Modification of graphene with silica nanoparticles for use in hybrid network formation from epoxy, novolac, and epoxidized novolac resins by sol-gel method: Investigation of thermal properties

A. Mousavi¹, H. Roghani-Mamaqani^{1,2*}, M. Salami-Kalajahi^{1,2}, S. Shahi¹, A. Abdollahi¹

¹Department of Polymer Engineering, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran

²Institute of Polymeric Materials, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran

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Abstract. Thermal stability of hybrid composites prepared from epoxy, novolac, and epoxidized-novolac resins and also modified graphene oxide (SFGO) was studied. SFGO was prepared by covering graphene oxide with silica nanoparticles and a bifunctional silane modifier. The first hybrid was prepared from SFGO and silane-modified epoxy resin. The second one was prepared from SFGO, and silane-modified epoxy and novolac resins. The third hybrid was formed from SFGO, silane-modified novolac, and epoxidized novolac resins. Fourier transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) results showed that modification of graphene oxide was carried out successfully. TGA results show that degradation temperature and char residue of resins were increased through their incorporation into hybrid network with SFGO. In addition, the most increase of char residue was observed for the hybrid composites formed from SFGO and modified novolac and epoxy resins.

Keywords: polymer composites, graphene, silica nanoparticle, epoxidized novolac resin, sol-gel

1. Introduction

Epoxy resins are thermosetting polymers widely used in coating, adhesive, electrical, and composite industries due to their excellent physical properties [1, 2]. However, their low flame resistance and low thermal stability restricted their applications [3, 4]. Thermal characteristics of this organic polymer can be improved by using various methods. Flame retardants with boron, phosphorous, and other inorganic moieties can result in improved thermal characteristics of epoxy resins [5, 6]. Additionally, thermal improvement of epoxy resins was reported by their curing with other thermally stable resins [7, 8]. Using phenolics as curing agents for epoxy resins can result in high thermal properties [9]. These products com-

bine the characteristics of phenolics such as high thermal resistance and properties of epoxy resins like flexibility and low shrinkage [10]. Void-free phenolic networks prepared by epoxy functionalization of phenolic novolacs are known as epoxidized phenolic resins [11]. Epoxy, phenolic, and epoxidized phenolic resins show even higher thermal characteristics by incorporation of carbon fillers like graphene and nanotube (CNT) [12–15]. Here, fillers content, their degree of dispersion, and their interaction with the host matrix are important factors.

An important class of polymeric hybrid composites was commonly prepared via sol-gel process, which provides covalent interactions between polymer chains and various fillers by incorporation of polymer

*Corresponding author, e-mail: r.mamaghani@sut.ac.ir
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chains and fillers into silica/siloxane domains. These organic-inorganic hybrid materials can be prepared by *co*-condensation of modified polymers with metal alkoxides and formation of covalent bonding between the organic and inorganic components [16]. In sol-gel methods, hydrolysable alkoxysilanes are commonly used as coupling agents and pH, alkoxide type, water amount, temperature, and drying methods are important factors controlling the hydrolysis and condensation reactions [17–20]. Uniform distribution of silica/siloxane domains within a polymer matrix in *co*-condensation process may result in higher thermal and mechanical properties in such hybrid materials. Organic-inorganic hybrids of epoxy resin were prepared by Wu and co-workers with incorporation of modified epoxy resin and 3-(isocyanatopropyl) triethoxysilane (IPTEOS)-modified CNT into silica/siloxane network through the sol-gel method [21, 22]. Najafi-Shoa and co-workers also reported preparation of hybrid networks from silane-modified epoxy resin with CNT and graphene by the sol-gel method [23, 24]. They showed that char residue is increased 17.54% by loading only 4 wt% of functionalized-CNT in silane-modified epoxy resin matrix. Additionally, char residue is increased by 16.93% by loading only 1 wt% of functionalized-GO in silane-modified epoxy resin matrix. In addition, modified CNT and novolac resin with alkoxysilane modifiers was incorporated into silica/siloxane network through the sol-gel method using tetraethyl orthosilicate (TEOS) by Noparvar-Qarebagh *et al.* [18]. They showed that 11.94% increase of char yield was achieved by incorporation of functionalized-CNT in silane-modified novolac resin matrix. A similar method was also used by this group for incorporation of (3-amino-propyl) triethoxysilane (APTES)-modified graphene and (3-glycidyloxypropyl)trimethoxysilane (GPTMS)-modified novolac resin into silica/siloxane network [19]. They obtained high char value of 70.58% by incorporation of functionalized-graphene layers in silane-modified novolac resin matrix. Additionally, graphene-reinforced polyurethane hybrids were prepared by Hu and coworkers through covalent siloxane bonding between polyurethane and APTES-modified graphene using the sol-gel method [25]. Wu and co-worker reported the preparation of CNT-containing poly(urea urethane) nanohybrids by functionalization of CNT and poly(urea urethane) with silane

