



# Preparation of organic-inorganic hybrid nanocomposites from chemically modified epoxy and novolac resins and silica-attached carbon nanotubes by sol-gel process: Investigation of thermal degradation and stability

Amin Abdollahi<sup>a</sup>, Hossein Roghani-Mamaqani<sup>a,b,\*</sup>, Mehdi Salami-Kalajahi<sup>a,b,\*</sup>, Alireza Mousavi<sup>a</sup>, Bahareh Razavi<sup>a</sup>, Sina Shahi<sup>a</sup>

<sup>a</sup> Department of Polymer Engineering, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran

<sup>b</sup> Institute of Polymeric Materials, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran

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## ABSTRACT

Here, three hybrid composites with high char yield and thermal stability were prepared from tetraethyl orthosilicate (TEOS)-modified epoxy resin (MER), (3-glycidyloxypropyl) trimethoxysilane (GPTES)-modified novolac resin (MNR), epoxidized novolac resin (ENR), and silica-grafted carbon nanotube (SFCNT) by a sol-gel method. The first class was prepared from MER and SFCNT. The second class was prepared from MER, MNR, and SFCNT. And the third class was prepared from MNR, ENR, and SFCNT. TEOS was used as covalent coupling agent in the sol-gel process. Results of Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy confirmed successful modification of epoxy and novolac resins, modification of silica nanoparticles with (3-Aminopropyl)triethoxysilane (APTES), and also functionalization of CNT with amine-modified silica nanoparticles. Results of thermogravimetric analysis confirmed that the hybrid composite containing 4 wt% of SFCNT, MNR, and ENR shows the highest char yield of 58.4%. The hybrid composite containing 4 wt% of SFCNT and MER shows the highest degradation temperature of 442.7 °C. Finally, the hybrid composite formed from 4 wt % of SFCNT, MER, and MNR shows degradation temperature of 439.0 °C and char yield of 47.2%. Microscopic images and X-ray diffraction results confirmed attachment of silica particles at the surface of CNT by chemical bonding.

## 1. Introduction

In the past few decades, polymeric composites with high thermal stability have received much attentions in scientific studies and researches because of their unique properties and extensive application in different industries [1–3]. Among them, organic-inorganic hybrid materials displayed remarkable physical and chemical properties such as mechanical strength and high thermal-chemical stability. Such materials were generally prepared by sol-gel method, that its mechanism is based on a polymerization process between inorganic materials and the most usable inorganic components are silica-based particles and networks [4–9]. Actually, in this method, firstly a stable dispersion of colloidal silica domains was prepared in a solvent as a sol and then, it was used to form a three-dimensional continuous network as a gel compound in acidic, basic, or acidic-basic conditions [4,8,10–12]. A wide range of different factors such as water content, metal alkoxides, solvent, pH of media, temperature, and drying methods affect the formation of gel and also gel microstructure [5]. On the other side, xerogel

materials can be prepared by evaporation of solvent of sol-gel compound in ambient pressure, hence in some researches and studies, surface of the used materials were modified for easy removal of solvent molecules [9,12].

Epoxy, novolac, and epoxidized novolac resins can be used in preparation of organic-inorganic hybrids with potential applications in coating, adhesive, electrical, and composite industries because of their excellent chemical and mechanical properties. For this propose, neat resins should be modified chemically with different silane modifiers such as tetraethyl orthosilicate (TEOS) oligomers and (3-glycidyloxypropyl) trimethoxysilane (GPTMS). The modified resins undergoes sol-gel process and chemically bonded to silica network by Si–O–Si bonds [13–16]. Incorporation of inorganic silica particles or network into the polymeric matrices can lead to improvement of physical and chemical properties of the final hybrid. In the other side, epoxy resins notwithstanding that displays unique physical, chemical, and mechanical properties, its thermal stability is low which led to restriction of epoxy composites application in different industries. Increase of thermal

\* Corresponding authors at: Department of Polymer Engineering, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran.  
E-mail addresses: [r.mamaghani@sut.ac.ir](mailto:r.mamaghani@sut.ac.ir) (H. Roghani-Mamaqani), [m.salami@sut.ac.ir](mailto:m.salami@sut.ac.ir) (M. Salami-Kalajahi).

stability of epoxy resins was achieved by different chemical and physical modifications. Addition of novolac or epoxidized novolac resins as high thermal stable polymer additives, incorporation of inorganic nanoparticles into the matrix to form polymer composites, introducing of graphene nanolayers (GO) and carbon nanotube (CNT) into the composites by chemical or physical bonds, and chemical modification of resin with different silane modifiers and hybrid formation of them with silica network are some well-known procedures. Each of these approaches can be used for increase of thermal stability in organic-inorganic hybrid materials based on epoxy or novolac resins.

