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Novolac phenolic resin and graphene aerogel organic-inorganic nanohybrids: High carbon yields by resin modification and its incorporation into aerogel network

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ABSTRACT

Graphene oxide (GO) modified with furfuryl alcohol and (3-aminopropyl) triethoxysilane (GOFASi) was used in two separate ways for preparation of novolac resin nanohybrids. In the first procedure, graphene-containing silica aerogel (GA) was obtained by incorporation of GOFASi into silica aerogel network using tetraethyl orthosilicate (TEOS). Then, GA was used as an additive in novolac resin matrix. In the second procedure, the synthesis of a hybrid novolac resin was accomplished by network formation via the reaction of GOFASi with (3-glycidyloxypropyl)trimethoxysilane-modified novolac resin and TEOS. The thermal stability and the carbon yield of the hybrid resins obtained by the two procedures were compared. Fourier transforms infrared spectroscopy, X-ray photoelectron spectroscopy, and thermogravimetric analysis showed that both GO and the novolac resin were successfully modified. Aerogel formation was proved by Raman, X-ray diffraction, N_2 adsorption and desorption isotherms, and by scanning and transmission electron microscopies.

1. Introduction

Organic-inorganic hybrids materials have been have been extensively studied in the past few decades because of their unique properties. Polymer matrices can be improved remarkably in their thermal, mechanical, physical, and other characteristics by incorporation of metal oxide clusters via various coupling agents [1–3]. Content of additive, its dispersion uniformity, and interaction with the host polymer matrix are important factors in properties of such products. These hybrid materials were commonly prepared via sol–gel process, which provides the possibility of polymer chains incorporation into silica domains. Inorganic domains are mainly formed from the hydrolysable multifunctional alkoxysilanes. Interconnected networks are formed by using appropriate coupling agents which provide covalent bonding between a polymer matrix and inorganic domains.

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 [4,5]. Microstructure of aerogels is constructed by hydrolysis and condensation processes, which 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 [6]. In addition to pH, alkoxide type, water amount, temperature, and drying methods are the other important factors in microstructure of aerogels.

Reinforcement of silica aerogels was previously carried out by multifunctional coupling agents of alkoxysilanes [7]. Also, alkoxysilanes were used to incorporate SWCNT and graphene into the silica aerogel network for improving its mechanical properties [8,9]. However, preparation of graphene aerogels with high surface area and low density were reported by hydrothermal [10,11], resorcinol and formaldehyde sol–gel polycondensation [12], and chemical reduction methods [13–15]. Self-assembly of graphitic layers into three-dimensional aerogel structure is observed in these

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methods, which prevents from restacking of layers in various polymer matrices. The latter is very attractive because of its simple reaction conditions and no requirement of binder moieties. It is noteworthy that preparation of carbon nanotube and graphene-carbon nanotube aerogels were also reported [16–19].

Phenolic resins were commonly synthesized from the source of a phenol and an aldehyde in two forms of resol and novolac, which is different in phenol and formaldehyde ratio and also type of the acidic or basic catalyst. Phenolics can be used in ablative thermal protection applications as thermal resistant thermosets. Structural modification of phenolics results in high thermal stability and high carbon yield values upon pyrolysis in nitrogen (TGA). Incorporation of boron and phosphorous moieties [20–24] and inorganic modifiers [6,25,26] into the phenolics structure are some important examples of structural modification methods. Additionally, thermal properties of phenolics were improved by the addition of graphene and carbon nanotube as carbon fillers [27–30].

In this study, phenolic resin structural modification with inorganic silane moieties by sol–gel process, incorporation of silane- and furfuryl alcohol-modified graphene and silane-modified phenolic resin into a silica network, and addition of GA into phenolic resin has been considered to increase the thermal properties and carbon yields of phenolic resin products. Herein, GA has been prepared by a sol–gel process. Also, graphene and phenolic resin formed a network by a sol–gel process similar to GA. Silane coupling agents of (3-glycidyloxypropyl) trimethoxysilane (GPTES) for phenolic resin and (3-aminopropyl) triethoxysilane (APTES) for furfuryl alcohol-modified graphene were used to increase phenolic resin and graphene compatibility and also network formation. This can also result in lowering phase separation between the organic and inorganic media. Designation of samples is given in Table 1.