modifiers and their incorporation into silica/siloxane network [26]. Qian *et al.* [27], reported preparation of phosphorous and silica-containing organic-inorganic epoxy nanohybrids by the sol-gel and thermocuring processes. According to their thermo-oxidative degradation results, organic/inorganic networks improve the char residue from 1.1 to 23.8 wt% at 700 °C. They also carried out a similar research for preparation of organic-inorganic epoxy flame retardants containing exfoliated graphene [28]. They showed that with incorporation of modified graphene into epoxy matrix, a maximum of 4.7 wt% increment in char residue was obtained.

Recently, various hybrid materials were prepared to finely tune thermal stability of epoxy and novolac resins [13, 14, 18, 19, 23, 24, and 29]. But, there is not any feasible report on preparation of organic-inorganic hybrid networks from epoxy and novolac resins via the sol-gel method. Here, we planned a highly feasible sol-gel approach for incorporation of modified graphene into thermoset matrix of epoxy, epoxy and novolac, and also novolac and epoxidized novolac resins with covalent interactions. The main goal is preparation of hybrid composites with high value of char residue at high temperatures. Designation of samples is presented in Table 1.

Table 1. Description of samples

Sample code	Description
HDBTMSPU	1,10-(hexane-1,6-diyl)bis(3-(3-(trimethoxysilyl)propyl)urea)
FGO	HDBTMSPU-functionalized GO
SiO ₂ -NH ₂	APTES-functionalized silica nanoparticles
SFGO	FGO with grafted SiO ₂ -NH ₂
ER	Epoxy resin
MER	TEOS-functionalized Epoxy resin
NR	Novolac resin
CER	Cured epoxy resin
MERH	Hybrid network of MER and TEOS
CNR	Cured novolac resin
MNR	GPTMS-functionalized novolac resin
ENR	Epoxidized novolac resin
CENR	Cured epoxidized novolac resin
SGEHX	SFGO and MER hybrid composite (x denotes wt% of SFGO)
SGNEHX	SFGO, MNR, and MER hybrid composite (x denotes wt% of SFGO)
SGMNENHX	SFGO, MNR, ENR hybrid composite (x denotes wt% of SFGO)

2. Experimental

2.1. Materials

Epoxy resin (EP 418, Resitan, Iran, Eq.g⁻¹ = 700–800), novolac resin (IP502, Resitan, Iran), epichlorohydrin (Merck, 99%), graphite (Merck), potassium permanganate (KMnO₄, Sigma-Aldrich, 99%), sodium nitrate (NaNO₃, Sigma-Aldrich, 99%), sulfuric acid (H₂SO₄, Merck), (3-aminopropyl)trimethoxysilane (APTMS, Sigma-Aldrich, 97%), (3-glycidyloxypropyl) trimethoxysilane (GPTMS, Aldrich, 99%), (3-aminopropyl)triethoxysilane (APTES, Sigma-Aldrich, 95%), tetraethyl orthosilicate (TEOS, Merck), hexamethylene diisocyanate (HMDI, Sigma-Aldrich, 98%), hexamethyltetramine (HMTA, Sigma-Aldrich, 99%), ethylenediamine (Sigma-Aldrich, 99%), formic acid (Sigma-Aldrich, 95%), *N,N'*-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-dimethylaminopyridine (DMAP, Aldrich, 99%), furfuryl alcohol (Sigma-Aldrich, 98%), and trimethylamine (TEA, Sigma-Aldrich, 99%) were used as received. Ethanol, hydrochloric acid, n-hexane, acetone, and tetrahydrofuran were purchased from Merck Company.

2.2. Preparation of graphene oxide (GO)

GO was prepared according to Hummer's method [30]. NaNO₃ (1.5 g) and graphite (3 g) were poured into a 300 mL three-necked flask which was placed in an oil bath. H₂SO₄ (180 mL) was added and the mixture was stirred in 0 °C for 15 min. After that, KMnO₄ (9 g) was poured slowly into the flask and stirring was continued at 35 °C for 7 h. In the second part, KMnO₄ (9 g) was added into the reactor and stirring was continued at 35 °C for 12 h. Then, the mixture was diluted by deionized water (600 mL) and remained KMnO₄ was reduced by the addition of H₂O₂ (30 mL). After centrifugation of the mixture and its washing with deionized water for three times, the graphite oxide dispersion in water was exposed to sonication for 30 min. Finally, GO was obtained by filtration of the product and its vacuum drying at 65 °C for 24 h.

