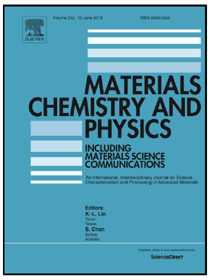

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Grafting of silica nanoparticles at the surface of graphene for application in novolac-type phenolic resin hybrid composites

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ABSTRACT

Hybrid composites of novolac resin were prepared by using graphene oxide (GO) which was functionalized with furfuryl alcohol and silica nanoparticles (SiO_2). For this purpose, SiO_2 was modified with silane coupling agent of (3-aminopropyl)triethoxysilane (APTES) to obtain SiO_2-NH_2 and subsequently attached at the surface of furfuryl alcohol-modified GO (GOFA) to obtain SGOFA. The SGOFA was incorporated into the novolac resin matrix in two different contents of 4 and 8 wt% of the matrix. Successful modification processes of GO with furfuryl alcohol, SiO_2 with APTES, and GOFA with SiO_2-NH_2 were confirmed by Fourier-transform infrared

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spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. TGA results showed that char residue of novolac resin was increased by incorporation of SGOFA from 58.4 to 61.3 and 65.4% by the addition of 4 and 8 wt% of SGOFA, respectively. Additionally, degradation temperature of novolac resin was increased by incorporation of SGOFA from 445.4 to 460.0 and 467.4°C by the addition of 4 and 8 wt% of SGOFA, respectively.

Keywords: Novolac resin; graphene; silica nanoparticle; char residue.

1. INTRODUCTION

Phenolic resins as thermosetting polymers are commonly used in thermally stable hybrid composites [1, 2]. Phenolic resins are synthesized from a phenol and formaldehyde. Considering the ratio of the phenol and formaldehyde and also catalyst type, these thermosetting resins can be categorized as highly viscous liquid resol and solid novolac. Furfuryl alcohol is used for viscosity control and improvement of processing condition of phenolic resins. Novolac-type phenolic resin represents high mechanical properties, dimensional stability, and thermal stability. Therefore, its application in ablation resistant composites can be prominent by increase of its carbon yields at high temperatures. Carbon yield of novolac-type phenolic resin was commonly increased by its structural modification and also use of additives. Boron, phosphorous, and other inorganic materials are commonly used for increase of thermal characteristics of novolac-type phenolic resins [3, 4]. Additionally, silica nanoparticles are an important class of inorganic materials in preparation of thermally stable novolac composites [5]. In such hybrid composites, sol-gel reaction results in covalent grafting of novolac chains on inorganic components [6-9]. These hybrid composites are commonly prepared by co-condensation of silane-modified novolac chains in the presence of metal alkoxides. Finally, covalent bonding of the organic and inorganic parts results in formation of a hybrid composite. These covalent interactions resulted in appropriate dispersion of fillers in the phenolic matrix.

Carbon nanomaterials such as graphene and nanotube were used in phenolic matrix for improvement of thermal stability [10-14]. Layered structure of graphene, its carbon characteristics, and low cost make it an appropriate component in polymer composites with high thermal stabilities. Graphene and CNT were also employed for incorporation into modified novolac resin by the sol-gel reaction for preparation of organic/inorganic hybrids [15-17]. In such hybrid composites, carbon-based fillers and novolac resin have been incorporated into silica/siloxane networks using sol-gel reaction. In these products, the problems of dispersion of carbon-based fillers and interfacial interaction of constituents are completely resolved. Silica-attached graphitic layers were also used for incorporated into silica/siloxane networks with novolac resins by sol-gel reaction [18, 19]. However, in these products silica/siloxane networks played the important role in determination of thermal properties. So, preparation of thermally stable novolac-type phenolic composites without silica/siloxane network seems to be beneficial.

In this research, a highly feasible approach was used for incorporation of graphene decorated with silica nanoparticles into novolac matrix with strong interactions. For this purpose, graphene oxide (GO) was functionalized with furfuryl alcohol moieties from its carboxyl groups. This was mainly carried out for improving dispersion of graphene layers in novolac matrix and also its interaction with the matrix through the furfuryl alcohol moieties. Additionally, amine-modified silica nanoparticles were attached on graphene layers by a nucleophilic ring opening reaction. This hybrid product was used as composite agent in preparation of novolac composites. The final goal is increase of novolac resin's char residue by incorporation of silica-containing graphene, which is capable of covalent bonding with the novolac matrix in the composites. Therefore, char residue and thermal degradation behavior of the prepared hybrids were compared. Sample's names with their description are summarized in Table 1.

Table 1

2. EXPERIMENTAL

2.1. Materials

Silica nanoparticles (SiO_2, particle average size: 10-15 nm, specific surface area: 150-226 m^2/g) were purchased from Tecnan-Nanomat company (Spain). Potassium permanganate

($KMnO_4$, Sigma-Aldrich), (3-aminopropyl)triethoxysilane (APTES, Sigma-Aldrich), hexamethylenetetramine (HMTA, Sigma-Aldrich), furfuryl alcohol (Sigma-Aldrich), sodium nitrate ($NaNO_3$, Sigma-Aldrich), and N,N'-Dicyclohexylcarbodiimide (DCC, Aldrich) were used as received. Graphite, sulfuric acid (H_2SO_4), ethanol, hydrochloric acid (HCl), and tetrahydrofuran (THF) were received from Merck Company.

2.2. Preparation of graphene oxide (GO)

GO was prepared using Hummer's method [20]. In a 300-mL flask, 1.5 g $NaNO_3$ and 3 g graphite were added. After addition of 180 mL H_2SO_4, stirring of the mixture at 0 °C for 15 min, addition of 9 g of $KMnO_4$, stirring at 35 °C for 7 h, feeding an additional 9 g of $KMnO_4$, stirring was applied for 12 h. After dilution of the mixture by deionized water, the remained $KMnO_4$ was reduced by addition of 30 mL H_2O_2. After centrifugation of the product, it's washing with deionized water, sonication for 30 min, filtration, and drying at 65 °C for 24 h, GO was obtained.

