# Enhancement of the mechanical properties of an epoxy composite through inclusion of graphene oxide nanosheets functionalized with silica nanoparticles through one and two steps sol-gel routes

S.Z. Haeri[a], M. Asghari[a], B. Ramezanzadeh[b],*

[a] Separation Processes Research Group (SPRG), Department of Engineering, University of Kashan, Kashan, Iran
[b] Department of Surface Coatings and Corrosion, Institute for Color Science and Technology (ICST), PO 16765-654, Tehran, Iran

ABSTRACT

Silica-functionalized graphene oxide (GO) nanosheets (GONs) were synthesized through a two-step sol-gel route. The chemical structure and morphology of the $SiO_2$-GONs were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and Field emission-scanning electron microscopy (FE-SEM). Then, the effect of $SiO_2$-GONs on the mechanical properties of epoxy coating (EP) was studied by dynamic mechanical thermal analysis (DMTA) and tensile test. Interestingly, when 0.1 wt.% of the silica modified GO nanosheets was added to the epoxy matrix, the tensile strength, energy at break, storage modulus, cross-linking density and glass transition temperature ($T_g$) of the coating were remarkably increased.

## 1. Introduction

Nowadays "polymers" have been extensively used in variety of industrial applications due to their favorable mechanical, thermal, chemical and electrical properties. Among different kinds of polymers, the epoxy based coatings have attracted lots of attentions due to theirs high mechanical strength, stiffness, stability and resistance against chemicals [1]. Apart from these advantages, the serious weaknesses of the epoxy based coating are its poor resistance against stress, and crack propagation as well as high brittle nature, limiting its application in many industrial cases. So, the researchers have tried to improve the mechanical strength and fracture toughness of the epoxy coating by addition of a second phase [2,3]. There are a plenty of works reporting the effect of different forms of fillers and additives on the coating reinforcement. It has been shown that the inclusion of conventional fillers i.e silica [4,5], carbon black [6], silicon carbide [7] mica and calcium carbonate [5] into the epoxy coating can considerably improve its mechanical properties. Recently, a considerable attention of the researchers has been directed toward the use of nanoparticles as advanced materials for the coating reinforcement. Owing high specific surface area, small particle size, they are introduced as good alternatives for the conventional micro particles [8] to reinforce the epoxy coating. Adding nanoparticles to the epoxy coating, due to the greater surface to volume ratio than micro particles, results in better physical, mechanical and thermal properties compared with the pure epoxy coating or the one reinforced with conventional micro particles [9]. In recent years a variety of nanoparticles are added to the epoxy resin to improve its mechanical and electrical properties [10–14]. In a work done by He et al. the effect of addition of nano-$CaCO_3$ particles on the mechanical and thermal properties of the epoxy coating was studied [15]. In another study, the thermal stability and dynamic mechanical properties of the epoxy composites reinforced with nano-$TiO_2$ particles were considered [16]. Foroutan et al. [17] studied the effect of nano-size $Al_2O_3$ filler on the mechanical properties of the epoxy coating. The results showed that the flexural and tensile strengths were considerably increased in the presence of nano-size $Al_2O_3$ particles. The mechanical properties of a carbon fiber epoxy composite were significant increased after addition of nano-$SiO_2$ particles [18].

Recently, carbon nano-materials, in particular graphene oxide, have attracted the researchers' attentions. Graphite, fullerenes, diamond and amorphous carbon are the most well-known allotropes of carbon. Among these, the graphene oxide, a one-atom-thick carbon nanosheet, has been largely considered as a useful nanomaterial for the reinforcement of many polymers. Owing high surface area and many oxygen containing groups [19], the GO has been used for the polymers properties enhancement [20]. Graphene oxide has large number of C-C bonds and many functional groups i.e hydroxyl, carboxylic and epoxide. The carboxyl and carbonyl groups are located at the edges of the GO sheets but the hydroxyl and epoxide groups can be seen on the basal plane of the nanosheet [21,22]. The GO is attractive for the