2.3. Synthesis of 1,1'-(hexane-1,6-diyl)bis(3-(3-(trimethoxysilyl)propyl)urea) (HDBTMSPU)

HDBTMSPU was synthesized according to the literature [31]. APTMS (4.6 g) and THF (28 mL) were poured into a 100 mL two-necked flask. Then, solution of HMDI (2.18 g) in THF (28 mL) was added slowly into the mixture under nitrogen atmosphere.

After filtration of the obtained white dispersion and vacuum drying of the product at 40 °C for 24 h, HDBTMSPU (6.78 g) was obtained as a white powder.

2.4. Functionalization of GO by HDBTMSPU to yield FGO

Functionalization of GO by HDBTMSPU was carried out according to the literature [32]. GO (0.25 g) was dispersed in ethanol (50 mL) and ultrasonically agitated for 30 min. GO dispersion and TEA (10 mL) were poured in a 250 mL flask, and the mixture was stirred for 2 h at 40 °C. Then, mixture of HDBTMSPU (4.86 g) and ethanol (50 mL) was added dropwise at 40 °C during 12 h. After sonication and precipitation of the product in *n*-hexane (100 mL), washing the solid by acetone, filtration by a 0.2 µm PTFE filter, and drying the product at 60 °C, black powder of FGO (0.19 g) was obtained.

2.5. Preparation of hydroxylated SiO₂

SiO₂ (4 g) were added into the solution of NaOH (2 g) and deionized water (100 mL) and stirred at 65 °C for 24 h. Then, the mixture was titrated by dropwise addition of acetic acid solution. After removal of excess liquid by centrifugation, washing the solid with fresh ethanol for three times, and drying the product in vacuum oven at 80 °C for 24 h, hydroxylated SiO₂ was obtained.

2.6. Functionalization of hydroxylated SiO₂ with (3-Aminopropyl)triethoxysilane (APTES) to obtain SiO₂-NH₂

Hydroxylated SiO₂ (4 g) were dispersed in ethanol and water solution (volumetric ratio of 95:5) and sonicated for 1 h. APTES (3 g) was added into the mixture and pH of solution was adjusted around 5 by dropwise addition of acetic acid. After stirring the mixture at ambient temperature for 24 h, the solid was removed by centrifugation and washed with ethanol for three times. SiO₂-NH₂ nanoparticles were finally obtained by drying the product in vacuum at 80 °C for 24 h.

2.7. Modification of FGO by SiO₂-NH₂ to obtain SFGO

Functionalization of FGO by SiO₂-NH₂ was carried out according to the literature [33, 34]. FGO (0.25 g) was dispersed in DMF (100 mL) and stirred for 2 h. After sonication of the dispersion for 30 min, DCC

(0.3 g) was added. In another balloon, $\text{SiO}_2\text{-NH}_2$ (0.25 g) was dispersed in DMF (50 mL) and the mixture was exposed to sonication for 30 min. This mixture was added dropwise into the FGO dispersion under nitrogen atmosphere and stirred for 24 h. After centrifugation of the reaction content, the solid was washed three times by acetone and then dried in vacuum at 60 °C for 24 h to yield SFGO.

2.8. Preparation of TEOS oligomer and modification of epoxy resin by TEOS oligomer to obtain MER

TEOS oligomer was prepared according to the literature [35]. For preparation of TEOS oligomer, TEOS (10 g) and ethanol (8.83 g) were transferred into a 100 mL round bottom flask. Then, deionized water (0.86 g) and HCl (0.02 g) were added and the mixture was left under stirring for 4 days at room temperature. In another 100 mL round-bottom flask epoxy resin solution (6 g) in THF (9 g) and TEOS oligomer (0.6 g) were added and the mixture was left under stirring for 3 days at 40 °C to obtain MER.

2.9. Modification of novolac resin with (3-glycidyloxypropyl)trimethoxysilane (GPTMS) to obtain MNR

Novolac resin modification was carried out by a ring opening reaction between epoxy groups of GPTMS and hydroxyl groups of novolac resin, as reported previously [29]. Novolac resin (5 g) was dissolved in THF (5 mL) in a 100 mL round-bottom flask. Subsequently, GPTMS (2 g) was added dropwise into the flask and the mixture left under stirring at 70 °C for 24 h. The solution of modified resin was subsequently used in the preparation of hybrid composites.

