



Designing a multi-functionalized clay lamellar-co-graphene oxide nanosheet system: An inventive approach to enhance mechanical characteristics of the corresponding epoxy-based nanocomposite coating

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ABSTRACT

Clay nano-platelets (NC) and Graphene oxide nanosheets (GO) are functionalized by the aid of 1,4- butanediol diglycidyl ether (BDDE) through an aminosilane coupling agent, i.e. 3-Triethoxysilyl propylamine (APTES). The products obtained from the modification process are characterized by visual assessment, FTIR, XRD, TGA, UV–vis, AFM and FE-SEM analyses. The results clearly demonstrate the epoxide ring of BDDE is chemically attached on the surface of the fillers. Furthermore, the process is causing the stacks of layers expand and d-spacing increases. The functionalized NC and GO, i.e. MNC and MGO, are then impregnated into an undiluted clear di-functional bisphenol A/epichlorohydrin derived liquid epoxy resin at 0.3% weight concentration by simple mechanical mixing. The films are also morphologically studied by FE-SEM. Dynamic and static mechanical properties are investigated by DMA and tensile testing. The outcomes demonstrate that there exists an optimum mixing ratio of MGO and MNC to obtain the best mechanical properties, i.e. MGN (70:30). Besides, almost all the modified samples show improved mechanical properties compared to their unmodified counterparts.

1. Introduction

Epoxy resins are one the key materials in heavy-duty protective coatings and are widely consumed in different industries, e.g. adhesives, composites and most important of all coatings, thanks to their intrinsic auspicious characteristics among which high hardness, good chemical resistance, excellent thermal stabilities and high tensile and compression moduli are noteworthy. Accompanied by these promising attributes, some unfavorable properties do exist for epoxy resins, for instance brittleness and insufficient barrier effect in various environment, which limit their uses [1–9].

Reinforcing epoxy resins by the aid of layered nanoparticles has attracted broad attentions by myriad of researchers on account of the opportunity of achieving enhanced attributions such as stiffness, fire resistance and dimension stability. Furthermore, some of the drawbacks of the resin, e.g. lack of barrier property, is being removed in the reinforced resin. Layered silicate nano-platelets, very well known as clay, and graphene oxide nano-sheets are enticing many considerations in order to be used as nano-fillers inside epoxy matrix to improve physical and mechanical properties [10–15].

Clay is a tactoid particle made of nano-sized layered silicate and due

to its natural abundance is easy to access. Possessing extremely large aspect ratio, provides very high specific surface area potentially offers countless interactions between the lamellae and the polymer chains. Notwithstanding, the compact lamellar structure of the clay in conjunction with its hydrophilic substance made it almost impossible to obtain an individually separated layers, i.e. exfoliated morphology, inside the epoxy matrix. Hence, vigorously mechanical and ultrasonic agitations are of essential necessity which confines large-scale quantity productions [16–18].

On the other hand, graphene oxide nano-sheets obtained from harsh oxidizing of graphite, are graphitic lamellar nano-filler consisted of stacks of graphene oxide layers strongly attached together through Van der Waals attractive forces. The layers are made of sp^2 hybridized carbon atoms together organized in honeycomb configurations and functionalities such as hydroxide, carboxyl and epoxide groups are situated on the surface principally at the edges. Graphene and its derivatives are famous owing to their fabulous physical, mechanical, thermal and electrical properties. For instance, they show excellent gas and ion permeability and have extremely high specific surface area as $2630 \text{ m}^2 \text{ g}^{-1}$. A single defect-free sheet of graphene possesses a Young's modulus of 1.0 TPa and its thermal conductivity goes up to 5300

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$\text{Wm}^{-1}\text{K}^{-1}$. Graphene also displays a remarkable electrical conductivity up to $25000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which correlated to resistivity as low as $10^{-6}\ \Omega\cdot\text{cm}$ [19–31].

To exploit the extraordinary beneficial properties of both clay and graphene oxide, the stacks of the layers must be transformed into individual sheets which in turn a tough goal to reach. To this aim, different approaches have been proposed in various studies ranging from mechanical and ultrasonic agitations that smashes down the micron-sized stacks to chemical delamination of the layers. One tactic is to surface functionalize the layers through which intercalation of the stacks and consequently exfoliated morphology becomes more accessible. Besides, the modified sheets inside the polymeric matrix tend less to gather back together to make aggregations [32–42].

Authors in their previous studies demonstrated that a promising method to surface functionalize the clay to obtain an exfoliated morphology simply through facile mechanical stirring is modification by hyperbranched dendritic polymers [1,6]. Significantly improved electrochemical and relatively enhanced mechanical characteristics attained for corresponding nanocomposite epoxy based coatings. In the current study, we have designed a new methodology through which epoxide rings are covalently grafted on the clay and graphene oxide sheets by the aid of an organosilane coupling agent and the nano-fillers as neat and modified are added to the epoxy matrix. In addition, mixtures of the fillers at several mixing ratio impregnated into the epoxy. The filled epoxy was then applied as nanocomposite coatings and physical-mechanical and electrochemical properties are being investigated. In the present paper physic-mechanical properties have been focused and electrochemical ones are simultaneously presented in another article.

To the best of the authors' knowledge, no study has ever focused on the effects of co-existence of both clay lamellae and graphene oxide sheet inside an epoxy based nanocomposite coating and investigating the mechanical characteristics.

