB

Thermal gravimetric analysis, of Pristine and modified glassy CB was made through similar experimental procedure (25 - 800^{o}C with heating rate 10^{o}C/ min). TGA of Pristine-glassy CB (Fig 10) showed thermal stability till almost 700^{o}C and afterwards it starts decomposing. On the contrary modified sample MPTS-glassy CB (Fig 10) showed slight degradation at around 250^{o}C and afterwards it showed thermal stability till 800^{o}C.

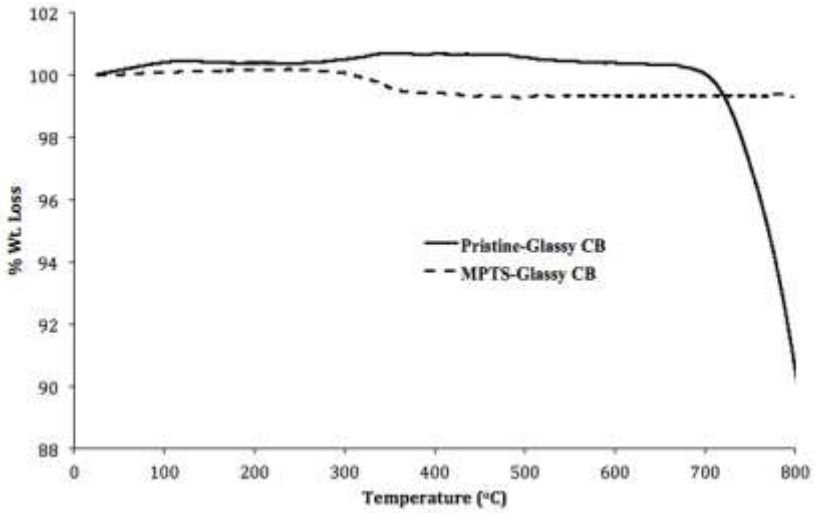


Figure 10: TGA of Pristine- and MPTS-Glassy CB

According to the previos chemical and structural analyses, the photochemical method has altered CB surface chemistry. This surface modification is expected to make CB particles easily dispersible in a range of solvents. Figure 14 demonstrates a comparison of dispersion stability between unmodified and photochemically modified CB particles, immediately as well as after 30 minutes from formulation. Pristine CB executed poor dispersability whereas modified CB established better and universal dispersion in polar and non-polar solvents.

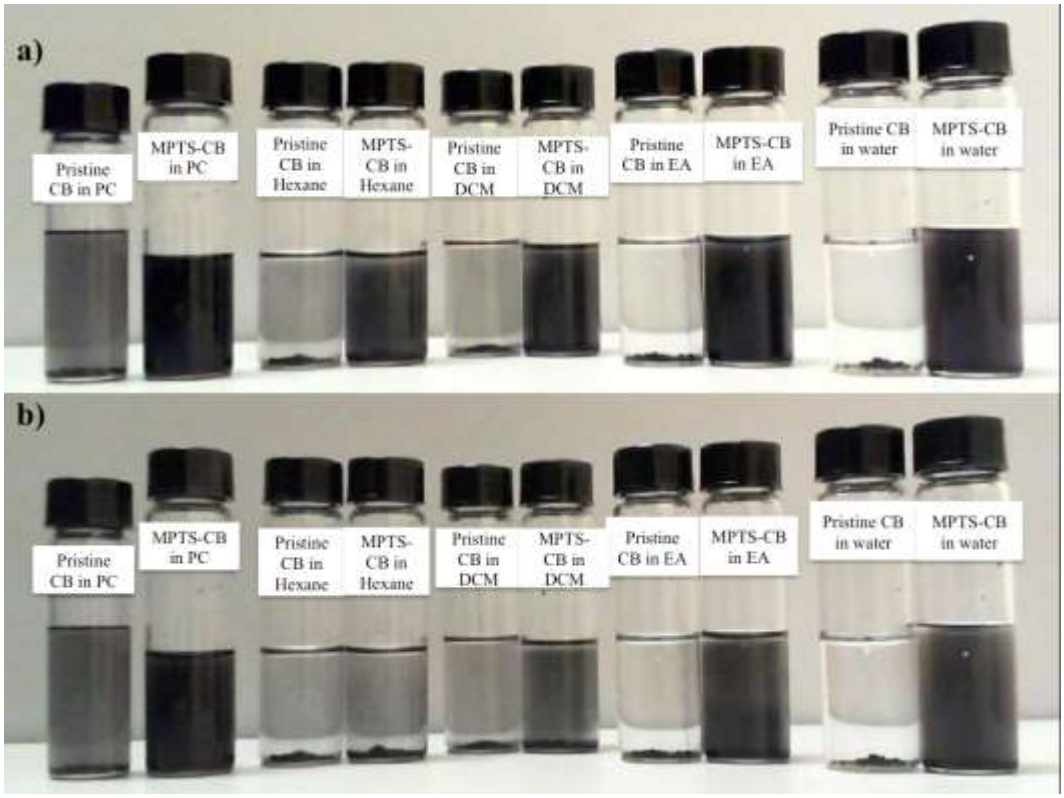


Figure 14: Pristine-CB and m-CB dispersion (10 mg/5 mL): a) immediately after mixing, b) 30 minutes after mixing.

