



Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

The role of functionalized graphene oxide on the mechanical and anti-corrosion properties of polyurethane coating

Pooneh Haghdadeh^a, Mehdi Ghaffari^a, Bahram Ramezanzadeh^{b,*}, Ghasem Bahlakeh^c,
 Mohammad Reza Saeb^d

^a Polymer Group, Faculty of Technical and Engineering, Golestan University, P.O. Box 155, Gorgan, Golestan, Iran

^b Department of Surface Coatings and Corrosion, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

^c Department of Engineering and Technology, Golestan University, Aliabad Katool, Iran

^d Department of Resins and Additives, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

ARTICLE INFO

Article history:

Received 13 November 2017

Revised 6 February 2018

Accepted 7 February 2018

Available online xxx

Keywords:

PU coating

Mechanical properties

GO

corrosion

DMTA

EIS

ABSTRACT

Polyurethane (PU) has been commonly used in a wide range of applications due to its high flexibility and good UV resistance. Attempts have been extensively carried out to improve the corrosion resistance and mechanical properties of this coating through inclusion of nanomaterials. In this study the graphene oxide nanosheets, covalently functionalized by (3-glycidyloxypropyl) trimethoxysilane, were introduced into the PU matrix to enhance the mentioned weaknesses. The modified (fGO) and unmodified-graphene oxide nanosheets (GO) were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) analysis, field emission-scanning electron microscopy (FE-SEM), UV-vis and thermal gravimetric analysis (TGA). The physical-mechanical properties of the PU coatings reinforced with GO and fGO nanosheets were characterized by dynamic mechanical thermal analysis (DMTA) and tensile test. The influence of GO and fGO nanosheets on the fractured surface morphology of the PU coating after tensile test was studied by SEM analysis. In addition, the corrosion protection properties of the mild steel panels coated with PU coatings were characterized by salt spray test and electrochemical impedance spectroscopy (EIS). The results affirmed the physical-mechanical and anti-corrosion properties enhancement of the PU coating after incorporation of fGO nanosheets. The tensile stress, energy at break, loss factor and storage modulus values were significantly increased by addition of fGO nanosheets. The fGO stability and dispersion in the PU matrix was improved after modification with (3-glycidyloxypropyl) trimethoxysilane. The interfacial bonds between the polyurethane coating-fGO nanosheets were significantly enhanced. Besides the experiments, theoretical quantum mechanics approaches were utilized to examine the interactions of trimethoxysilane with polyurethane and GO surface.

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1. Introduction

Polyurethane is a popular thermoplastic polymer, with hard and soft blocks, and has been widely used as a part of different applications such as foams, coatings, elastomers and adhesives [1,2]. Although the PU has outstanding properties such as good abrasion and UV resistance, great flexibility and strong adhesion to the substrates [3], but it has also some weaknesses like low thermal stability and mechanical strength which limit its extensive applications in many industries [4]. The low resistance of

PU against external stresses, *i.e.* thermal shocks and mechanical damages, results in the creation of defects in the coating matrix, which would be diffusion pathways for corrosive electrolyte. So, to overcome this unsatisfactory event the coating mechanical properties should be improved. Recent findings have showed that incorporation of nanoparticles into the PU matrix is one applicable strategy for overcoming these weaknesses, thanks to the high specific surface area and modulus of the nanoparticles. Various nanoparticles such as TiO₂ [5], silicon carbide [6], Fe₂O₃, BaTiO₃ [7], montmorillonite [8] and ZnO [9] have been added to the PU coating for mechanical properties reinforcement. Recently the PU matrix based on carbon allotropes has attracted the high attention of the researchers. Among various carbon allotropes, graphene is the most novel nanomaterial and its use has been dramatically increased over past five years. With its unique properties, graphene has gained a special place in the production of polymer

* Corresponding author.

E-mail addresses: Ramezanzadeh@aut.ac.ir, Ramezanzadeh-bh@icrc.ac.ir (B. Ramezanzadeh).

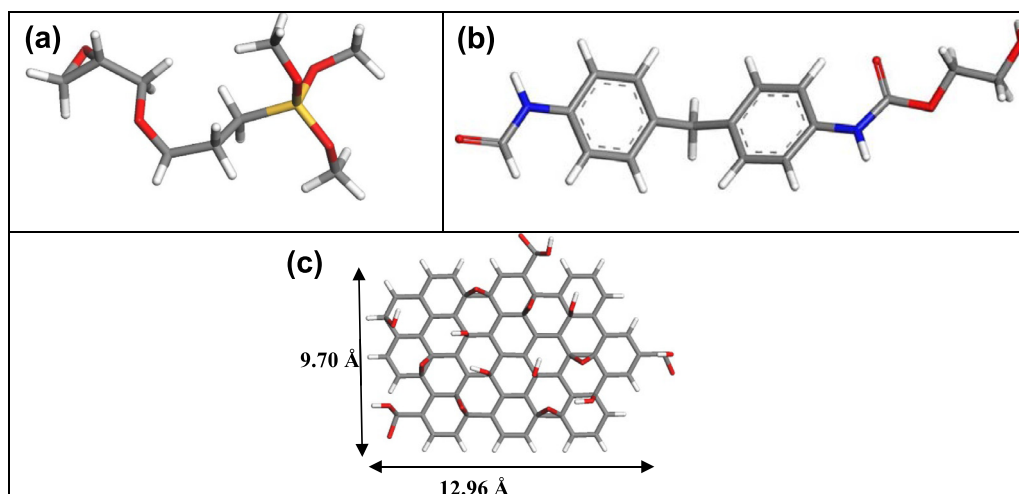


Fig. 1. Molecular structure of (a) (3-glycidyloxypropyl) trimethoxysilane (GPTS), (b) polyurethane monomer, and (c) graphene oxide. Atoms are shown in Stick style.