2.10. Preparation of hybrid composites of SGEH

Various amounts of SFGO (0.02 and 0.04 g for samples with 1 and 2 wt% of SFGO with respect to resin (MER)) were dispersed in THF (5 mL) and ultrasonically agitated for 30 min. Then, solution of MER (2 g) in THF (10 mL) was added to the SFGO and THF dispersion in a flask. After that, TEOS (0.28 mL), deionized water (0.125 mL), and formic acid (0.015 mL) were added to the mixture and left under stirring for 1 h. Then, temperature was increased to 90 °C for evaporation of solvent. Finally, ethylene diamine (0.20 g) was added into the mixture as curing agent

and the curing reaction was completed in five heating steps: (1) 90 °C for 30 min, (2) 120 °C for 60 min, (3) 140 °C for 30 min, (4) 180 °C for 180 min, and (5) 200 °C for 180 min. Hybrid composite composed of MER and TEOS (MERH) was prepared similar to this procedure but without SFCNT.

2.11. Preparation of hybrid composites of SGENH

Various amounts of SFGO (0.02 and 0.04 g for samples with 1 and 2 wt% of SFGO with respect to resins (MNR and MER)) were dispersed in THF (5 mL) and ultrasonically agitated for 30 min. Then, solutions of MNR (1 g) in THF (5 mL) and MER (1 g) in THF (5 mL) were added to the SFGO and THF dispersion in a flask. After that, TEOS (0.28 mL), deionized water (0.125 mL), and formic acid (0.015 mL) were added to the mixture and left under stirring for 1 h. Then, temperature was increased to 90 °C for evaporation of solvent. Finally, ethylene diamine (0.16 g) was added into the mixture as curing agent and the curing reaction was completed in five heating steps: (1) 90 °C for 30 min, (2) 120 °C for 60 min, (3) 140 °C for 30 min, (4) 180 °C for 180 min, and (5) 200 °C for 180 min.

2.12. Preparation of hybrid composites of SGMNENH

Various amounts of SFGO (0.02 and 0.04 g for samples with 1 and 2 wt% of SFGO with respect to resins (MNR and ENR)) were dispersed in THF (5 mL) and ultrasonically agitated for 30 min. Then, solutions of MNR (1 g) in THF (5 mL) and ENR (1 g) in THF (5 mL) were added to the SFGO and THF dispersion in a flask. After that, TEOS (0.28 mL), deionized water (0.125 mL), and formic acid (0.015 mL) were added to the mixture and left under stirring for 1 h. Then, temperature was increased to 90 °C for evaporation of solvent. Finally, ethylene diamine (0.20 g) was added into the mixture as curing agent and the curing reaction was completed in five heating steps: (1) 90 °C for 30 min, (2) 120 °C for 60 min, (3) 140 °C for 30 min, (4) 180 °C for 180 min, and (5) 200 °C for 180 min. ENR was cured similar to epoxy resins because of its epoxy functionalities. Therefore, after addition of ethylene diamine (0.042 g) to the mixture, curing reaction was completed in four steps: (1) 90 °C for 30 min, (2) 120 °C for 1 h, (3) 140 °C for 30 min, and (4) 160 °C for 2 h.

2.13. Curing of ER and NR to obtain CER and CNR

For preparation of CER, ER (2 g) was dissolved in THF (4 mL) and then ethylene diamine (0.042 g) was added into the ER solution. Finally, the curing reaction was completed in four steps: (1) heating at 90 °C for 30 min, (2) 120 °C for 1 h, (3) 140 °C for 30 min, and (4) 160 °C for 2 h. For preparation of CNR, NR (5 g) was dissolved in furfuryl alcohol (7 mL). After addition of HMTA (0.7 g) to the mixture and agitation for 10 h, curing of NR was carried out as follows: temperature was increased to 80 °C by the rate of 2 °C·min⁻¹ and remained at this temperature for 2 h. Temperature was held at 120 °C for 4 h and 180 °C for 2 h for curing and 230 °C for 8 h for post-curing.