2. Experimental

2.1. Materials

Novolac resin (IP502, Resitan), graphite (Merck), potassium permanganate ($KMnO_4$, Sigma–Aldrich, 99%), sodium nitrate ($NaNO_3$, Sigma–Aldrich, 99%), sulfuric acid (H_2SO_4, Merck), furfuryl alcohol (Sigma–Aldrich, 98%), N,N′-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-dimethylaminopyridine (DMAP, Aldrich, 99%), (3-aminopropyl) triethoxysilane (APTES, Sigma–Aldrich, 99%), tetraethoxysilane (TEOS, Merck), (3-glycidyloxypropyl) trimethoxysilane (GPTES, Aldrich, 99%), hexamethyldisilazane (Aldrich, 99%), and hexamethyltetramine (HMTA, Sigma–Aldrich, 99%) were used as received.

Table 1
Designation of the samples.

Sample	Description
APTES	(3-aminopropyl) triethoxysilane
GPTES	(3-glycidyloxypropyl) trimethoxysilane
G	Graphite
GO	Graphene oxide
GOFA	Furfuryl alcohol-functionalized GO
GOFASi	APTES-functionalized GOFA
GA	Graphene-containing silica aerogel
SA	Silica aerogel
R	Novolac resin
MR	GPTES-functionalized R
CR	Cured R
RGAX	GA/R cured composite with X wt% of GA
MRGAX	GOFASi/MR cured composite with X wt% of GOFASi

2.2. Oxidation of graphite to prepare graphene oxide (GO)

Modified Hummers' method was used for preparation of GO [31]. Accordingly, graphite (3.0 g) and $NaNO_3$ (1.5 g) were mixed with H_2SO_4 (180 mL) in a 300-mL flask for 15 min at room temperature. Subsequently, $KMnO_4$ (9.0 g) was slowly added to the flask and stirring was continued at 35 °C for 7 h. After addition of the second part of $KMnO_4$ (9.0 g), stirring was continued for 12 h. Subsequent addition of deionized water (600 mL) and H_2O_2 (30 v%, 30 mL) results in the reduction of unreacted $KMnO_4$. Wet graphite oxide with pH of about 7 was obtained by centrifugation, washing the paste with HCl solution (10 v%), and washing the product three times with distilled water. Exfoliation of graphite oxide dispersion by a probe ultrasonic, filtration, and drying the product in vacuum at 65 °C gives GO.

2.3. Preparation of furfuryl alcohol-functionalized GO (GOFA)

Furfuryl alcohol was attached to the edge of GO by an esterification reaction. Accordingly, GO (0.2 g) and DMF (120 mL) were stirred in a flask for 24 h and then ultrasonically agitated for 30 min to reach a homogeneous dispersion. Subsequently, furfuryl alcohol (0.47 mL, 5.41 mmol) was added into the flask and the dispersion was stirred for another 30 min. Then, DCC (4.0 g, 20.87 mmol) and DMAP (0.3 g, 2.46 mmol) were added slowly and the mixture was agitated for 16 h. At the end, GOFA (0.16 g, 80%) was obtained after filtration, washing the product with DMF for three times, and drying the solid in vacuum at 65 °C for 24 h (Fig. 1, Part I).

2.4. Preparation of (3-aminopropyl) triethoxysilane-functionalized GOFA (GOFASi)

APTES was attached to the surface of GOFA by addition of amine moieties of APTES on the epoxy groups which frequently occur on GOFA surface [32]. Accordingly, GOFA (0.1 g) and ethanol (50 mL) were stirred in a flask for 24 h and then ultrasonically agitated for 30 min to reach a homogeneous mixture. Subsequently, after addition of DCC (0.1 g, 0.52 mmol), APTES in ethanol (1.6 in 10 mL) was slowly added into the flask and stirring was continued at 70 °C for 20 h. Then, the product was filtered through a 0.2 μm PTFE filter and washed with ethanol for three times. After drying the product in oven at 65 °C, GOFASi was obtained (0.072 g, 72%) (Fig. 1, Part II).

2.5. Preparation of graphene-containing silica aerogel (GA) and silica aerogel (SA)

GA was prepared by an acid-catalyzed sol–gel process. GOFASi (0.25 g) and furfuryl alcohol (8 mL) were stirred in a flask for 24 h and then ultrasonically agitated for 30 min 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. Then, GA was obtained by letting the mixture to remain at the room temperature for 12 h and 60 °C for 72 h (Fig. 1, Part III). 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.