2.3. Functionalization of GO by furfuryl alcohol to yield GOFA

GOFA was prepared by an esterification reaction of furfuryl alcohol hydroxyl groups and GO carboxylic acid groups [10, 11]. The mixture of 0.2 g GO and 100 mL DMF were stirred into a 250-mL flask and sonicated for 15 min. After addition of furfuryl alcohol (0.472 mL, 5.46 mmol) and agitation for 15 min, DCC (4.0 g, 20.87 mmol), and DMAP (0.3 g, 2.46 mmol) and agitation for 16 h, washing the product with DMF for several times, and drying at 65 °C for 24 h, GOFA was obtained.

2.4. Functionalization of SiO_2 with APTES to yield SiO_2-NH_2

At first, 4 g SiO_2 was added into the solution of 2 g NaOH in 100 mL deionized water and stirred at 65 °C for 24 h. After titration of the dispersion by dropwise addition of acetic acid, centrifugation of the mixture, washing the product with ethanol, and drying the product at 80 °C for 24 h, hydroxylated SiO_2 was obtained [18, 19]. Then, 4g of hydroxylated SiO_2 was dispersed in ethanol and water solution (volumetric ratio of 95:5) and sonicated for 30 min. Then, 3g APTES was added into the mixed solution and pH of solution was adjusted around 5 by dropwise addition of acetic acid. After stirring at ambient temperature for 24 h and centrifugation of the product, the resulted solid was washed with ethanol and dried at 80 °C for 24 h to yield SiO_2-NH_2 [18, 21].

2.5. Modification of GOFA by SiO_2-NH_2 to yield SGOFA

Functionalization of GOFA by SiO_2-NH_2 was carried out through a nucleophilic ring opening reaction [19, 22]. At first, 0.25 g GOFA was mixed in 100 mL DMF and stirred for 2 h. Then, 0.3 g DCC was added into the dispersion and the mixture was sonicated for 30 min. In another flux, 0.25 g SiO_2-NH_2 was dispersed in 50 mL DMF under nitrogen purging and the mixture was sonicated for 30 min. After that, SiO_2-NH_2-containing dispersion was added gradually into the GOFA dispersion in N_2 atmosphere and stirred for 24 h. Finally, centrifugation of the mixture, washing the solid with acetone, and drying the product at 60 °C for 24 h yield SGOFA.

2.6. Preparation of composites

Curing of novolac resin in the presence of SGOFA was carried out according to the literature [10, 11]. SGOFA (4 and 8 wt% of resin) was mixed in 10 mL THF and sonicated for 30 min. After addition of 6.2 g novolac resin dissolved in 10 mL THF and 0.9 g HMTA into the SGOFA dispersion and agitation for 24 h, the resin compound was prepared. After that, the mold was heated to 90 °C and the temperature remained unchanged for evaporation of THF. Finally, the curing was completed by increasing temperate to 135 °C with a ramp of 3.7 °C/h, further heating to 200 °C with a ramp of 12 °C/h, and keeping the temperature constant at 200 °C for 4 h.

2.7. Characterization

The Fourier-transform infrared spectrum (FT-IR) using the KBr pellet technique was conducted with a Bruker spectrometer to study the chemical structure of silica nanoparticles and graphitic layers after modification processes. X-ray diffraction (XRD) measurements for powder samples were performed on a D5000 X-ray diffractometer (Siemens, Germany) using a Cu Kα radiation. Thermo-gravimetric analysis (TGA) was performed on a Polymer Laboratories-TGA (TGA 1000, Shropshire, UK) at temperature increasing rate of 10 °C/min in N_2 for study of thermal degradation characteristics of the silica, graphitic, polymeric, and composite samples. The samples for scanning electron microscopy (SEM) were prepared by deposition of a layer from dispersion of GO and GOG in ethanol on a mica surface and sputtering with gold. The Vega-SEM (Tescan, Czech Republic) was employed for SEM imaging. Before this step, specimens were ultrasonically agitated for 30 min using an ultrasonic homogenizer (Development of Ultrasonic Technology, Iran). For transmission electron microscopy (TEM) and morphological study of silica, G, GO, and SGOFA, Philips EM 208 (Philips, Eindhoven, the Netherlands) was used. Samples were prepared by deposition of a sample layer on lacy grids. Before this step, specimens were ultrasonically agitated for 30 min using an ultrasonic homogenizer (Development of Ultrasonic Technology, Iran).

3. RESULTS AND DISCUSSION

Silica-containing graphene and novolac resin composites were prepared with the aim of increase in char residue and thermal degradation temperature. For this purpose, SiO_2 was firstly modified with APTES to prepare SiO_2-NH_2, as shown in Figure 1 (A). Then, GO was modified with furfuryl alcohol and SiO_2-NH_2 to yield GOFA and SGOFA, respectively (Figure 1(B)). Finally, hybrid composites of novolac resin were prepared by incorporation of SGOFA and its subsequent curing by hexamethylenetetramine (HMTA).