researchers due to its low density, large specific surface area and extraordinary electronic, thermal and mechanical properties [23]. In addition, it has been reported that inclusion of GONs into the polymers can improve their mechanical and protective performance. Ansari at al. [24] has reported the advantages of addition of GO nanosheets to the epoxy coating on its mechanical properties enhancement. The GO has active epoxide rings and many hydroxyl groups which can participate in the curing reaction and make covalent bonding with the curing agent of epoxy resin. However, the nanoparticles dispersion and stability in the polymer matrix is still a big challenge when fabrication of a nanocomposite. The improvement of the mechanical and physical properties of the composites can be only obtained through uniform dispersion of nanoparticles in the composites. The presence of many oxygen containing groups on the edge and basal plane of GO is responsible for the great hydrophilicity and therefore poor compatibility with inorganic solvents and polymers. Literature survey returns numerous reports on the effect of surface modification of GO nanosheets on their dispersion and compatibility in a polymer coating. In addition, the surface modification of GO nanosheets can influence the interfacial interactions at the GO/polymer interface and affect the composite physical and mechanical properties. In our previous study [25] the GO nanosheets were covalently functionalized by P-phenylenediamine (FGO) and then added to the epoxy coating. It was shown that addition of 0.1 wt.% FGO nanosheets to the epoxy coating significantly increased its barrier performance. In another work the GO was functionalized by polyisocyanate (PI-GO) and incorporated into a polyurethane matrix. It was found that addition of 0.1 wt.% PI–GO significantly increased the mechanical properties of the coating [26]. Li et al. [27] synthesized silane-functionalized graphene oxide (GO) nanosheets by methacryloxy propyltrimethoxy silane (MPTS). The tensile test indicated that the MPTS-GO/BMI nanocomposites (BMI resin) showed higher modulus and tensile strength than the neat coating and the impact strength of the composites was considerably improved. The effect of surface functionalization of graphene oxide (FGO) by vinyl trimethoxy silane (VTMS) on the mechanical and thermal properties of a silicone polymer was studied. Results showed that the tensile strength, thermal stability and thermal conductivity of the silicone polymer composite were remarkably improved [28]. To improve the mechanical properties of liquid silicone rubber (LSR), Triethoxyvinylsilane (TEVS)-graphene oxide (GO) was used. Results showed significant enhancement in tear strength of the TEVS-GO/LSR composites compared with the neat LSR [29]. There are plenty of reports on the effect of surface modified GO nanosheets on the polymers mechanical properties enhancement. However, this study reports the influence of GO nanosheets decorated with silica nanoparticles on the mechanical properties of the epoxy coating.

This paper reports simple one (I) and two-step (II) sol-gel routes of making nanosheets of GO covered with $SiO_2$ nanoparticles using mixture of TEOS and APTES silane precursors. The $SiO_2$-GONs obtained from two methods were characterized by FT-IR, XPS and FE-SEM analyses. The effect of addition of $SiO_2$-GONs-I and II on the mechanical properties of the epoxy coating was studied by DMTA and tensile test.

## 2. Experimental

### 2.1. Raw materials

Graphite powder (40 μm) was purchased from Sigma-Aldrich Co. Epoxy resin (diglycidyl ether of bisphenol A, Epon 828) and polyamine hardener (Cycloaliphatic polyamine hardener; Epikure F205) were prepared from Shell; USA and Kian Co., respectively. Tetraethyl orthosilicate (TEOS, Merk Co.), 3-Aminopropyltrimethoxysilane (APTES, 97%, Sigma-Aldrich Co.), sulfuric acid (Merck Co.), sodium nitrate (Merck Co.), hydrochloric acid (Merck Co.), dimethylformamide (Merck Co.), hydrogen peroxide (Merck Co.) and acetic acid (Merck Co.) were the other materials used in this study