2.14. Characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out in wavelengths between 4000 and 400 cm⁻¹ on a Bruker spectrometer (Karlsruhe, Germany) at a resolution of 4 cm⁻¹. An average of 24 scans was taken from the samples dispersed in KBr pellets. X-ray photoelectron spectroscopy (XPS) was performed on a Gammatdata-Scienta Esca 200 (Uppsala, Sweden) equipped with an Al K α (1486.6 eV photons) X-ray source in an ultra-high vacuum. X-ray diffraction (XRD) was performed at the step scan mode in diffraction angles between 10 and 80° by a D5000 X-ray diffractometer (Siemens, Germany) equipped with a Cu K α radiation ($k = 0.1540$ nm). Thermogravimetric analysis (TGA) was carried out on a PL thermal analyzer (Polymer Laboratories, TGA 1000, UK). All the data were recorded at a heating rate of 10 °C/min under nitrogen atmosphere. Scanning electron microscopy (SEM) was performed on a Vega SEM instrument (Tescan, Czech Republic). Samples were prepared by deposition of a thin sample layer on a mica surface using a spin coater. Before this step, specimens were ultrasonically agitated for 30 min using an ultrasonic homogenizer (Development of Ultrasonic Technology, Iran). Transmission electron microscopy (TEM) was carried out on a Philips EM 208 (Eindhoven, the Netherlands) with an accelerating voltage of 80 kV. Samples were prepared by deposition of a thin 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

Here, GO was modified with a bifunctional silane coupling agent of HDBTMSPU and amine-functionalized SiO₂ (Figure 1). Epoxy and novolac resins were modified with TEOS oligomer and GPTMS, respectively (Figure 2). Finally, three hybrid composites were prepared as follows: (I) Introduction of SFGO into MER using sol-gel method, (II) incorporation of SFGO into the matrix composed of MNR and MER using the sol-gel method (Figure 3), and (III) Introduction of SFGO into the matrix composed of MNR and ENR. After curing of epoxy groups by ethylenediamine, all the hybrid composites were compared from the viewpoint of thermal properties such as char residue and thermal degradation temperature.

FT-IR spectra of GO, FGO, SiO₂, SiO₂-NH₂, and SFGO are shown in Figure 4a. The peaks at 3398 and 1716 cm⁻¹ in GO spectrum are assigned to stretching vibration of hydroxyl and carbonyl groups, respectively. In addition, two peaks at 1051 and 853 cm⁻¹ are ascribed to the oxirane moieties of oxidized graphene. FGO spectrum shows some additional bands compared with GO, such as stretching vibration of secondary amide group at 3421 cm⁻¹, asymmetric and symmetric stretching mode of C–H bonds respectively at 2920 and 2854 cm⁻¹, bending vibration of N–H and stretching vibration of C–O units respectively at 1571 and 1258 cm⁻¹, and Si–O–C vibration at 795 cm⁻¹, which confirm successful functionalization of GO with HDBTMSPU moieties [32, 36]. However, partial hydrolysis of alkoxy groups results in a band at 1098 cm⁻¹ due to bending vibration of Si–O–Si units. In addition, stretching vibration of carbonyl groups in GO and HDBTMSPU is observed at 1714 and 1626 cm⁻¹, respectively [37, 38]. In the spectrum of SiO₂, absorption bands at 3450, 1100, and 950 cm⁻¹ correspond to the stretching, asymmetric stretching, and bending vibrations of surface silanol groups (Si–OH), respectively. Also, asymmetric stretching and bending vibrations of siloxane groups (Si–O–Si) appear at 1100–1200 and 467 cm⁻¹, respectively. The bands observed at 2947 and 1384 cm⁻¹ are attributed to the Si–CH₂ stretching and bending vibrations, respectively. Stretching vibration of adsorbed water and bending vibration of moisture appear at 3500–3400 and 800 cm⁻¹, respectively. Absorption bands at 3400 and 1616 cm⁻¹ signify the stretching and bending vibrations of aliphatic amine (N–H) groups, respectively. In the

Figure 1. Schematic illustration for the synthesis of (a) HDBTMSPU, (b) FGO, and (c) SFGO

spectrum of $\text{SiO}_2\text{-NH}_2$, the bands of N–H and C–H vibrations at 3400 cm^{-1} are overlapped with siloxane and silanol group's bands. However, appearance of weak band in the region of $2850\text{--}2950\text{ cm}^{-1}$ due to

Figure 2. Schematic illustration for the modification of (a) novolac and (b) epoxy resins to obtain MER and MNR, respectively

the symmetric vibration of C–H groups confirms substitution of APTES at the surface of SiO_2 in $\text{SiO}_2\text{-NH}_2$ [39–41]. SFGO spectrum shows all the characteristic peaks of FGO, such as stretching vibration of carbonyl groups of GO and HDBTMSPU at 1714 and 1626 cm^{-1} and asymmetric and symmetric stretching mode of C–H units at 2920 and 2854 cm^{-1} . In addition, intensity of two peaks at 1051 and 853 cm^{-1} (due to oxirane moieties of oxidized graphene) decreased in the spectrum of SFGO due to ring opening reaction of primary amines of SiO_2 and oxirane moiety of FGO.