Figure 1

Figure 2

FT-IR results for GO, GOFA, SiO_2, SiO_2-NH_2, SGOFA, and SGNH8 are shown in Figure 2. Accordingly, the peaks at 3398, 1716, and 1250 cm^{-1} in the spectrum of GO are assigned to the stretching mode of hydroxyl, carbonyl, and C–O groups vibration, respectively [23-26]. The two peaks observed at 1051 and 853 cm^{-1} are due to oxirane moieties of GO. In the case of GOFA, appearance of a signal at 1112 cm^{-1} as a result of ether linkage of furfuryl alcohol and also intensification of C–H stretching at 2920 and 2851 cm^{-1} are two evidences for successful functionalization of GO with furfuryl lacohol [11, 27]. In the SiO_2 spectrum, the bands at 1100 and 950 cm^{-1} originates from the asymmetric stretching and bending vibrations of surface Si–OH groups, respectively. Also, asymmetric stretching and bending vibrations of Si–O–Si units appeared at 1100–1200 and 467 cm^{-1}, respectively. The bands in the vicinity of 2950 and 1380 cm^{-1} are attributed to the Si–CH_2 stretching and bending vibrations, respectively. In the spectrum of modified silica (SiO_2-NH_2), vibration of N–H units is overlapped with siloxane and silanol groups at 3400 cm^{-1}. However, appearance of a low-intensity peak in 2840–2960 cm^{-1} as a result of the symmetric vibration of the C–H groups confirmed successful substitution reaction of APTES at the surface of SiO_2 [28-30]. In the case of SGOFA, stretching vibration of carbonyl groups at 1714 cm^{-1}, asymmetric and symmetric stretching vibrations of C–H units at near 2920 and 2850 cm^{-1}, asymmetric stretching vibrations of Si–O–Si units at 1100–1200 cm^{-1}, and also bending vibrations of Si–O–Si units at 467 cm^{-1} confirm grafting of SiO_2-NH_2 on GOFA. In addition, the intensity of two peaks at 1051 and 853 cm^{-1} (assigned to the oxirane moieties of GO) are decreased in SGOFA spectrum, which is attributed to the ring opening reaction of primary amines present at the surface of SiO_2-NH_2 with oxirane moieties of GOFA. In the spectrum of SGNH8, all distinctive peaks of SGOFA are observed. However, the peaks for stretching vibrations of C–H units, stretching vibrations of non-conjugated C=C units, and C-O vibrations of phenol ether groups are observable at 2918, 1609, and 1054 cm^{-1}, respectively. This exhibited that a large number of cross-linked novolac networks are present in the composite structure [11, 31]. In addition, a large content of Si–O–Si units in the composites matrix results in methylene and methyl peaks with lower intensities [32].

Figure 3

Figures 3 (A) shows TGA thermograms of SiO_2, G, GO, GOFA, SiO_2-NH_2, SGOFA, CNR, SGNH4, and SGNH8. According to the results, SiO_2 and G represent the most thermally stable behavior with the final char residues of 99.4 and 93.3% at 600 °C, respectively. In the case of GO, the mass loss at below 120 °C is due to the release of absorbed water. A large content of GO mass was lost in 160-230 °C due to decomposition of its oxygen functionalities which was resulted in formation of CO and CO_2. Oxygen functionalities with higher thermal stabilities were decomposed in 230-320 °C [33-35]. Finally, GO reached to the char residue of 37.9% at 600 °C. After modification of GO with furfuryl alcohol, thermal decomposition of GOFA followed a different pattern, because some of oxygen functionalities of GO were participated in esterification reaction with hydroxyl groups of furfuryl alcohol. Consequently, GOFA shows higher char content of 42.8% with respect to GO [11]. Modification of SiO_2 with APTES moieties resulted in SiO_2-NH_2 sample with char content of 91.5%. This shows that about 7.9 wt% of SiO_2-NH_2 is composed of APTES moieties. Further functionalization of GOFA with SiO_2-NH_2 resulted in a higher char content of 64.4% with respect to GOFA, which originates from chemical attachment of SiO_2-NH_2 at the surface of GOFA via a nucleophilic ring opening reaction. The large difference between char contents of GOFA and SGOFA shows that partial reduction of GOFA happened during its functionalization with SiO_2-NH_2. A large content of CNR degradation is shown in 250-400 °C as a result of methylene bridges decomposition into methyl, phenol, and cresol groups. Degradation of phenol units are observed in the next stage [36, 37]. CNR shows char residue of 58.4% which is increased to 61.3 and 65.4% by the addition of 4 and 8 wt% of SGOFA content, respectively. Figures 3 (B) shows DTG thermograms of GO, GOFA, SGOFA, CNR, SGNH4, and SGNH8. After incorporation of SGOFA into the matrix of novolac resin, onset decomposition temperature of the composites showed insignificant increase. However, maximum degradation temperature is shifted to higher temperatures. This shows that incorporation of SGOFA into the matrix of novolac resin enhances its thermal stability. The summarized data from TGA and DTG curves are exhibited in Table 2.

Table 2

Figure 4

XRD spectra of G, GO, GOFA, SFGOA, SGNH8, are exhibited in Figure 4. Accordingly, narrow and sharp diffraction peak of G appeared at 26.1° indicating an interlayer distance of 0.34 nm. GO displays a broader and weaker peak at 10.3°, which corresponds to the interlayer distance of 0.85 nm. Interlayer expansion of GO is due to the reduction of graphene layers stacking order upon oxidation process. During oxidation of graphene, size of sp^2-hybridized domains was decreased by appearance of oxygen functionallities at the surface of graphene layers [38-40]. The interlayer distance of GOFA is about 11.04 nm ($2\theta=8°$). This shows that interlayer distance of GO was increased by its functionalization with furfuryl alcohol moieties. Interlayer distance of graphene layers in SGOFA is further increased ($2\theta=6.9°$) with respect to GOFA by insertion of SiO_2-NH_2 between the layers. A weak amorphous peak is also observed in the vicinity of 19° which may be due to delamination of some layers during functionalization processes. The amorphous peak of phenolic resins was appeared around 19°. In the case of SGNH8, novolac domains resulted in a broad diffraction peak in the vicinity of 19° [41]. Disappearance of the diffraction peak of SGOFA at $2\theta=6.9°$ shows that SGOFA layers were fully dispersed in the novoalc matrix.

