Organic-inorganic nanohybrids of novolac phenolic resin and carbon nanotube: high carbon yields by using carbon nanotube aerogel and resin incorporation into aerogel network

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ABSTRACT

CNTCOOH was prepared from oxidation of carbon nanotube. Subsequently, CNTSi was prepared by grafting (3-glycidyloxypropyl) trimethoxysilane (GPTES) to the surface of CNTCOOH by a ring opening reaction of epoxy groups. Then, CNTA was obtained by formation of silicon oxide network between CNTSi and tetraethyl orthosilicate (TEOS). Finally, CNTA was used as an additive in novolac resin matrix to yield RCNTA composites with high carbon yield values. Additionally, modification of novolac resin by GPTES gives MR with silicon ethoxide moieties on its structure. Then, MRCNTA composites were obtained by

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formation of silica/siloxane network from MR, CNTSi, and TEOS. RCNTA composites were thermally compared with MRCNTA composites. Results from Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and thermogravimetric analysis showed that CNT and novolac resin were successfully modified. Aerogel formation was proved by Raman, X-ray diffraction, and scanning and transmission electron microscopies. BET shows that incorporation of CNT into the aerogel network results in lower cumulative pore volume value. The pore size of SA and CNTA ranges from 2 to about 100 nm which shows that both of them can be included in the mesoporous materials category. Finally, MRCNTA composites reached to the maximum increase of char yields; 11.94% increase of char yield was achieved by MRCNTA4 composite.

Keywords: Novolac phenolic resin; Carbon nanotube aerogel; Carbon yield.

1. Introduction

Phenolic resins are synthesized from a phenol and an aldehyde in two forms of resol and novolac, which are different in phenol and formaldehyde ratio and also type of catalyst. Phenolics can be used in ablative thermal protection applications as thermal resistant thermosets. Structural modification of phenolics results in high thermal stability, flame retardancy, oxidation resistance, and high carbon yield values. In this context, boron and phosphorous compounds [1-5] and inorganic materials [6-9] are some important examples of structural modifiers of phenolics. In the case of boron compounds, boron phenolic resin which is synthesized from boric acid, phenol, and formaldehyde is thermally resistant due to a greater quantity of B–O–Ph structures with higher bonding energy of B–O with respect to C–C [2]. Also, thermal resistant hyperbranched polyborate (HBPB) is another boron compound which improves processability, thermal stability, and toughness of phenolic resins matrix. Increase of char content by the addition of HPBP can be attributed to the higher thermal stability of HBPB and formation of BC_3 and B_2O_3 which promotes graphitization [2, 3]. Additionally, thermal properties of phenolics can be improved by addition of carbon fillers of graphene and nanotube (CNT) [10-13].

Polymer matrices can be improved remarkably in their thermal, mechanical, physical, and other characteristics by incorporation of metal oxide clusters via coupling agents [14, 15]. Additive content, its dispersion quality, and its interaction with the polymer matrix are important factors in properties of such products. Sol-gel process is one of the common methods for preparation of these hybrid materials, which provides the possibility of polymer chains incorporation into silica domains. Inorganic domains are formed from the hydrolysable alkoxysilanes. Interconnected networks are formed by using appropriate coupling agents which provide covalent bonding between a polymer matrix and inorganic domains. According to the

studies of Haraguchi et al., sol-gel process is used to incorporate inorganic parts into the phenolic resins to modify their physical properties [6, 7]. Ma et al. also used similar routes for this purpose [8].

Sol-gel process is commonly used for synthesis of silica-based mesoporous materials known as aerogels. Silica aerogels because of high porosity, large pore volume, low density, and high surface area were commonly used as thermal and acoustic insulators in hybrid composites with polymers [16, 17]. Microstructure of aerogels is constructed by hydrolysis and condensation processes, which is mainly controlled by pH of the reaction medium. At lower pH values, higher hydrolysis rates results in a highly extended network structures. In contrast, higher condensation rates results in a highly condensed structures at higher pH values [8]. Water content, temperature, and drying methods are other important factors in determination of aerogels microstructure. Reinforcement of silica aerogels was previously carried out by multifunctional coupling agents of alkoxysilanes [18]. Also, alkoxysilanes were used to incorporate SWCNT and graphene into the silica aerogel network for improving its mechanical properties [19, 20].

Although some efforts have been made to prepare phenolic resins with high char yields, but there is not any report on incorporation of resin chains into a network to increase its char yield. Here, phenolic resin chains were incorporated into a CNT-containing silica/siloxane network. To this end, alkoxysilane-modified phenolic resin and alkoxysilane-modified CNT form a network in the presence of tetraethyl orthosilicate by hydrolysis and silica/siloxane bonds formation. Char yield of the formed hybrid was compared with CNT-containing silica aerogel (CNTA)-loaded phenolic resin. Thus, (3-glycidyloxypropyl) trimethoxysilane was used as alkoxysilane to increase the compatibility between the organic and inorganic phase. Increase of carbon yield

value of the phenolic resin and also comparison of the two methods to reach higher carbon yield values are the main objectives of this work. Designation of samples is given in Table 1.