Table 1

The ratio of various peaks obtained from FT-IR spectra of GO and fGO nanosheets.

Ratio of the peaks	$\frac{\text{O}-\text{H}}{\text{C}=\text{C}}$	$\frac{\text{C}-\text{H}}{\text{C}=\text{C}}$	$\frac{\text{C}=\text{O}}{\text{C}=\text{C}}$	$\frac{\text{C}-\text{O}}{\text{C}=\text{C}}$	$\frac{\text{C}-\text{O}-\text{C}}{\text{C}=\text{C}}$	$\frac{\text{C}-\text{O}(\text{Alkoxy})}{\text{C}=\text{C}}$
GO	2.44	1.30	0.52	0.67	0.93	1.07
fGO	1.74	0.90	0.28	-	0.21	-

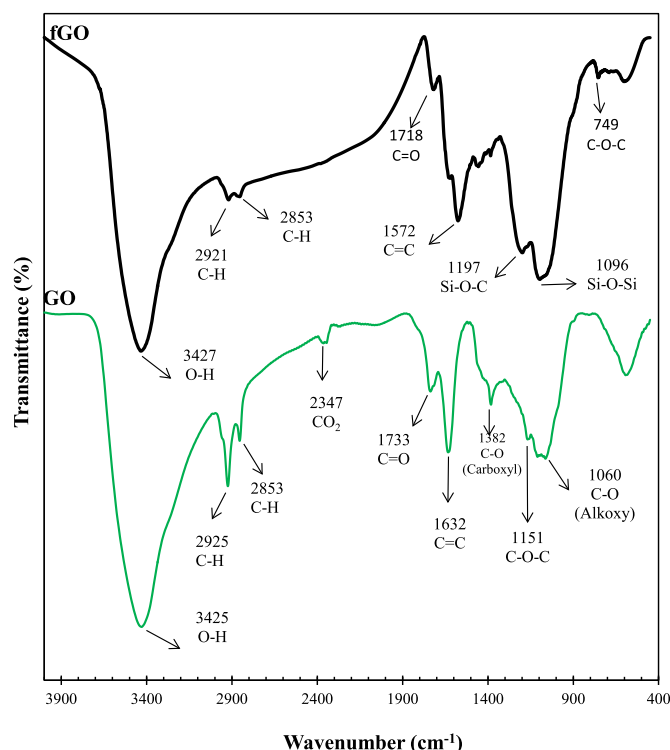


Fig. 2. FT-IR spectra for the GO and GO-GPTS nanosheets.

[14,15]. As a widely used derivatives of graphene, graphene oxide (GO) has been under large consideration for acquiring graphene-based composites [14]. Similar to graphene nanosheets, GO has attracted the high consideration of the scientists. Owing high specific surface area, high thermal conductivity, good mechanical properties, and excellent barrier against oxygen and water it has been turned into a significant nanomaterial for improving the properties of polymeric coatings [16,17]. GO contains massive oxygen containing groups such as hydroxyl, epoxide, carboxyl and carbonyl at the edge and basal planes [18,19]. These functional groups provide high polarity for the graphene derivatives and make it incompatible with most of the non-polar solvents and polymers. So, the covalent and non-covalent functionalizations of GO are required to enhance the nanosheets compatibility with non-polar solvent and organic polymers. Shifeng et al. studied the GO and reduced GO (rGO) functionalization with N (trimethoxysilylpropyl) ethylenediaminetriacetic (EDTA). The EDTA/graphene presented enhanced dispersion in water and the EDTA/graphene film with a well-layered structure and high conductivity was manufactured [20]. 3-amino-propyltriethoxysilane (APTS) is another molecule that is used for functionalization of GO (APTS-f-GO). Yang et al. functionalized GO with APTS and the outcomes revealed that the incorporation of APTS-f-GO increased the compressive failure strength of silica monoliths [21]. Also the use of APTS in Wang's study resulted in the enhancement of epoxy coating tensile properties [22]. (3-glycidyloxypropyl) trimethoxysilane (GPTS) is another kind of silane coupling agent which Wan et al. used in their study. They indicate that using silane-fGO nanosheets increased the compatibility between the silane-fGO and the epoxy matrix, leading to the increase of storage modulus, glass transition temperature, thermal stability, tensile and flexural properties, and fracture toughness of epoxy coatings [23]. In our previous paper the beneficial role of GO functionalization by silane coupling agent [24] and polyaniline nanofibers [25] on the mechanical and anti-corrosion properties of the epoxy coating has been demonstrated. Surface functionalization of GO resulted in the GO/Polymer interfacial interactions enhancement as well as good dispersion of particles in the poly-

composites with enhanced properties. Some of the outstanding properties of the graphene, including high thermal and electrical conductivity, good mechanical strength, and superior impermeability to gasses make it a perfect platform for reinforcement of polymeric coatings [10–13]. Graphene nanosheets can affect the interfacial interactions between the graphene sheets and polymer chains and produce nanocomposites with outstanding properties

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