Figure 5

Figure 5 exhibits SEM images of G, SiO_2, and SGOFA. All the images were recorded from the samples precipitated on mica surface. As shown in Figure 5 (A), G shows layers with smooth and uniform surface. However, agglomerated spherical SiO_2 particles with bumpy structure are clearly observed in Figure 5 (B). According to the images presented in Figures 5 (C) and (D), smooth and uniform surface of graphene is covered by a large number of SiO_2, which shows that grafting of silica at the surface of graphene was done successfully and a coarse graphene surface was observed after modification with SiO_2.

Figure 6

To confirm SEM results, TEM images of G, SiO_2, and SGOFA are exhibited in Figure 6. TEM results were recorded by deposition of samples on lacy carbon grids. As displayed in Figure 6 (A), G shows a layer structure with smooth and uniform surface. Graphene layers were crumpled during sever oxidation process. In Figure 6 (B), folded GO layers with lots of creases are clearly displayed. Figure 6 (C) shows that SiO_2 nanoparticles with diameters of less than 10 nm are agglomerated. The presence of silica nanoparticles grafted to graphene layers is observable in Figure 6 (D), which confirms successful modification of GOFA with SiO_2-NH_2.

4. CONCLUSION

Silica-containing graphene and novolac resin composites with high char residue and thermal degradation temperature were prepared. For this purpose, SiO_2 was modified with APTES and then incorporated at the surface of furfuryl alcohol-modified GO to obtain SGOFA. The results of FT-IR, XRD, TGA, SEM, and TEM show that grafting of APTES on SiO_2, furfuryl alcohol at the edge of GO, and APTES-modified silica at the surface of GOFA was performed successfully. Functionalization of GOFA with SiO_2-NH_2 resulted in a higher char content of 64.4% with respect to GOFA (42.8%), which originates from chemical attachment of SiO_2-NH_2 on GOFA. CNR shows char residue of 58.4% which is increased to 61.3 and 65.4% by the addition of 4 and 8 wt% of SGOFA content, respectively. Additionally, degradation temperature of novolac resin was increased by incorporation of SGOFA from 445.4 to 460.0 and 467.4°C by the addition of 4 and 8 wt% of SGOFA, respectively. The grafted silica on graphene layers surface is observable in SEM and TEM images of SGOFA.

5. ACKNOWLEDGMENT

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6- CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Figure 1- Schematic illustration for preparation of (A) SiO_2-NH_2 and (B) SGOFA

Figure 2- FT-IR spectra of GO, GOFA, SiO_2, SiO_2-NH_2, SGOFA, and SGNH8

Figure 3- (A) TGA thermograms of SiO_2, G, GO, GOFA, SiO_2-NH_2, SGOFA, CNR, SGNH4, and SGNH8 and (B) DTG thermograms of GO, GOFA, SGOFA, CNR, SGNH4, and SGNH8

Figure 4- XRD results for G, GO, GOFA, SGOFA and SGNH8

Figure 5. SEM images of (A) G, (B) SiO_2, and (C and D) SGOFA in various enlargements

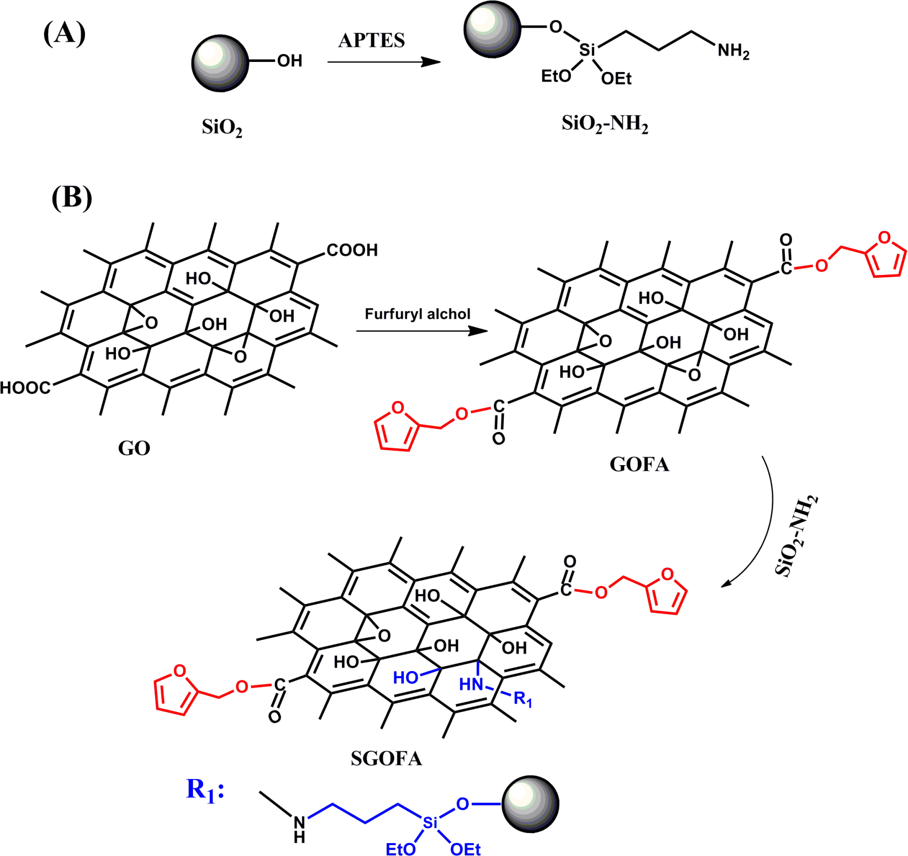
Figure 6. TEM images of (A) G, (B) GO, (C) SiO_2, and (D) SGOFA