Table 1

2. Experimental

2.1. Materials

Multi-walled CNT (Shenzhen Nanoport Company, China), novolac resin (IP502, Resitan), furfuryl alcohol (Sigma-Aldrich, 98%), hexamethyltetramine (HMTA, Sigma-Aldrich, 99%), (3-glycidyloxypropyl) trimethoxysilane (GPTES, Aldrich, 99%), tetraethoxysilane (TEOS, Merck), hexamethyldisilazane (Aldrich, 99%), and nitric acid (HNO_3 , Merck) were used as received.

2.2. Oxidation of CNT to obtain CNTCOOH

CNTCOOH was prepared from acid treatment of CNT. Due to the harsh acidic conditions, oxidation and solubilization of amorphous carbon originating from CNT synthesis in combination with the removal of catalytic metal impurities have been carried out [21]. Accordingly, CNT (2.0 g) was agitated in a 60% HNO_3 aqueous solution (100 mL) under reflux for 24 h. Then, filtration of the paste through a 0.2- μm PTFE filter and drying in a vacuum at 50 °C yield CNTCOOH. Finally, carboxyl functional groups were created on the convex surface and end caps of CNT.

2.4. Functionalization of CNTCOOH by GPTES to yield CNTSi

GPTES was grafted to the surface of CNTCOOH by ring opening reaction of its epoxy groups [8]. Accordingly, CNTCOOH (0.2 g) and ethanol (40 mL) were stirred in a flask for 24 h and then ultrasonically agitated for 30 min by a bath sonicator. Subsequently, GPTES (2 in 10 mL in

ethanol) and KOH (1 mg) were added into the flask and stirring was continued at 70 °C for 24 h. Then, the mixture was filtered through a 0.2 µm PTFE filter and washed with ethanol for three times. Finally, drying the product in oven at 60 °C gives CNTSi (0.16 g, 80%).

2.5. Preparation of CNTA and SA

CNTA was prepared by an acid-catalyzed sol-gel process. CNTASi (0.25 g) and furfuryl alcohol (8 mL) were stirred in a flask for 24 h and then ultrasonically agitated for 30 min by a bath sonicator to reach a homogeneous mixture. Then, TEOS (1.25 g) and deionized water (0.024 g) were added to the flask. Subsequently, HCl was added in 0.03 wt% of the solution as the catalyst and stirring was continued for 1 h. Finally, the mixture was hold at the room temperature for 12 h and 60 °C for 72 h to reach CNTA. SA was also prepared by an acid-catalyzed sol-gel process similar to GA. Accordingly, TEOS (1.25 g) and deionized water (0.024 g) were added to a flask and after stirring for 30 min, HCl was added in 0.03 wt% of the solution as the catalyst. For simplification of drying process, surface modification was carried out by immersion of the product in hexamethyldisilazane (1.10 mL) and *n*-hexane (10 mL) for 24 h. SA was obtained after washing the product with *n*-hexane for three times and drying the product at 50 °C for 3 h, 150 °C for 2 h, and 200 °C for 1 h.

2.6. Modification of novolac resin with GPTES to yield MR

Novolac resin modification was carried out by a ring opening reaction between epoxy groups of GPTES and hydroxyl groups of novolac resin, as reported previously [8]. Novolac resin (5 g) was dissolved in THF (5 mL) in a flask. Subsequently, GPTES (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 CNTSi/MR composites.

2.7. Preparation of RCNTA and MRCNTA composites

For preparation of RCNTA samples, calculated amounts of CNTA (0.1 and 0.2 g for 2 and 4 wt % respectively) and furfuryl alcohol (5 mL) were stirred in a flask for 24 h and then ultrasonically agitated for 30 min by a bath sonicator to reach a homogeneous mixture. Resin compounds were obtained by the addition of novolac resin solution (5 g resin in 5 mL furfuryl alcohol) and 0.7 g HMTA to the mixtures after agitation for 24 h. The compounds are molded and cured as follows [8]: the mold temperature was increased to 80 °C by the rate of 2 °C/min for drying the samples and remained in this state for 2 h. Then, the mold 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. In the case of MRCNTA composites, calculated amounts of CNTSi (0.1 and 0.2 g for 2 and 4 wt % respectively) and furfuryl alcohol (8 mL) were stirred in a flask for 24 h and then ultrasonically agitated for 30 min by a bath sonicator to reach a homogeneous mixture. Modified novolac resin solution (5 g modified resin in 5 mL THF) and HMTA (0.7 g) were added into the flask and agitated for 24 h. In a beaker, TEOS (1.25 g) and deionized water (0.024 g) were agitated. HCl was added in 0.03 wt% of the solution as the catalyst and stirring was continued for 1 h. The resin compounds were obtained by the addition of flask and beaker contents. The compounds were molded and cured as the procedure used for CNTA.

2.8. Characterization

A Fourier transformed infrared (FTIR) spectrophotometer (Bruker, Germany) was used to collect the spectra at a 4 cm⁻¹ resolution. An average of 24 scans for each sample was taken in a constant cell pathlength at room temperature. Samples were dispersed in KBr pellets and dried in vacuum desiccators.

Surface composition of the samples was analyzed by an X-ray photoelectron spectroscopy (XPS, Gammatdata-Scienta Esca 200) equipped with an Al K α (1486.6 eV photons) x-ray source in an ultra high vacuum at pass energies of 20 and 100 eV for region and survey scan spectra.