FT-IR spectra of ER, MER, NR, MNR, SGEH2, SGNEH2, and SGMNENH2 are shown in Figure 4b. ER shows stretching vibrations of hydroxyl units and C–H of oxirane rings at 3415 and 3041 cm^{-1} , respectively. The bands at 2964 and 2870 cm^{-1} are related to stretching vibration of C–H groups. Two peaks appear at 1610 and 1505 cm^{-1} which are assigned to aromatic C=C and aryl–C units, respectively. Moreover, stretching vibration of ether groups is observed at 1037 cm^{-1} . Also, C–O and C–O–C segments of oxirane rings show stretching vibrations at 905 and 828 cm^{-1} , respectively. Appearance of weak and

Figure 3. The proposed schematic illustration for the structure of SGNEH composites

broad Si–O–Si peak at 1026 cm^{-1} in the spectrum of MER confirms successful modification of ER by TEOS oligomer [24, 42]. In the spectrum of NR, asymmetric bending vibration of C–H units, stretching vibration of C=C groups, and C–O vibration of phenol groups appear at 1511 , 1611 , 1098 cm^{-1} , respectively. Appearance of Si–O vibration in the

spectrum of MNR at 1048 cm^{-1} confirms successful grafting of GPTMS to NR backbone [14, 29]. In the spectra of hybrid composites, all distinctive peaks of MER, MNR, and SFGO are observed. However, intensity of C–H at 3041 , C–O at 905 , and C–O–C at 828 cm^{-1} are reduced as a result of ring opening curing reaction between epoxy groups of resin and

Figure 4. FT-IR spectra of (a) GO, FGO, SiO₂, SiO₂-NH₂, and SFGO and (b) ER, MER, NR, MNR, SGEH₂, SGNEH₂, and SGMNENH₂

amine groups of the hardener. In addition, high proportion of silica/siloxane moieties results in lower intensity of methylene and methyl peaks [43].

In Figure 5, surface elemental composition of GO and SFGO was investigated using XPS. Compared with survey scan spectrum of GO, SFGO shows additional components at binding energies of 105.4 and 403.0 eV assigned to Si 2p and N 1s bands, respectively. Presence of silicon and nitrogen atoms in the SFGO spectrum confirms successful grafting of HDBTMSPU and SiO₂-NH₂ at the surface of GO [44–46]. The molar content of silicon and nitrogen atoms in SFGO is 11.1 and 2.6%, respectively. High content of silicon atom results from attachment of SiO₂-NH₂ at the surface of GO. Increase of carbon to oxygen ratio from 1.59 to 2.99 by functionalization of GO with HDBTMSPU and SiO₂-NH₂ also confirms partial reduction of GO upon the functionalization process [33, 44]. The C 1s band spectra of GO and FGO are shown at higher resolutions (Figure 5b). C 1s band spectrum of SFGO appears at higher binding energies compared with GO, which can be related to covalent grafting of HDBTMSPU to GO [47]. In addition, the peak area of C 1s band is higher in SFGO compared with GO due to reduction of GO upon the functionalization process. The C 1s band spectrum for SFGO is deconvoluted into six peak components in Figure 5c. Carbon-containing groups of Si–C, C–C and C=C, C–N, C–O, C=O, and N–C=O and O–C=O with their binding energies are also displayed. Presence of Si–C, C–N, and N–C=O peaks at the binding energies of 288.8, 290.2, and 291.8 eV confirms that HDBTMSPU were successfully attached at the surface of GO [48].