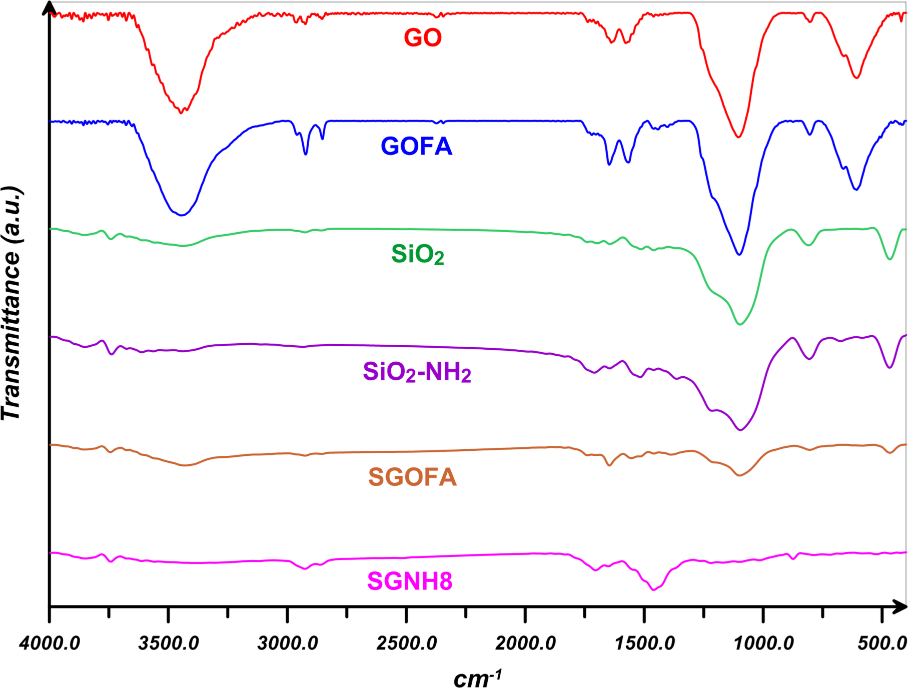
Table Captions:

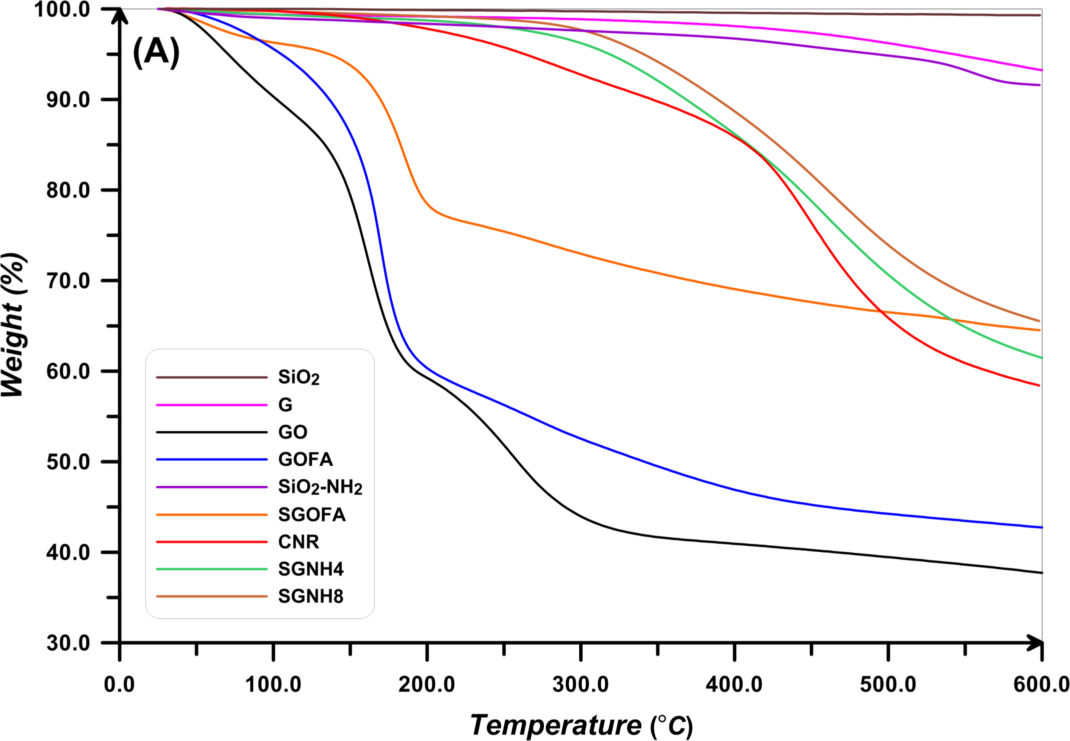
Table 1- Designation of the samples

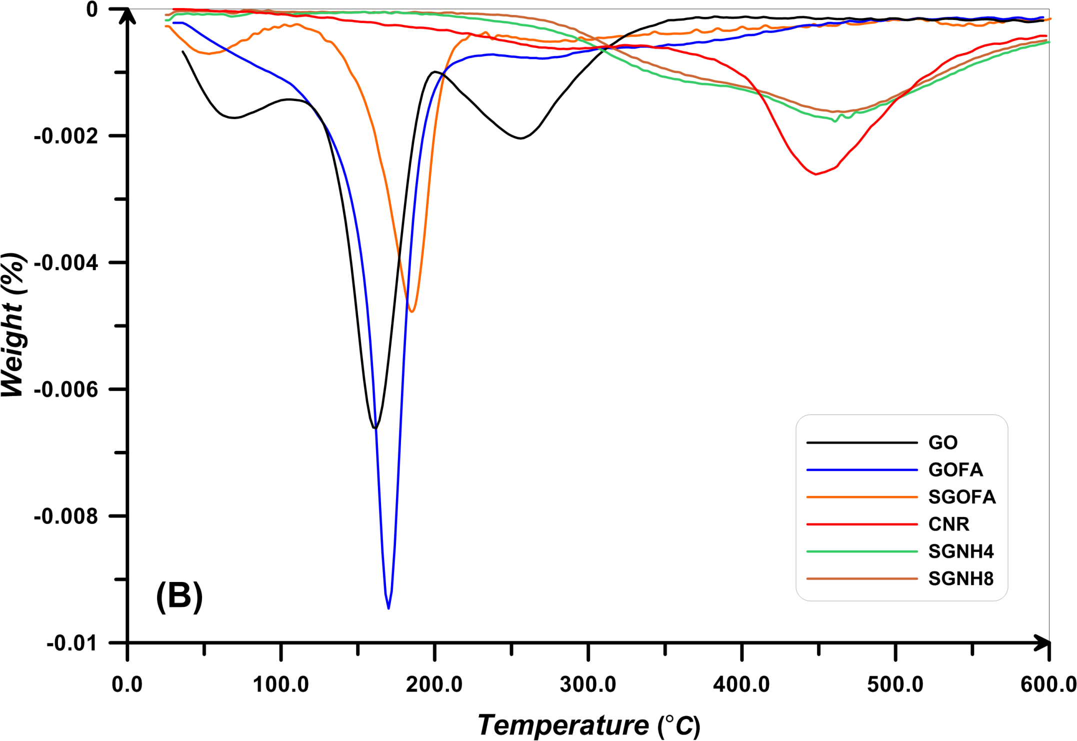
Table 2- The summarized data from TGA and DTG curves

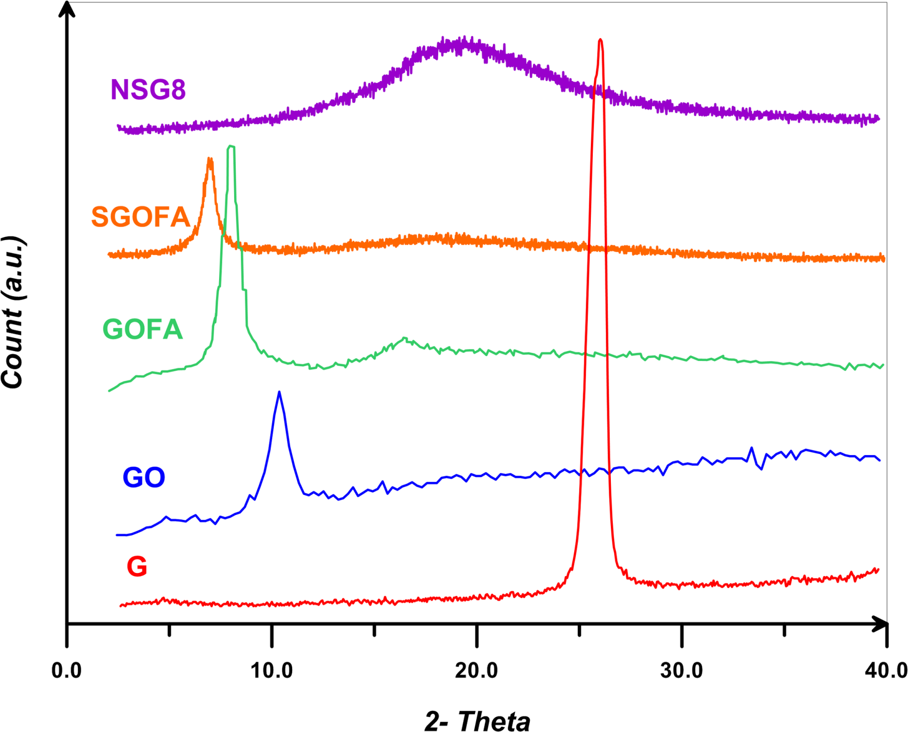
- Surface modification of GO by furfuryl alcohol and APTES-modified silica resulted in SGOFA.
- Novolac-type phenolic resin composites were prepared by incorporation of 4 and 8 wt% of SGOFA.
- Char residue was increased by incorporation of SGOFA to 65.4% by the addition of 8 wt% of SGOFA.
- Degradation temperature was increased to 467.4°C by the addition of 8 wt% of SGOFA.

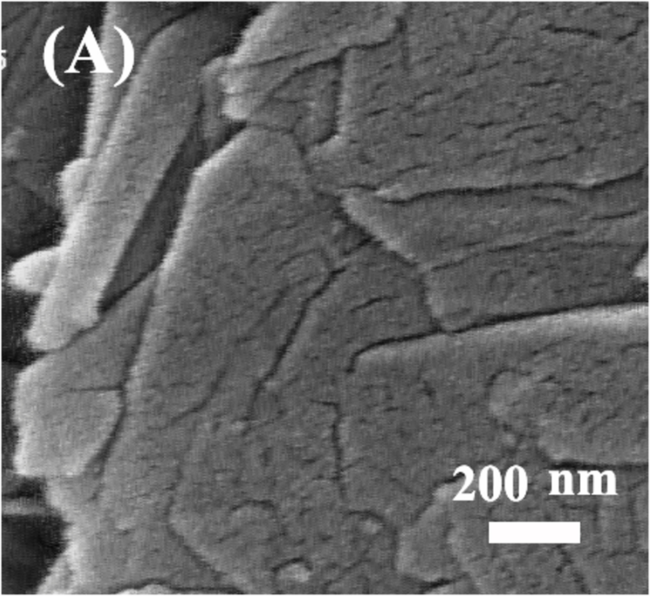

(A)
OH
SiO2
APTES
O
Si
NH2
EtO
OEt
SiO2-NH2
(B)
COOH
HO
OH
O
HOOC
GO
Furfuryl alchol
GOFA
SiO2-NH2
HO
HN
R1
SGOFA
R1:
N
H
Si
O
EtO
OEt