Raman spectra were obtained on a Senterra Dispersive Raman spectroscope (Bruker Optics, Germany) fitted with a 785 nm laser source, a CCD detector, and a confocal depth resolution of 2 μm . Laser power at the sample and spectral resolution was 50 mW and 3-5 cm^{-1} respectively. The laser beam was focused on the sample using an optical microscope.

Powder X-ray diffraction (XRD) spectra were recorded by a D5000 X-ray diffractometer (Siemens, Germany) equipped with a scintillation counter and Cu K α radiation ($\lambda=0.1540\text{ nm}$) at an accelerating voltage of 35 kV and a current of 20 mA. Samples were scanned from 10 to 80° at the step scan mode. The basal spacing of the samples was calculated using the Bragg's equation ($\lambda=2d\sin \theta$).

Thermo gravimetric analysis (TGA) was carried out with a PL thermal analyzer (Polymer Laboratories, TGA 1000, Shropshire, UK) on a sample of about 10 mg. All TGA data were recorded from ambient temperature to 600 °C at a heating rate of 10 °C/min and under N₂ atmosphere at a flow rate of 50 mL/min.

Nitrogen gas adsorption and desorption measurements were carried out using a Micromeritics ASAP 2010 surface analyzer (Micromeritics Instrument Corporation, USA) at 76.09 K. Adsorption-desorption isotherms, BET (Brunauer-Emmett-Teller) and Langmuir specific surface area, BJH (Barret-Joyner-Halenda) surface/volume mesopore analysis were obtained. Removal of any adsorbed species from the samples was carried out prior to the analysis at 250 °C and low vacuum for 12 h.

Morphology of CNT, SA, and CNTA samples was studied by scanning electron microscopy (Vega Tescan SEM instrument, Czech Republic). The specimens were prepared by precipitation of a thin sample layer on a mica surface using a spin coater (Modern Technology Development Institute, Iran) and its subsequent gold-coating using a sputtering coater.

The transmission electron microscope (Philips EM 208, Eindhoven, the Netherlands) with an accelerating voltage of 80 kV was used to study the morphology of CNT and CNTA. Specimens were prepared by deposition of a thin sample layer on lacy grades from the ultrasonically agitated sample and ethanol dispersions.

Figure 1

Figure 2

3. Results and discussion

CNT and silicon oxide moieties were incorporated into novolac resin matrix by two different methods for increasing carbon yield value of novolac matrix. As shown in Figure 1, CNTCOOH was prepared from oxidation of CNT. Subsequently, CNTSi was prepared by grafting GPTES to the surface of CNTCOOH by a ring opening reaction of epoxy groups in the presence of KOH as catalyst. Then, CNTA was obtained by formation of silicon oxide network between CNTSi and TEOS. Finally, CNTA was used as an additive in novolac resin matrix to increase its carbon yield value. In the second procedure as shown in Figure 2, modification of novolac resin by GPTES gives MR with silicon ethoxide moieties on its structure. Subsequently, MRCNTA composites were obtained by formation of silicon oxide network from MR, CNTSi, and TEOS. This finally results in incorporation of novolac resin and CNT into a hybrid material.

FTIR spectra of CNTCOOH, CNTSi, CNTA, R, MR, RCNTA2, and MRCNTA2 are shown in Figure 3. In comparison with CNTCOOH, CNTSi shows intensified stretching vibration of C–H units in the region of 2837–2980 cm^{-1} as a result of CH_2 units of GPTES [22, 23]. CNTSi also shows two bands at 1020 and 1445 cm^{-1} assigned to C–O–C group and methylene C–H bending vibration of GPTES respectively [24, 25]. The appearance of the intense band at 1089 cm^{-1} which is assigned to the vibration of the Si–O–C group of GPTES or hydrolyzed Si–O–Si groups provided more evidence for successful modification process [24, 26]. Asymmetric stretching of Si– CH_2 is observed at 801 cm^{-1} for CNTSi and CNTA [27, 28]. CNTA shows a band at 1615 cm^{-1} which confirms remaining of carbon double bonds in the aerogel structure. The bands at about 1621 and 1092 cm^{-1} for R, MR, RCNTA2, and MRCNTA2 are ascribed to stretching vibration of carbon double bonds and C–O vibration of phenol groups respectively [10, 29, 30]. According to the fact that different hydroxyl group types are generated by the ring opening reaction after modification of R with GPTES, appearance of hydroxyl peak in 3000–3700 cm^{-1} varies [8]. A peak at 1048 cm^{-1} is assigned to Si– OC_2H_5 vibration of GPTES moieties. These observations clearly show that GPTES moieties are successfully attached to the backbone of R. The vibration of Si–O groups is also observed in RCNTA1 and MRCNTA1 spectra at 1015 cm^{-1} , which confirms the presence of siloxane (or silica) network in both of the samples.

Figure 3

Figure 4

XPS was used to evaluate surface elemental composition of CNTSi, as shown in Figure 4. Survey scan spectrum for CNTSi is displayed in Figure 4 (A). Additionally, Si 2p and O 1s core-level spectra of CNTSi are presented at higher resolution. Appearance of the bands for Si 2p at 104.7 and Si 2s at 157.8 eV is a result of successful functionalization of CNTCOOH with

GPTES moieties by ring opening of epoxy groups [31, 32]. In Figure 4 (B), C 1s core-level spectrum is deconvoluted to five distinguished peak components of C–Si at 285.7, C=C and C–C at 286.2, C–O at 286.7, C=O at 287.3, and O–C=O at 288.2 eV. Appearance of C–Si component at 285.7 eV is another confirmation for the successful grafting of GPTES moieties [33-35]. Table 2 summarizes the results of XPS as the amount of each functional group and atom content. Carbon to oxygen ratio is decreased after functionalization of CNT, which is a result of oxidation of CNT and its functionalization with GPTES moieties with a large amount of oxygen atoms.