In the past few decades, a wide range of studies have focused on preparation and investigation of different types of silica/siloxane-based hybrid materials. A fast review of these literatures displays that epoxy resin and CNT were modified with 3-(isocyanatopropyl) triethoxysilane (IPTEOS) and finally incorporated into silica/siloxane network via sol-gel method by Wu and coworkers [17,18]. In this case, Cui et al. reported preparation of phenolic resin composites with pristine and carboxylated CNTs by using in situ polymerization methods, which the obtained composites displayed high thermal stability [19]. It should be pointed that the incorporation of CNT into the curing reaction of phenolic resin can lead to its better dispersion, and therefore, improved thermal properties. In the recent years, our group reported extensive approaches for preparation of silica-based hybrid materials by using modified resins and incorporation of GO and CNT into the matrix [13–16]. An abnomenment between all of these studies is chemical modification of the used resins by silica-based components and also using of CNT and GO as reinforcement nanomaterials. For instance, Noparvar-Qarebagh and coworkers modified the carboxylated CNTs with furfuryl alcohol by esterification reaction and then incorporated it into the novolac resin for increase of char yield [20]. A few time later, they have prepared the xerogel materials by chemical modification of carboxylated CNT with (3-glycidyloxypropyl) triethoxysilane (GPTES) and then prepared hybrid network from silane-modified CNTs and novolac resin using TEOS as linker between two materials [16]. Thermal investigation results illustrate that incorporation of CNT into the novolac resin leads to increase of thermal stability and char yield of the host matrix. Additionally, Noparvar-Qarebagh and coworkers prepared the similar hybrid composites by chemical modification of GO with (3-aminopropyl) triethoxysilane (APTES) and hybrid network formation with TEOS in the presence of novolac resin as polymeric matrix [15]. Najafi-Shoa and coworkers prepared a new type of organic-inorganic hybrids by using of modified CNT and GO, and epoxy resin at the presence of silane-based materials to form silica/siloxane networks in order to improve of thermal stability of epoxy resin [13,14]. As a summery, increase of thermal stability of thermoset resins was achieved by using of silica/siloxane networks and also incorporation of CNT or GO into the hybrid networks, in which the organic and inorganic phases were bonded together through chemical Si–O–Si bonds. Novolac resin displays high thermal characteristics compared with epoxy resin, but the epoxy resin has unique mechanical, chemical, and physical properties [21,22]. Epoxidized novolac resin is the best candidate for using in epoxy-based polymer composites in order to increase of thermal stability and char yield.

Herein, we have developed a new type of organic-inorganic hybrid materials containing silica nanoparticles-grafted CNT as reinforcement agent and also modified epoxy resin (MER), modified novolac resin (MNR), and finally epoxidized novolac resin (ENR) as polymeric matrices. At the first, silica nanoparticles ( $\text{SiO}_2$ ) were chemically modified with APTES to form  $\text{SiO}_2\text{-NH}_2$ . Then, CNTs were oxidized to form carboxylic functional groups (COOH) at their surface and obtain carboxylated CNT (CNTCOOH). Then, CNTCOOH was further modified with 3-(methacryloyloxy)propyl trimethoxysilane (MPS) to form functionalized CNT (FCNT). In a most important modification reaction, combination of FCNT and  $\text{SiO}_2\text{-NH}_2$  was carried out by an amidation reaction between amine functional groups of  $\text{SiO}_2\text{-NH}_2$  and carboxylic acid groups in FCNT to yield SFCNT, as presented in Fig. 1. In the