Figure 6 shows TGA diagrams of SiO₂, SiO₂-NH₂, GO, FGO, and SFGO. According to the results of Figure 6a, SiO₂ with char content of about 99.3% at 600 °C shows the highest thermal stability. Thermal stability of SiO₂-NH₂ decreased in comparison with SiO₂ and its char residue reached to 91.8% at 600 °C. Using the results of Figure 6b, SiO₂-NH₂ shows a two stage mass loss diagram related to evaporation of absorbed water at the silica surface, partial decomposition of un-reacted APTES at lower than 100 °C, degradation of residual starting materials, and decomposition of organo-functional groups in 500–600 °C [41]. Some mass loss in below 100 °C is observed for GO, which is due to the loss of absorbed water. GO lost most of its mass in 150–220 °C due to decomposition of oxygen-containing functional groups accompanied by the formation of carbon monoxide and carbon dioxide vapors [49, 50]. Oxygen functionalities of GO with higher thermal stabilities decomposed in 230–320 °C [51]. Finally, char residue of GO reaches to 42.3% at 600 °C. However, due to the partial reduction of oxygen functionalities during modification process, char residue of FGO is higher than GO. Increasing $T_{0.05}$ (the temperature threshold for 5 wt% of mass loss) and char residue of FGO are confirmation for grafting of HDBTMSPU at the surface of GO [52]. DTG results show that degradation of FGO takes place at four steps: (I) loss of absorbed water at temperatures lower than 100 °C, (II) loss of oxygen-containing groups in 100–208 °C, (III) loss of nitrogen-containing groups in 208–430 °C, and (IV) loss of skeletal carbon and silicon. SFGO shows a similar decomposition behavior to FGO with char residue of 67.3%. Interestingly, its char residue is

Figure 5. (a) Survey scan XPS spectra of GO and SFGO, (b) C 1s band spectra of GO and SFGO, and (c) deconvoluted C 1s band of SFGO

higher than GO and FGO as a result of presence of higher content of silica/siloxane groups. Therefore, higher char residue and thermal stability of SFGO can be attributed to grafting of $\text{SiO}_2\text{-NH}_2$ and reduction of oxygen-containing groups at the surface of SFGO. Figure 7a shows TGA and DTG thermograms of CER, MERH, SGEH1, and SGEH2. Results show that maximum decomposition of ER occurs at 298.9 °C. After modification of ER with TEOS oligomer and formation of hybrid composite, maximum decomposition temperature increases to 314.5 °C. Incorporation of SFGO into the hybrid structure results in

degradation temperature of 321.7 and 318.1 °C in the case of SGEH1 and SGEH2, respectively. The hybrid composite formed from MER shows char residue of 16.8%, which is higher than the char residue of CER (12.6%). Char residue of SFGO-containing hybrids was increased to 18.8 and 20.4% in the case of SGEH1 and SGEH2, respectively. Presence of silica/siloxane moieties and covalently bonded graphene layers in the structure of hybrid composites composed from MER, SGEH2, and SGEH4 caused such high char residues and also enhanced thermal stabilities [52]. It is clear that char residue increases by

Figure 6. (a) TGA and (b) DTG thermograms of SiO_2 , $\text{SiO}_2\text{-NH}_2$, GO, FGO, and SFGO

increasing SFGO content from 1 to 2 wt% in hybrid composites (SGEH). As shown in Figure 7b, by addition of MNR into hybrid network of MER and SFGO (SGNEH), onset of decomposition was shifted to lower temperatures and char content was increased considerably in comparison with SGEH composites. Such considerable increase of char residue is due to the introduction of resin with high thermal stability (MNR) into the hybrid network. Considering thermal degradation of novolac resin at the region of 250–400 °C, methylene bridges decomposed into methyl, phenol, and cresol groups and degradation of phenol group occurs at the next stage. Therefore, mass loss in SGNEH composites occurs at lower temperatures compared with CER and MERH [53, 54]. Maximum decomposition temperature of CNR, SGNEH1, and SGNEH2 is shown at 449.4, 423.1, and 416.1 °C, respectively. Reduction of the DTG peak area in SGNEH in comparison with SGEH composites confirms improvement of thermal stability by incorporation of MNR in the hybrid composite structure. Finally, char residue of CNR, SGNEH1, and SGNEH2 is 58.3, 58.7, and 61.3%, respectively. According to the Figure 7c, by incorporation of ENR into hybrid network with MNR and SFGO, a product with high thermal stability was achieved. Maximum decomposition temperature of CENR, SGMNENH1, and SGMNENH2 is shown at 398.8, 437.4, and 442.9 °C, respectively. Also, char residue of CENR, SGMNENH1, and SGMNENH2 is 44.8, 48.1, and 54.1%, respectively. CENR shows the lowest thermal degradation temperature and also char content due to its thermally unstable epoxy groups. A comparison between three hybrid networks shows that increasing SFGO content in hybrid composites results in higher char contents. Incorporation of novolac resin into the hybrid networks results in higher char

contents and also degradation temperatures. SGMNENH with 2 wt% of SFGO shows the highest degradation temperature and SGNEH with 2 wt% of SFGO shows the highest char residue. This can be related to engagement of SFCNT, MNR, and MER in the silica/siloxane network. Finally, all the epoxy-containing hybrid networks were thermally more stable than the cured epoxy and show high char residues.