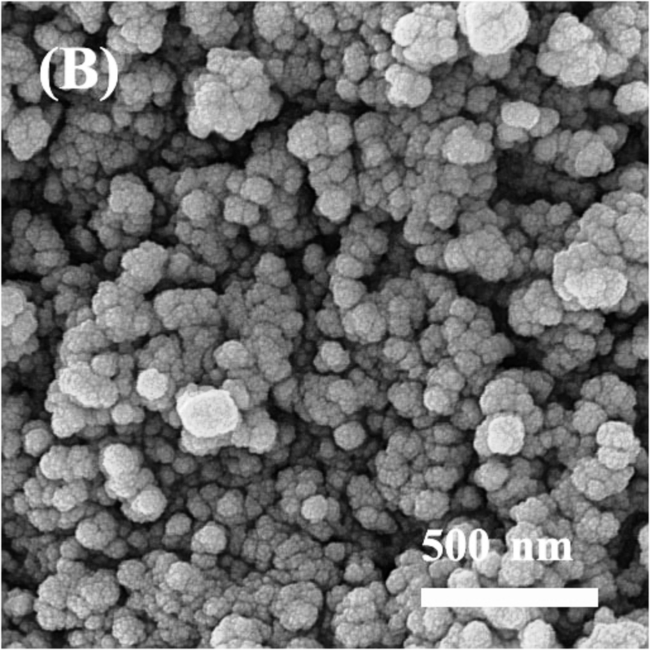

GO
GOFA
SiO₂
SiO₂-NH₂
SGOFA
SGNH8
Transmittance (a.u.)
4000.0
3500.0
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
cm⁻¹

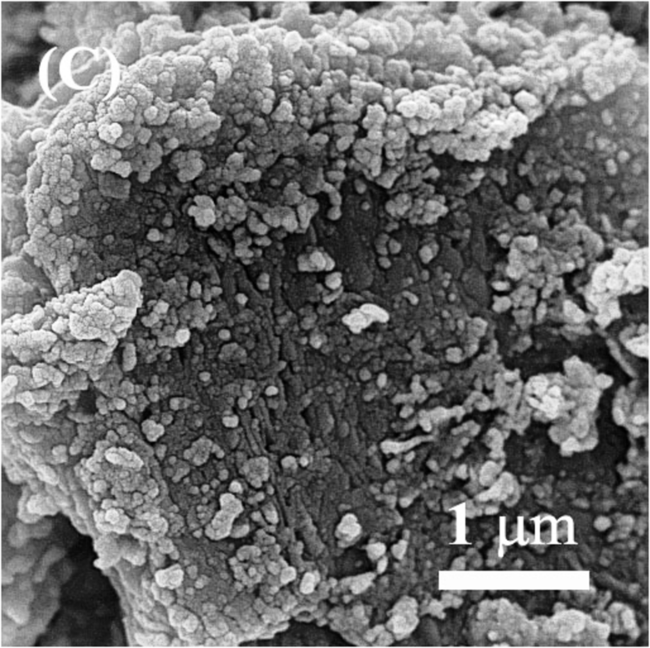

(A)
Weight (%)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
0.0
100.0
200.0
300.0
400.0
500.0
600.0
Temperature (°C)
SiO2
G
GO
GOFA
SiO2-NH2
SGOFA
CNR
SGNH4
SGNH8

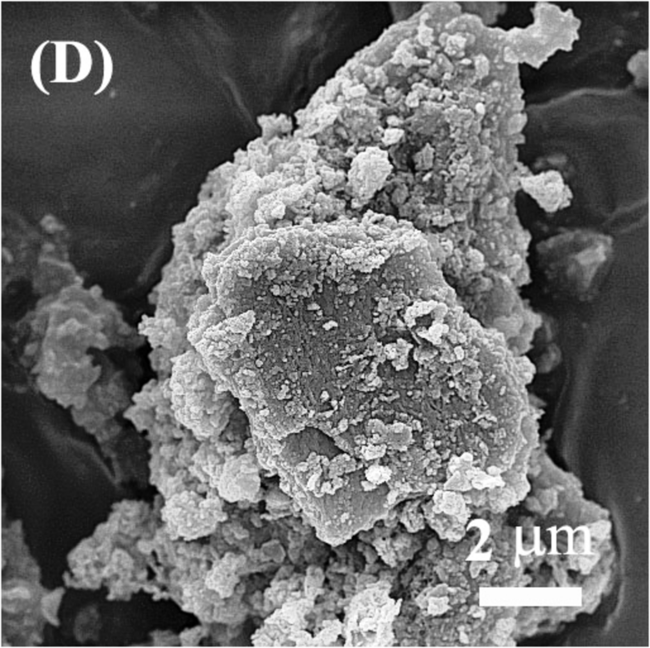

0
-0.002
-0.004
-0.006
-0.008
-0.01
Weight (%)
0.0
100.0
200.0
300.0
400.0
500.0
600.0
Temperature (°C)
(B)
GO
GOFA
SGOFA
CNR
SGNH4
SGNH8