second step, three types of resins were prepared by chemical modification of epoxy and novolac resins; MER was prepared by modification of epoxy resin (ER) with TEOS oligomers, MNR was obtained by modification of novolac resin (NR) with GPTES, and ENR was obtained by modification of NR with epichlorohydrin. Then, different types of hybrid composites containing SFCNT were prepared by mixing and hybrid network formation of the modified resins by sol-gel method. Here, SFCNT and epoxy hybrids (CSEH) were formed from MER and SFCNT (2 and 4%wt). SFCNT, novolac, and epoxy hybrids (CSNEH) were formed from a mixture of MER and MNR with SFCNT (2 and 4% wt). Finally, SFCNT, MNR, and ENR hybrids (CSMNEH) were formed from a mixture of MNR and ENR with SFCNT (2 and 4%wt). For comparison of hybrid composites with hybrid-based materials without SFCNT, MER was set in hybrid network using TEOS to yield MERH, ER was cured with ethylenediamine to form CER and also NR was cured with HMTA to yield CNR. The prepared hybrids were evaluated from the viewpoint of thermal stability and char residue. To the best of our knowledge, it should be pointed that the obtained hybrid materials and the related results were reported by our group in current study for the first time.

## 2. Experimental

### 2.1. Materials

Silica nanoparticles ( $\text{SiO}_2$ , particle average size: 10–15 nm, specific surface area: 150–226  $\text{m}^2/\text{g}$ ) were purchased from Tecnan-Nanomat company (Spain). Multi-walled carbon nanotube was purchased from Shenzhen Nanoport Company (China). The resins were epoxy resin (EP 418, Resitan,  $\text{Eq}^{-1} = 700\text{--}800$ ) and novolac resin (IP502, Resitan, Iran). Most of the chemicals such as potassium permanganate ( $\text{KMnO}_4$ , 99%), sodium nitrate ( $\text{NaNO}_3$ , 99%), (3-aminopropyl) trimethoxysilane (APTMS, 97%), (3-aminopropyl) triethoxysilane (APTES, 95%), (3-glycidyloxypropyl) trimethoxysilane (GPTMS), 3-(trimethoxysilyl) propyl methacrylate (MPS, 98%), ethylenediamine (99%), formic acid,  $N,N'$ -Dicyclohexylcarbodiimide (DCC), hexamethyltetramine (HMTA, 99%), furfuryl alcohol (98%), and triethylamine (TEA, 99%) were purchased from Sigma-Aldrich and used without further purification. Tetraethyl orthosilicate (TEOS), benzoyl peroxide (BPO), hydrochloric acid, *n*-hexane, acetone, ethanol, and tetrahydrofuran were purchased from Merck Company. Deionized water and  $\text{N}_2$  gas purging were used in all recipes in current study.

### 2.2. Modification of $\text{SiO}_2$ with APTES to obtain $\text{SiO}_2\text{-NH}_2$

Firstly,  $\text{SiO}_2$  (4 g) were added to an aqueous solution of NaOH (2 g in 100 mL  $\text{H}_2\text{O}$ ) in a flask under stirring at 65 °C for 24 h. Then, the obtained dispersion was titrated by acetic acid, and centrifuged. Finally, the precipitates were separated, washed with methanol for three times, and dried in vacuum oven at 80 °C for 24 h to prepare the hydroxylated  $\text{SiO}_2$ . Hydroxylated  $\text{SiO}_2$  (4 g) was added in a mixture of Ethanol/ $\text{H}_2\text{O}$  (100 mL, 95/5 mL) under stirring and then APTES (3 g) was added to the mixture. The pH of the mixture was controlled at about 5 by addition of acetic acid. After ultrasonically agitation of the mixture for 60 min, it was kept in ambient temperature for 24 h under stirring. Then, the solids were separated by centrifugation and washed with methanol for three times. Finally,  $\text{SiO}_2\text{-NH}_2$  nanoparticles were obtained after drying at 80 °C in vacuum oven for 24 h.

### 2.3. Oxidation of CNT to obtain CNTCOOH

Oxidation of CNT was carried out according to the literature [23]. For this purpose, CNT (2.0 g) was dispersed in an aqueous solution of  $\text{HNO}_3$  (60%, 100 mL) and refluxed for 24 h. Then, the paste was separated by PTFE filter membrane with pore dimensions of 0.2- $\mu\text{m}$ , washed with deionized water for several times, and dried in vacuum oven at

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