Table 2

As shown in Figure 5, Raman spectroscopy is used to study the graphitic lattice structure of CNTs in CNT, CNTCOOH, CNTSi, and CNTA. The band of radial breathing mode at 265 cm^{-1} indicates diameter distribution of CNTs [36]. Moreover, three characteristic bands of D at 1311 cm^{-1} (the breathing mode of κ -point phonons of A_{1g} symmetry), G at 1578 cm^{-1} (the first order scattering of the E_{2g} phonons of sp^2 -carbon atoms), and 2D at 2640 cm^{-1} (the stacking order of carbon layers) can be observed [22, 37]. D band is referred to the disorder mode and G band is attributed to the ordered aromatic domains and therefore they are widely attributed to sp^3 - and sp^2 -hybridized carbons on the sidewall respectively [38]. CNT shows D and G bands at 1316 and 1589 cm^{-1} respectively. The intensity ratio of the D and G bands (I_D/I_G) is reciprocally related to the graphitic crystallite size [24, 37]. I_D/I_G values of 0.17, 0.38, 0.26, and 2.22 are obtained from peak area for CNT, CNTCOOH, CNTSi, and CNTA respectively. According to the results, decrease of I_D/I_G value of CNTCOOH by GPTES modification from 0.38 to 0.28 results from covalent attachment of GPTES moieties [24, 37]. Covalent bonding may cause in variation of Raman intensity change as a result of variation of carbon atoms hybridization [39]. Raman spectrum of CNTA differs from the spectra of CNT, CNTCOOH, and CNTSi. Decrease of 2D

band intensity, increase of D band intensity, severe decrease of G band intensity, and also appearance of some peaks at below 1000 cm^{-1} can be an evidence for aerogel formation. Severe increase of I_D/I_G to the value of 2.22 upon the formation of aerogel shows that size of continuous areas of sp^2 carbon is very small, while sp^3 carbon is dominant. Additionally, the peaks at 536 and 1047 cm^{-1} are assigned to Si–O network [40, 41] and the bands at 745 and 954 cm^{-1} are attributed to Si–C group [42, 43].

Figure 5

XRD results of CNTCOOH, CNTSi, CNTA, RCNTA2, MRCNTA2, RCNTA4, and MRCNTA4 are displayed in Figure 6. Accordingly, CNTCOOH and CNTSi exhibit two characteristic peaks at 26.5° and 44.2° which are attributed to the graphite (002) and (101) reflection respectively [44-46]. CNTA shows a broad peak at diffraction angle of 20.13° which originates from the coherent diffraction of Si–O based domains and is an evidence for the formation of aerogel structure [47-49]. It is also observed that no characteristic peak of CNTSi is displayed in the diffraction pattern of CNTA, which is an indication of a good dispersion of CNTs in the aerogel matrix [50, 51]. In the case of CNTA/novolac composites, the amorphous peak at around 19.6° is characteristic of phenolic resin [52].

Figure 6

Figure 7

Thermogravimetric analysis results for various CNTs, SA, R, and its composites are presented in Figure 7 and Table 3. According to the results of Figure 7 (A), CNT is almost stable till 600°C with char yield of about 98.5%. CNTCOOH exhibits its mass loss in the region of $100\text{-}300^\circ\text{C}$ as a result of decomposition of its carboxyl groups and finally reaches to char yield of 94.9%.

Modification of CNTCOOH with GPTES results in a lower char yield of 86.5 %, which is ascribed to the degradation of GPTES moieties. Considering that CNTCOOH and CNTSi reach to a constant char yield near 500 °C, the difference between their char yields can be related to the degradation of grafted GPTES moieties in CNTSi. Consequently, degradation value of about 8.4 wt% can be estimated as grafting quantity of GPTES. SA displays its mass loss in the region of 325-575 °C as a result of decomposition of its carbon containing groups and finally reaches to char yield of 90.8%. Interestingly, weight loss and its derivative thermograms for CNTA are different from CNT, CNTCOOH, CNTSi, and also SA. CNTA decomposition occurs at two steps. The weight loss of about 19.4% at 192.3 °C can be assigned to the decomposition of unreacted carboxylic groups (similar to CNTCOOH decomposition pattern) and also remained solvent in the pores according to the incomplete solvent exchange reactions. However, 24.4% degradation at 430.1 °C relates to carbon skeleton degradation and also pyrolysis of Si–O groups in aerogel network (similar to SA decomposition pattern) [20, 48]. DTG thermogram of GA (Figure 7(C)) shows that the second degradation step is placed at lower temperatures compared with SA, which is resulted from decomposition of carbon skeleton. The weight ratio of GPTES moieties at the surface of CNTCOOH is calculated to be 9.17×10^{-2} using Equation 1 [22, 53].

$$G_{r,GPTES}(\text{weight ratio of GPTES on CNTCOOH}) = \frac{w\%_{GPTES}}{100 - w\%_{GPTES}} \quad (1)$$

where, $w\%_{GPTES}$ denotes the weight loss of CNTSi. By dividing $G_{r,GPTES}$ to the molecular weight of GPTES ($236.34 \text{ g.mol}^{-1}$), molar ratio of GPTES moieties at the surface of CNTCOOH is calculated to be $388 \text{ } \mu\text{mol/g}$.