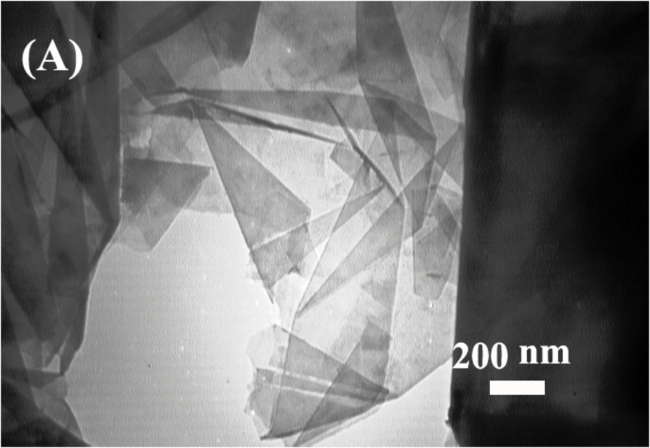

NSG8
SGOFA
GOFA
GO
G
Count (a.u.)
0.0
10.0
20.0
30.0
40.0
2- Theta

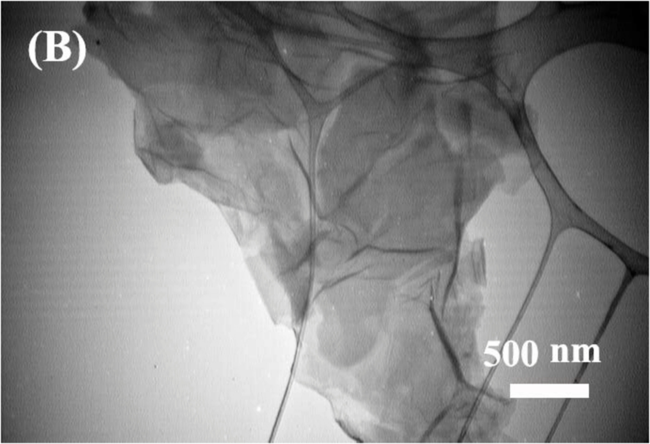

(A)
200 nm

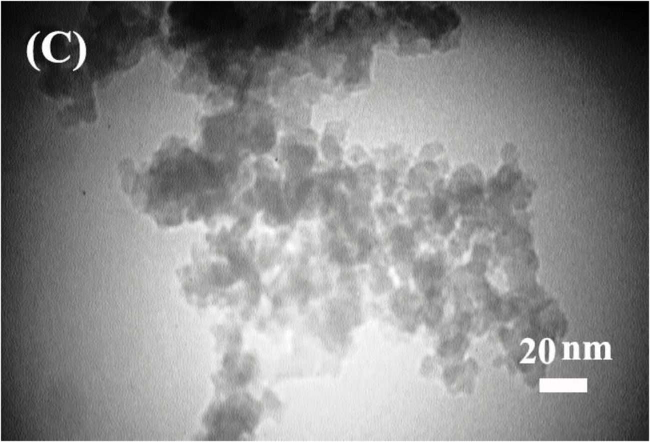

(B)
500 nm

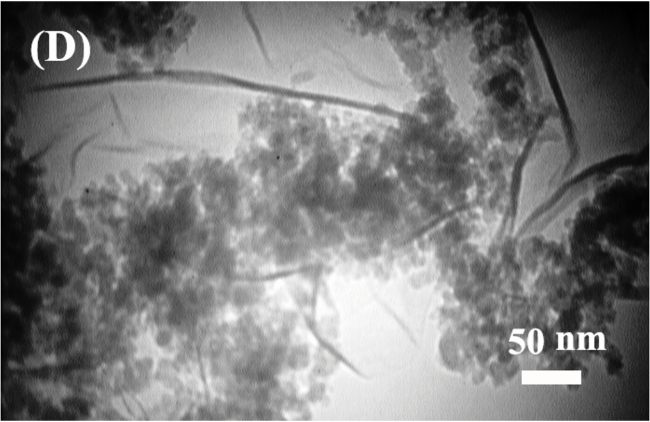

(C)
1 μm


(D)
2 µm


(A)
200 nm


(B)
500 nm


(C)
20 nm


(D)
50 nm

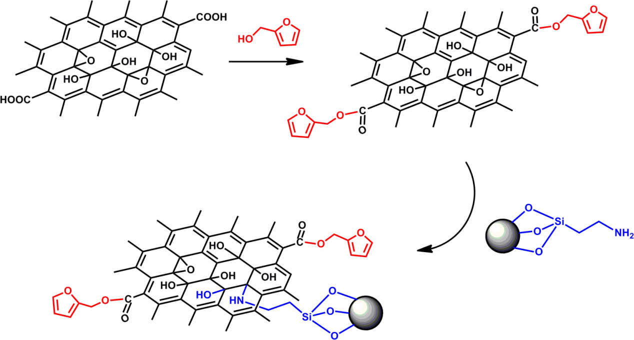

COOH
HOOC
HO
OH
O
HO
NH2
Si
HN

Table 1- Designation of the samples

Sample	Description
GO	Graphene oxide
GOFA	Furfuryl alcohol-grafted GO
SiO_2	Silica nanoparticles
SiO_2-NH_2	(3-Aminopropyl)triethoxysilane-modified SiO_2
SGOFA	SiO_2-NH_2-attached GOFA
CNR	Cured novolac resin
SGNH4	SGOFA and novolac resin hybrid composite with 4 wt% of SGOFA
SGNH8	SGOFA and novolac resin hybrid composite with 8 wt% of SGOFA

Table 2- The summarized data from TGA and DTG curves

Sample	T_d (°C)	Char residue (%)
SiO_2	---	99.4
GO	161.4 and 256.7	37.9
GOFA	170.6 and 273.2	42.8
SiO_2-NH_2	---	91.5
SGOFA	186.1 and 276.8	64.4
CNR	445.4	58.4
SGNH4	460.0	61.3
SGNH8	467.4	65.4