2. Materials and methods

2.1. Materials

Materials needed to synthesis graphene oxide were gathered as follows. Hydrochloric acid (HCl) and sodium hydroxide (NaOH), were acquired from Mojallali Co., Iran. Sulfuric acid (H_2SO_4 , 98%), potassium permanganate (KMnO_4) and hydrogen peroxide (H_2O_2 , 30%) both Sigma-Aldrich were purchased from domestic sources. Expandable graphite, EG, (carbon content = 98–99.5%, grain size as $d_{80\%} > 300\ \mu\text{m}$ and expansion rate = $350\text{--}700\ \text{cm}^3/\text{g}$) was procured from Kropfmuehl Graphite Co.

CLOISITE 20A clay (from Southern Clay Products Inc. which is now a part of BYK Additives Inc.) was procured from domestic sources. This mineral is an organically modified phyllosilicates. CLOISITE 20 is bis (hydrogenated tallow alkyl)dimethyl, salt with bentonite ($\rho = 1.77\ \text{g}/\text{cm}^3$, $d_{001} = 3.16\ \text{nm}$, Moisture < 3%). Further decontaminated using ethanol washing through a two-hour agitation and centrifugation process (at the rate of 4000 rpm). The procedure was repeated three times to ensure the removal of all undesirable dirt and impurities on the surfaces of the clay. APTES, 3-(Triethoxysilyl)propyl amine, precursor (from Merck Millipore) was purchased and readily used without extra purification. 1,4-Butanediol diglycidyl ether, BDDE, (from Sigma-Aldrich) was bought and utilized in its pristine form. An undiluted clear difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin (EPON™ Resin 828 from HEXION Inc.) and a low viscosity, modified cycloaliphatic amine curing agent (EPIKURE™ Curing Agent F205 from HEXION Inc.) were obtained from local providers. The appropriate solvents, i.e. dimethylformamide (DMF), ethanol, etc., were achieved from Sigma-Aldrich and used without further purification.

2.2. Graphene oxide (GO) synthesis and functionalization

2.2.1. Synthesis

Graphene oxide nano-sheets are synthesized from the expandable graphite (EG) through the well-known modified Hummers' method. Acid delamination of EG is conducted by H_2SO_4 (1 g EG poured to 120 g H_2SO_4) under vigorous agitation at ambient temperature for at least an hour. In the following step 3 g of the oxidizer, i.e. KMnO_4 , is added to the mixture at temperatures below $20\ ^\circ\text{C}$ and the stirring continues for 12 more hours at ambient temperature. Then, 600 ml of distilled deionized water is discharged into the reactants mixture while strong stirring is continued. Finally, to put an end to the oxidizing reaction 5 ml of H_2O_2 and mixing continues for an extra hour. The attained suspension undergoes a centrifugation process at 4000 rpm and 20 min. The product then is washed twice by 1 M HCl and three times by deionized water.

2.2.2. Functionalization

After having synthesized the graphene oxide sheets, they were undergone an acid washing process by the aid of a molar HCl solution (40 ml HCl into 7 ml of GO suspension) for 3 times followed by a rinsing process with deionized water. Eventually the material went through a sonication procedure enduring 3 min at 150 W. In the next level, a solvent exchange process was carried out in order to make it compatible with the epoxy solution. To this end, HCl was added to GO (2 ml of HCl into 20 ml of GO suspension) and the mixture experienced a centrifugation process for 20 min at 4000 rpm. The latter was repeated once more to ensure removing the whole water.

Later on, the concentration of the resulted GO suspension was calculated by measuring the solid content of the suspension according to ASTM D2369 and an equivalent weight of APTES correlated to GO was gradually added to the suspension. The mixture was stirred for 24 h at 400 rpm and $40\ ^\circ\text{C}$. Then the washing procedure with ethanol was carried out twice to remove all the physically adsorbed reactant. Afterwards, the concentration of APTES-modified GO in the suspension and also the number of moles of APTES were calculated. In the following step BDDE was added twice as the mole number of APTES and the stirring process was continued at $40\ ^\circ\text{C}$ and 400 rpm for 24 h. In the end the obtained Modified GO (MGO) suspension underwent the ethanol washing twice to eliminate the unreacted and physically adsorbed reactants. The attained suspension was centrifuged at 4000 rpm for 20 min and kept in sealed container for consequent consumption.

2.3. Nanoclay (NC) modification

The ethanol washed NC was poured into ethanol to make a 1 wt% suspension, i.e. $C = 0.01\ \text{g}/\text{ml}$, and the functionalization process with APTES and surface modification by BDDE was performed exactly the same as for the GO sheets.

2.4. Epoxy nanocomposite fabrication

The prepared nano-fillers were impregnated into the epoxy resin to obtain a 0.3 wt% mixture. The mixture was vigorously agitated under a lab-sized mixer for two hours at 2500 rpm. No further sonication process was used since it was believed that the modification process had been already enough to enhance the dispersion of the fillers inside the epoxy matrix. Then, the appropriate amount of polyamine hardener (Epoxy/Polyamine = 1.8) was weighed and poured into the filled resin and thoroughly blended to obtain full consistency. The product was applied on glass substrate and pre-treated steel ones by the aid of an applicator. The wet film thickness of the samples was elected as $60\ \mu\text{m}$. The samples on glass substrates were used in order to make free films.

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