Table 3

According to the results of Figure 7 (B), char yield of CR is increased from 55.29 to 63.58% by the addition of 2 wt% of CNTA. However, resin modification with GPTES results in a higher char yield of 67.23% in the presence of 4 wt% of CNTSi. This clearly shows that char yield not only increases by the addition of CNTA content, but also it is increased by structural modification of novolac resin and its incorporation into the CNT-containing silica aerogel network. Covalent bonding between of GPTES and CNTs in CNTSi and also GPTES and novolac resin in MR, and finally silica network formation between MR, CNTSi, and TEOS results in a hybrid composite with covalent interaction between the fillers and novolac matrix. Subsequent curing of the composite gives a product with a high char yield and thermal degradation point. In comparison, CNTA-loaded composites show lower char contents because of physical interaction between the novolac matrix and filler. Thermal stabilities of the composites are higher than R and it increases by the addition of CNTA content.

A comparison is carried out between this new hybrid composite and other novolac resins with a focus on their char yield (Table 4). Table 4 shows increase of carbon yield value in various novolac resins with the addition of chemical additives or nanofillers. Commonly, boron- and phosphorous-containing chemicals were used in chemical additives method in a large content compared with the nanofiller method. According to the presented data, 11.94% increase of char yield is achieved only by the addition of 4 wt% of CNTSi and also silica aerogel network formation. We propose that the final carbon yield value of this resin network can be increased by using resins with higher char yields or using structural modified resins with boron- or phosphorous-containing materials. It is an ongoing work in our group to use a structural-modified phenolic resin with boron and silane moieties to form aerogel with furfuryl alcohol-

and silane-modified CNTCOOH for more increase of final carbon yield value. It is expected to reach a higher carbon yield values in comparison with MRCNTA4.

Table 4

Figure 8

As shown in Figure 8 (A, B), microstructure of SA and CNTA are investigated by multilayer nitrogen adsorption-desorption isotherms at 76.11 K. The isotherms are type IV with a pronounced type H3 hysteresis loop attributed to the capillary condensation and suggesting mesoporous structures [49, 54]. According to IUPAC, pores with diameters in the range of 2 and 50 nm are mesopores. Micropores are pores with diameters less than 2 nm and pores with diameters larger than 50 nm are macropores [55]. The similarity in the type and shape of isotherms originates from the similar aerogel structures in SA and CNTA. According to the rapid increase of N₂ adsorption at low relative pressures, SA and CNTA contain a little amount of micropores [28, 55]. Cumulative pore volume plot and also pore size distribution curve, dV/dD as a function of D, are obtained from the Barret-Joyner-Halenda (BJH) method using nitrogen adsorption-desorption data [56] and the curves for SA and CNTA are shown in Figure 8 (C and D). Interestingly, incorporation of CNT into the aerogel network results in lower cumulative pore volume value. The pore size of SA and CNTA ranges from 2 to about 100 nm; however, size of a large number of pores is between 2 and 10 nm in both of them. This shows that SA and CNTA can be included in the mesoporous materials category. Considering cylindrical pore geometry, pore diameter of a material can be estimated from the volume of the gas required to fill all the pores as $D=4V_p/S_{BET}$, where D is the average pore diameter and V_p is the pore volume [57-59]. BET and Langmuir surface area (S_{BET} and S_{Langmuir}) for SA and GA (SI: Figure 1 (A) and (B)) Specific surface area by BJH methods, pore volumes, and pore diameters are calculated from the

BET, Langmuir, and BJH plots and the results are presented in Table 5. Accordingly, the average pore sizes of 5.90 and 2.51 respectively for SA and CNTA show their mesoporous structure. High surface area and suitable pore size are characteristics of both SA and CNTA products.

Table 5

SEM images of CNT, CNTA, and SA are shown in Figure 9 (A-E). SEM results were recorded by precipitation of a thin sample layer on a mica surface using a spin coater. Figure 9 (A) shows CNTs with diameter of about 20 nm and length in the range of several micrometers. Figures 9 (B-D) show that CNTs are incorporated into the spongy silica aerogel matrix. In Figure 9 (E), spongy spherical SA particles with uniform size distribution in the aggregated form are observed which is characteristic of aerogel materials [28, 60, 61].

Figure 9

TEM images of CNT and CNTA are shown in Figure 10 (A, B). TEM results were obtained by putting a drop of CNT and CNTA dispersion in ethanol on a lacey carbon grid. Figure 10 (A) shows tubular structure of CNT with smooth surface and diameter of about 20 nm and length in the range of several micrometers. Interestingly, silica aerogel network in the presence of CNTs can easily be observed in the Figures 10 (B). Accordingly, silica aerogel has porous structure; whereas, CNTs are incorporated in silica aerogel network uniformly.