### 2.2. Fabrication of SiO2-GO nanohybrids

The GO nanosheets were synthesized through modified Hummer's procedure [30]. For this purpose, the graphite powder (2 g) was added to the concentrated $H_2SO_4$ (240 mL) and mixed for 2 h on stirrer. Then the $NaNO_3$ (2 g) for 2 min and $KMnO_4$ (12 g) during 1 h were gradually added to the solution and stirred for 72 h. In the next step, the solution was added to DI water (600 mL), then $H_2O_2$ (35%) was gradually added until getting a yellow solution, and the mixture was centrifuged at 4000 rpm and sonicated for 2 min and washed with a mixture of DI water and HCl (1 M). At the end, the $SiO_2$-GONs were synthesized by one and two steps sol-gel methods as described below:

#### 2.2.1. Synthesis of SiO2-GONs by one-step sol-gel route (Method I)

The GO nanosheets were modified by $SiO_2$ nanoparticles by a one-step sol-gel method using mixture of TEOS (60 wt.%) and APTES (40 wt.%) silane precursors. For this purpose, the silane bath containing 5 wt.% silane mixture, 80 wt.% alcohol and 15 wt.% deionized water was prepared and then 25 mg GO nanosheets was added to this mixture and sonicated for 2 min. The pH of the mixture was adjusted at 4 by adding acetic acid and mixed for 72 h at room temperature. In this step the silane precursors will be hydrolyzed, leading to the silanes interactions with the hydroxyl groups existed on the GO sheets through hydrogen bonding. Then, the pH and temperature of the GO-hydrolyzed silanes were increased up to 9 (by adding proper amount of NaOH (5 wt.%) solution) and 70 °C, respectively and the mixture was stirred for 1 h. At this condition the condensation reaction of the hydrolyzed silanes takes place on the GO sheets, leading to the creation of GO-$SiO_2$ nanohybrids. The schematic procedure of the GO functionalization by $SiO_2$ nanoparticles is displayed in Fig. 1. At the end, the residue was washed 5 times with a solution of ethanol and water (50/50%) to remove the unreacted and physically adsorbed silanes. The graphene oxide nanosheets covered with $SiO_2$ nanoparticles obtained in this method is named as GO-$SiO_2$-I.

#### 2.2.2. Synthesis of SiO2-GONs by two-step sol-gel route (Method II)

Similarly to the first method (I) a mixture of silanes containing 5% silanes mixture (TEOS–60 wt.% and APTES–40 wt.%), 80 wt.% alcohol and 15 wt.% deionized water was prepared. The pH of the mixture was fixed at 4 by addition of acetic acid. Unlike the first method the GO nanosheets were not added to the silane mixture at this step and the solution was kept for 72 h. In this method the silanes precursors hydrolysis takes place prior addition of GO. The hydrolyzed TEOS and APTES silane precursors interact with each other and form larger oligomers. Afterwards 25 mg GO nanosheets was added to the pre-hydrolyzed silane mixture and sonicated for 15 min and mixed for 3 h. Finally, the pH of the solution was increased up to 9 by adding NaOH–5 wt.% solution and the mixture was stirred for 1 h at temperature of 70 °C. In this way the $SiO_2$ nanoparticles were deposited on the GO surface. The schematic procedure of the GO functionalization by $SiO_2$ nanoparticles is displayed in Fig. 2. At the end, the final mixture was washed 5 times with a solution of ethanol and water (50/50%) to remove the physically adsorbed silanes. The nanosheets obtained in this method is named as GO-$SiO_2$-II.

### 2.3. Preparation of SiO2-GO/Epoxy nanocomposites

The $SiO_2$-GONs/Epoxy composites were prepared through a wet transfer method (WTM) [25]. To this end, the GO and $SiO_2$-GONs (0.2 wt.%) were sonicated in water for 5 min. Then, the mixtures were separately added to a solvent free epoxy resin (30 g). In the next step the GONs/Epoxy, $SiO_2$-GONs-I/Epoxy and $SiO_2$-GONs-II/Epoxy were mechanically mixed to obtain a uniform dispersion. The above mixtures were heated up to 80 °C in an oven for 24 h to remove the water from the mixture. In this way the $SiO_2$-GONs-I, II and GONs can be transferred from the water phase into the polymer matrix. Afterward,