4. CONCLUSION:

This research was planned over a photochemical method used to alter surface chemistry of colored particles which otherwise is impossible to modify with light. The work is based upon the concept of using active centers, generated by photoinitiator, to penetrate into shaded area of reaction mixture. Moreover, this effective photochemical treatment suggests possibility of working with molecules that can not be processed through thermal procedures as per their thermal instability.

Effectiveness of photochemical technique, with and without thermal support, has been verified, through instrumental analyses, which confirmed an ample amount of thiolation (2.5-7%) and silanization (3.3-10.8%) on CB to produce the surface framed with sulfur and silicon moieties. Data clearly revealed that CB particles have been decorated with 5-10 wt % of modifiers. Thermal decomposition has been observed in modifier molecules at higher temperature.

Dispersion comparison, between unmodified and modified CB particles, has proven increased reactivity of modified CB particles towards external media (solvent or polymer). Improved dispersion of CB particles signposts a strong interaction towards other constituents within composites, that is an essential prerequisite to produce required properties.

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REFERENCES:

1. Atif M, Bongiovanni R, Yang J. Cationically UV-Cured Epoxy Composites. Polym. Rev. 2015; 55(1):90-106
2. Soares M C F, Viana M M, Schaefer Z L, et al. Surface modification of carbon black nanoparticles by dodecylamine: Thermal stability and phase transfer in brine medium. Carbon. 2014; 72: 287–295.
3. Heo Y J, Yeon S H, Park S J. Defining contribution of micropore size to hydrogen physisorption behaviors: A new approach based on DFT pore volumes. Carbon. 2019;143:288-293.
4. Prado-Burguete C, Linares-Solano A, Rodriguez-Reinoso F, et al. Effect of carbon support and mean Pt particle size on hydrogen chemisorption by carbon-supported Pt catalysts. J. of Cata. 1991; 128(2):397-404.
5. Takanori T, Tomoharu S, Masahiro M, et al. Reducing Physical Adsorption of Enzymes by Surface Modification of Carbon Black for High-Current-Density Biofuel Cells. J. Electrochem. Soc. 2014;161(13):H3095-H3099. doi: 10.1149/2.0181413jes.
6. Verkuijlen R O F, Van Dongen M H A, Stevens A A E, et al. Surface modification of polycarbonate and Polyethylene Naphtalate foils by UV-ozone treatment and Plasma printing. App. Sur. Sci. 2014; 290:381–387.
7. Xin W, Yujie W, Jiang G, et al. Thermal and flammability properties of polypropylene/carbon black nanocomposites. Polymer Deg. & Stability. 2012; 97(5):793–801.
8. Atif M, Bongiovanni R, Giorcelli M, et al. Modification and characterization of carbon black with Mercaptopropyltrimethoxysilane. App. Sur. Sci. 2013; 286:1-430.

9. Li Q, Wu G, Ma Y, et al. Grafting modification of carbon black by trapping macroradicals formed by sonochemical degradation. Carbon. 2007;45: 2411–2416.
10. Tsubokawa N, Hosoya M, Kurumada J. Grafting Reaction of Surface Carboxyl Groups on carbon black with polymers having terminal hydroxyl or amino groups using N,N'-dicyclohexylcarbodiimide as a condensing agent. Reactive and Functional Polymers. 1995;27: 75-81.
11. Woointranont P, Pecharapa W. Effects of Surface Modification of Carbon Nanotubes on the Deposition of NiO/CNTs Nanocomposites. Journal of the Microscopy Society of Thailand. 2011;4:116-119.
12. Coates J P. Interpretation of infrared spectra: a practical approach, in: Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation, John Wiley & Sons, New York, 2000.
13. Socrates G. Infrared And Raman Characteristic Group Frequencies: Tables and Charts, Third Ed., John Wiley & Sons, New York, 2001.
14. Papirer E, Lacroix R, Donnet J B. XPS study of the halogenation of carbon black. Carbon. 1994;32:1341–1358.
15. Chang C H. Preparation and characterization of carbon–sulfur surface compounds. Carbon. 1981;19: 175–186.
16. Sugatri R I, Wirasadewa Y C, Saputro K E, et al. Recycled carbon black from waste of tire industry: thermal study. Microsystem Technologies. 2018;24(1): 749-755.