Figure 10

4. Conclusions

CNTSi was prepared by grafting GPTES to the surface of CNTCOOH by a ring opening reaction of epoxy groups. Then, CNTA was obtained by formation of silicon oxide network between

CNTSi and TEOS. Finally, CNTA was used as an additive in novolac resin matrix. Additionally, modification of novolac resin by GPTES gives MR. Then, MRCNTA samples were obtained by formation of silicon oxide network from MR, CNTSi, and TEOS. The product obtained from addition of CNTA in the novolac matrix was thermally compared with the composite obtained from the engagement of CNTSi and MR in silicon oxide network. Successful modification of CNTCOOH by GPTES moieties was confirmed by Si–O stretching and intensified stretching vibration of C–H units in FTIR and also appearance of XPS bands for Si 2p and Si 2s. Decrease of I_D/I_G value of CNTCOOH in Raman spectra by GPTES modification from 0.38 to 0.28 results from covalent attachment of GPTES moieties. Decrease of 2D band intensity, increase of D band intensity, severe decrease of G band intensity, and also appearance of some peaks at below 1000 cm^{-1} can be an evidence for aerogel formation in CNTA. CNTA shows a broad XRD peak at diffraction angle of 20.13° which originates from the coherent diffraction of Si–O based domains. Degradation value of about 8.4 wt% in CNTSi can be estimated as grafting quantity of GPTES. Decomposition of CNTA occurs at two steps with weight loss of about 19.4 and 24.4% assigned to the decomposition of remained oxygen functionalities, pyrolysis of Si–O groups, and also carbon skeleton degradation. Char yield of CR is increased from 55.29 to 63.58% by the addition of 2 wt% of CNTA. However, resin modification with GPTES results in a higher char yield of 67.23% in the presence of 4 wt% of CNTSi. Therefore, 11.94% increase of char yield is achieved only by the addition of 4 wt% CNTSi and also silica aerogel network formation. Incorporation of CNT into the aerogel network results in lower cumulative pore volume value. The pore size of SA and CNTA ranges from 2 to about 100 nm which shows that both of them can be included in the mesoporous materials category. SEM and TEM images show that CNTs with smooth surface are incorporated into the spongy silica aerogel matrix.

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6. References

- [1]. Y. Liu, X. Jing, Carbon 45 (2007) 1965–1971.
- [2]. P. Xu, X. Jing, Polym. Eng. Sci. 50 (2010) 1382–1388.
- [3]. P. Xu, X. Jing, Polym. Adv. Technol. 22 (2011) 2592–2595.
- [4]. K. Haraguchi, Y. Usami, Y. Ono, J. Mater. Sci. 33 (1998) 3337–3344.
- [5]. K. Haraguchi, Y. Usami, K. Yamamura, S. Matsumoto, Polymer 39 (1998) 6243–6250.
- [6]. S. Wang, X. Jing, Y. Wang, J. Si, Polym. Degrad. Stab. 99 (2014) 1–11.
- [7]. G.H. Hsiue, S.J. Shiao, H.F. Wei, W.J. Kuo, Y.A. Sha, J. Appl. Polym. Sci. 79 (2001) 342–349.
- [8]. C.L. Chiang, C.C.M. Ma, D.L. Wu, H.C. Kuan, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 905–913.
- [9]. J.M. Lin, C.C. Ma, F.Y. Wang, H.D. Wu, S.C. Kuang, J. Polym. Sci. Part B: Polym. Phys. 38 (2000) 1699–1706.
- [10]. H. Roghani-Mamaqani, V. Haddadi-Asl, M. Mortezaei, K. Khezri, J. Appl. Polym. Sci. 131 (2014) 40273.
- [11]. X. Zhao, Y. Li, J. Wang, Z. Ouyang, J. Li, G. Wei, Z. Su, ACS Appl. Mater. Interfaces 6 (2014) 4254–4263.
- [12]. B.J. Cui, Y. Yan, J. Liu, Q. Wu, Polym J. 40 (2008) 1067–1073.

- [13]. L. Liu, Z. Ye, Polym. Degrad. Stab. 94 (2009) 1972–1978.
- [14]. J. Wen, G.L. Wilkes, Chem. Mater. 8 (1996) 1667–1681.
- [15]. U. Schubert, N. Huesing, A. Lorenz, Chem. Mater. 7 (1995) 2010–2027.
- [16]. M. Reim, W. Körner, J. Manara, S. Korder, M. Arduini-Schuster, H.P. Ebert, J. Fricke, Solar Energy 79 (2005) 131–139.
- [17]. V. Gibiat, O. Lefevre, T. Woignier, J. Pelous, J. Phalippou, J. Non-Crystalline Solids 186 (1995) 244–255.
- [18]. J. Li, F. Wang, C. Liu, J. Colloid Interf. Sci. 382 (2012) 13–16.
- [19]. Y. Zhang, Y. Shen, D. Han, Z. Wang, J. Song, L. Niu, J. Mater. Chem. 16 (2006) 4592–4597.
- [20]. H. Yang, F. Li, C. Shan, D. Han, Q. Zhang, L. Niu, A. Ivaska, J. Mater. Chem. 19 (2009) 4632–4638.
- [21]. I.D. Rosca, F. Watari, M. Uo, T. Akasaka, Carbon 43 (2005) 3124–3131.
- [22]. H. Roghani-Mamaqani, V. Haddadi-Asl, M. Ghaderi-Ghahfarrokhi, Z. Sobhkhiz, Colloid Polym. Sci. 292 (2014) 2971–2981.
- [23]. H. Hemmatpour, V. Haddadi-Asl, H. Roghani-Mamaqani, Polymer 65 (2015) 143–153.
- [24]. H. Roghani-Mamaqani, V. Haddadi-Asl, K. Khezri, M. Salami-Kalajahi, Polym. Int. 63 (2014) 1912–1923.
- [25]. H. Roghani-Mamaqani, V. Haddadi-Asl, K. Khezri, E. Zeinali, M. Salami-Kalajahi, J. Polym. Res. 21 (2014) 333.
- [26]. H. Roghani-Mamaqani, V. Haddadi-Asl, Polym. Compos. 35 (2014) 386–395.
- [27]. X. Pu, H.B. Zhang, X. Li, C. Gui, Z.Z. Yu, RSC Adv. 4 (2014) 15297–15303.