XRD spectra of G, GO, FGO, SFGO, SGEH2, SGNEH2, and SGMNENH2 are shown in Figure 8. According to the results, G shows a narrow and sharp diffraction peak at 26.1°, which indicates an interlayer distance of 0.34 nm. GO shows a broader and weaker peak at diffraction angle of 10.3° with interlayer distance of 0.85 nm. Increase of interlayer spacing is due to the presence of oxygen functionalities in the interlayer upon the oxidation process and reducing the stacking order of layers. In the oxidation process, size of sp^2 -hybridized domains was decreased and oxygen-containing groups were created at the surface and edge of layers [55, 56]. A broader diffraction pattern of GO, FGO, and SFGO in comparison with the original graphite originates from destruction of graphitic layers during the oxidation and grafting of HDBTMSPU at the surface of GO and SiO_2 at the surface of FGO [57]. Silane-functionalization and attachment of SiO_2 prevents from restacking of the graphene layers [58]. These broad peaks are located at diffraction angles of near to the graphite diffraction peak, which may be due to partial reduction of GO by grafting reactions [57]. In the case of SGEH2, amorphous nature of hybrid structures composed of graphene, epoxy resin, and silica/siloxane network results in a broad diffraction peak in the region of 12–30°. Hybrid structure composed from SFGO, MER, MNR, and silica/siloxane network in SGNEH2 and the other hybrid structure composed

Figure 7. TGA and DTG thermograms of (a) CER, MERH, SGEH1, and SGEH2, (b) CER, MERH, CNR, SGNEH1, and SGNEH2, and (c) CNR, CENR, SGMNENH1, and SGMNENH2

from SFGO, MNR, ENR, and silica/siloxane network in SGMNENH2 results in similar diffraction patterns. Absence of the broad peak of SFGO in the hybrid composites spectra can be attributed to the complete exfoliation of SFGO in the cured matrices [55, 59].

Figure 9 shows SEM images of SiO_2 and SFGO in various magnifications. Images were recorded by precipitation of a thin sample layer on a mica surface using a spin coater. As shown in Figure 9a, spherical aggregated silica nanoparticles with uneven and bumpy surface can be observed. Figure 9b and 9c

Figure 8. XRD results for G, GO, FGO, SFGO, SGEH2, SGNEH2, and SGMNENH2

shows that grafting of SiO_2 at the surface of graphene was done successfully, which results in a coarse graphitic surface after modification with $\text{SiO}_2\text{-NH}_2$. TEM images of SiO_2 and SFGO are shown in Figure 10. Samples were prepared by putting a drop of samples dispersion in ethanol on a lacy carbon grid. According to Figure 10a, SiO_2 with size in the range of 5–10 nm formed aggregated structures. After modification of GOFA with $\text{SiO}_2\text{-NH}_2$, graphene layers were surrounded with SiO_2 .

4. Conclusions

Here, surface modification of GO by HDBTMSPU and APTES-modified silica were carried out to obtain SFGO. After modification of epoxy with TEOS oligomer and novalac resin with GPTMS and epichlorohydrine, sol-gel method and final curing were employed for incorporation of SFGO and modified resins into hybrid composite structures. XPS, FT-IR, SEM, and TEM results show that grafting of $\text{SiO}_2\text{-NH}_2$ onto FGO and formation of SFGO were done effectively. In addition, final curing reaction of epoxy groups by ethylenediamine was also approved by FT-IR. Broader XRD peak in GO, FGO, and SFGO in comparison with graphite shows that layers were destructed under the oxidation and grafting processes. TGA results show that modification of GO results in increase of char yield due to reduction of oxygen functionalities of GO. By modification of ER by TEOS oligomer and hybrid network formation with SFGO, maximum degradation temperature was shifted to higher temperature and char yield partially increased. In addition, by incorporation of MNR into MER and SFGO hybrid, onset of decomposition was

Figure 9. SEM images of (a) silica and (b and c) SFGO in various magnifications

Figure 10. TEM images of (a) silica and (b) SFGO

shifted to lower temperatures and char content was increased considerably. Additionally, by incorporation of ENR into hybrid network with MNR and SFGO, char residue and thermal degradation temperature were increased considerably. Comparing three hybrid networks shows that increasing SFGO content in hybrid composites results in higher char contents. Incorporation of novolac resin into the hybrid networks results in higher char contents and also higher degradation temperatures. The SGMNENH with 2 wt% of SFGO shows the highest degradation temperature and the SGNEH with 2 wt% of SFGO shows the highest char residue.

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