- [28]. S.A. Mirshafiei-Langari, V. Haddadi-Asl, H. Roghani-Mamaqani, M. Sobani, K. Khezri, *Polym. Compos.* 34 (2013) 1648–1654.
- [29]. F.Y. Yuan, H.B. Zhang, X. Li, H.L. Ma, X.Z. Li, Z.Z. Yu, *Carbon* 68 (2014) 653–661.
- [30]. M. Li, H. Song, X. Chen, J. Zhou, Z. Ma, *Phys. Chem. Chem. Phys.* 17 (2015) 3250–3260.
- [31]. Z. Li, R. Wang, R.J. Young, L. Deng, F. Yang, L. Hao, W. Jiao, W. Liu, *Polymer* 54 (2013) 6437–6446.
- [32]. H. Roghani-Mamaqani, V. Haddadi-Asl, K. Khezri, M. Salami-Kalajahi, M. Najafi, *Polym. Eng. Sci.* 55 (2015) 1720–1732.
- [33]. H. Yang, C. Shan, F. Li, D. Han, Q. Zhang, L. Niu, *Chem. Commun.* (2009) 3880–3882.
- [34]. W. Li, X.Z. Tang, H.B. Zhang, Z.G. Jiang, Z.Z. Yu, X.S. Du, Y.W. Mai, *Carbon* 49 (2011) 4724–4730.
- [35]. H. Roghani-Mamaqani, V. Haddadi-Asl, K. Khezri, M. Salami-Kalajahi, M. Najafi, M. Sobani, S.A. Mirshafiei-Langari, *Iran. Polym. J.* 24 (2015) 51–62.
- [36]. H. Peng, L.B. Alemany, J.L. Margrave, V.N. Khabashesku, *J. Am. Chem. Soc.* 125 (2003) 15174–15182.
- [37]. H. Roghani-Mamaqani, V. Haddadi-Asl, K. Khezri, M. Salami-Kalajahi, *RSC Adv.* 4 (2014) 24439–24452.
- [38]. A.G. Souza Filho, A. Jorio, G.G. Samsonidze, G. Dresselhaus, R. Saito, M.S. Dresselhaus, *Nanotechnology* 14 (2003) 1130.

- [39]. C.S. Lee, S.E. Baker, M.S. Marcus, W. Yang, M.A. Eriksson, R.J. Hamers, *Nano Lett.* 4 (2004) 1713–1716.
- [40]. Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, I.T. McGovern, B. Holland, M. Byrne, Y.K. Gun'Ko, J.J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A.C. Ferrari, J.N. Coleman, *Nat. Nanotechnol.* 3 (2008) 563–568.
- [41]. P.D. Adhikari, S. Jeon, M.J. Cha, D.S. Jung, Y. Kim, C.Y. Park, *Sci. Technol. Adv. Mater.* 15 (2014) 015007.
- [42]. X. Qi, G. Zhai, J. Liang, S. Ma, X. Liu, B. Xu, *Cryst. Eng. Commun.* 16 (2014) 9697–9603.
- [43]. J. Wasyluk, T.S. Perova, S.A. Kukushkin, A.V. Osipov, N.A. Feoktistov, S.A. Grudinkin, *Mater. Sci. Forum.* 645 (2010) 359–362.
- [44]. M. Cochet, W.K. Maser, A.M. Benito, M.A. Callejas, M.T. Martinez, J.M. Benoit, J. Schreiber, O. Chauvet, *Chem. Commun.* (2001) 1450–1451.
- [45]. X. Yao, H. Wu, J. Wang, S. Qu, G. Chen, *Chem. Eur. J.* 13 (2007) 846–853.
- [46]. Z. Lei, Y. Yan, J. Feng, J. Wu, G. Huang, X. Li, W. Xing, L. Zhao, *RSC Adv* 2015;5:25650–25656.
- [47]. Y. Qian, P. Wei, P. Jiang, J. Liu, *Sol. Energy Mater. Sol. Cells* 107 (2012) 13–19.
- [48]. Z. Wang, P. Wei, Y. Qian, J. Liu, *Composites: Part B* 60 (2014) 341–349.
- [49]. W.Y. Cheng, C.C. Wang, S.Y. Lu, *Carbon* 54 (2013) 291–299.
- [50]. S.B. Yang, X.L. Feng, S. Ivanovici, K. Mullen, *Angew. Chem. Int. Ed.* 49 (2010) 8408–8411.
- [51]. L. Chen, X. Wang, X. Zhang, H. Zhang, *J. Mater. Chem.* 22 (2012) 22090–22096.

- [52]. C. Wu, X. Huang, G. Wang, X. Wu, K. Yang, S. Li, P. Jiang, J. Mater. Chem. 22 (2012) 7010–7019.
- [53]. V.G. Ngo, C. Bressy, C. Leroux, A. Margaillan, Polymer 2009;50:3095–102.
- [54]. S.A. Mirshafiei-Langari, V. Haddadi-Asl, H. Roghani-Mamaqani, M. Sobani, K. Khezri, J. Polym. Res. 20 (2013) 163.
- [55]. R.R. Kohlmeyer, M. Lor, J. Deng, H. Liu, J. Chen, Carbon 49 (2011) 2352–2361.
- [56]. E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373–380.
- [57]. M.E. Plonska-Brzezinska, A. Molina-Ontoria, L. Echegoyen, Carbon 67 (2014) 304–317.
- [58]. S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309–319.
- [59]. S. Yamanaka, G.W. Brindley, Clays Clay Minerals 27 (1979) 119–124.
- [60]. M. Sobani, V. Haddadi-Asl, M. Salami-Kalajahi, H. Roghani-Mamaqani, S.A. Mirshafiei-Langari, K. Khezri, J. Sol-Gel Sci. Technol. 66 (2013) 337–344.
- [61]. M. Sobani, V. Haddadi-Asl, S.A. Mirshafiei-Langari, M. Salami-Kalajahi, H. Roghani-Mamaqani, K. Khezri, Designed Monom. Polym. 17 (2014) 245–254.

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Table 1- Designation of samples

Sample	Description
TEOS	Tetraethyl orthosilicate
GPTES	(3-glycidyloxypropyl) trimethoxysilane
CNT	Carbon nanotube
CNTCOOH	Oxidized CNT
CNTSi	GPTES-functionalized CNTCOOH
CNTA	CNT-containing silica aerogel
SA	Silica aerogel
R	Novolac resin
MR	GPTES-functionalized R
CR	Cured R
RCNTAX	CNTA/R cured composite with X wt% of CNTA
MRCNTAX	CNTSi/MR cured composite with X wt% of CNTSi

Table 2- Surface elemental composition of CNT and CNTSi resulted from XPS (Data of CNT is extracted from reference [22])

CNT type	XPS data					
	Composition (%)				Ratio	
	O	C	N	Si	C/O	C/Si
CNT	15.44	84.56	----	----	5.47	----
CNTSi	32.61	64.72	----	2.67	1.98	24.24

Table 3- Summary of TGA results

Sample	CNTSi	CNTA	SA	CR	RCNTA2	MRCNTA2	RCNTA4	MRCNTA4
DTG peak point (°C)	386.2	192.3, 430.1	494.6	285.5, 448.1	454.4	452.9	481.0	460.5
Char (%)	86.5	55.6	90.8	55.29	63.58	61.68	66.24	67.23

Table 4- Increase of carbon yield values in various structural modification of novolac resins and nanofiller addition

Method	Resin char (%)	Final char (%)	Additive content (wt%)	Increase (%)	Ref
Boron chemical	64.2	75.4	10	11.2	[1]
Boron chemical	63.8	73.1	20	9.3	[2]
Boron chemical	63.8	78.4	80	14.6	[3]
Boron modification	63.0	76.4	10	13.4	[4]
Phosphorus modification	12	47	7.79	35	[5]
FA-modified GO	55.29	62.09	0.4	6.8	[10]
Reduced GO	55.25	63.25	1	8.0	[11]
Carboxylated MWCNT	59.6	62.7	0.95	3.1	[12]
MWCNT	66	72.2	1	5.2	[13]
CNTA-containing	55.29	63.58	2	8.29	This Work
CNTSi and sol-gel	55.29	67.23	4	11.94	This Work

Table 5- Detailed results of nitrogen adsorption-desorption isotherms for SA and CNTA

Sample	S_{BET} (m^2g^{-1})	S_{Langmuir} (m^2g^{-1})	S_{BJH}^1 (m^2g^{-1})	V_{BJH}^2 (cm^3g^{-1})	D_{BJH}^3 (nm)	$D_{\text{ave, BET}}^4$ (nm)
SA	857.2	1275.5	1082.5 ^a 1172.7 ^d	1.324 ^a 1.297 ^d	4.89 ^a 4.42 ^d	5.90
CNTA	382.46	670.18	176.37 ^a 192.88 ^d	0.1464 ^a 0.1486 ^d	1.21 ^a 1.64 ^d	2.51

¹ BJH adsorption (*a*) and desorption (*d*) cumulative surface area of pores

² BJH adsorption (*a*) and desorption (*d*) cumulative pore volume of pores

³ BJH adsorption (*a*) and desorption (*d*) average pore diameter (4V/A)

⁴ Average Pore Diameter (4V/A by BET)

Graphical Abstract

CNTA was obtained by silica/siloxane network formation between (3-glycidyloxypropyl) trimethoxysilane (GPTES)-modified CNT (CNTSi) and tetraethyl orthosilicate (TEOS). Then, it was used as an additive in novolac resin matrix to obtain RCNTA composites. MRCNTA composites were obtained by network formation of GPTES-modified resin, CNTSi, and TEOS. Finally, RCNTA and MRCNTA composites were thermally compared.