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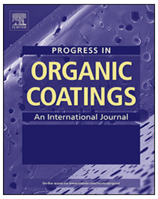

Screening the effect of graphene oxide nanosheets functionalization with ionic liquid on the mechanical properties of an epoxy coating

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ABSTRACT

Epoxy coatings are widely used in many industries due to the high anti-corrosion properties, good adhesion to metals and high cross-linking density. However, due to the high brittleness and poor resistance against crack propagation, the coating performance can be decreased in exposure with external stress. In this study the graphene oxide (GO) nanosheets were modified by 1-Butyl-3-methylimidazolium chloride (BMIM-Cl) ionic liquid and then introduced into an epoxy coating for the reinforcement of the mechanical properties. The BMIM-Cl adsorption on the GO surface was studied by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) analysis and Raman spectroscopy. The fracture surface morphology of the film without and with nanoparticles was studied by a scanning electron microscopy (SEM) to reveal the effect of GO-BMIM nanosheets dispersion on the coating mechanical properties. The GO-BMIM nanosheets were introduced into the coatings at different loadings. FT-IR test results confirmed that the BMIM molecules successfully attracted with GO sheets through physical/chemical bonds. XRD and Raman spectroscopy tests results revealed the role of BMIM molecules on the GO stacking reduction. The physical and mechanical properties of the coatings were investigated by tensile and dynamic mechanical thermal analysis (DMTA). Result showed that addition of 0.09% GO-BMIM nanosheets into the epoxy matrix significantly increased the glass transition temperature (T_g), storage modulus, tensile strength and energy at break. The coating brittleness was remarkably reduced by addition of GO-BMIM nanosheets, indicating that the BMIM molecules adsorption on the GO surface successfully improved the coating mechanical properties. Results revealed that the maximum flexural strength was obtained in the presence of 0.09% GO-BMIM, attributed to the good dispersion and high tensile strength of the nanosheets.

1. Introduction

Epoxy resin is one of the most important thermo-setting polymers with unique physical, anti-corrosion and chemical properties and has been widely used in the plenty of industrial applications such as coatings, composites, adhesives, construction materials, and syringe materials. The high anti-corrosion properties of the epoxy come from its high cross-linking density and good adhesion to the metal substrate. Large efforts have been performed to enhance the corrosion protection performance of the epoxy coating by incorporation of fillers, additive, pigments and corrosion inhibitors. It has been shown in our previous studies that incorporation of nanofillers into the epoxy coating is an effective approach for enhancing the corrosion resistance [1–6]. However, epoxy has some weaknesses including high brittleness and poor resistance to crack propagation [7–10]. Creation of cracks and defects as a result of mechanical damages can deteriorate the barrier and anti-corrosion properties of the coating. For this reason many studies have been done to improve the epoxy coating mechanical properties. There are various methods for the epoxy coating mechanical properties enhancement, among them addition of additives, fillers and pigments are the most effective methods [11–13]. Recently, the nanotechnology has attracted the researchers' attention to make nanocomposites with extraordinary results. The extremely high surface area of the nanoparticles provides strong interfacial interactions with the polymer chains and results in the coating fracture toughness enhancement. Various kinds of nanopigments have been used for this purpose [14,15].

Recently, the graphene oxide (GO) nanosheet has attracted considerable attention of the researchers. GO is one of the most famous carbon material with special properties such as high specific surface area, unique structure (a two-dimensional monolayer of sp^2- hybridized) and thermal and mechanical properties. So, GO is an effective option for the reinforcement of polymer composites [16–18]. The beneficial role of GO and functionalized GO nanosheets on the epoxy coating mechanical properties enhancement has been shown in the

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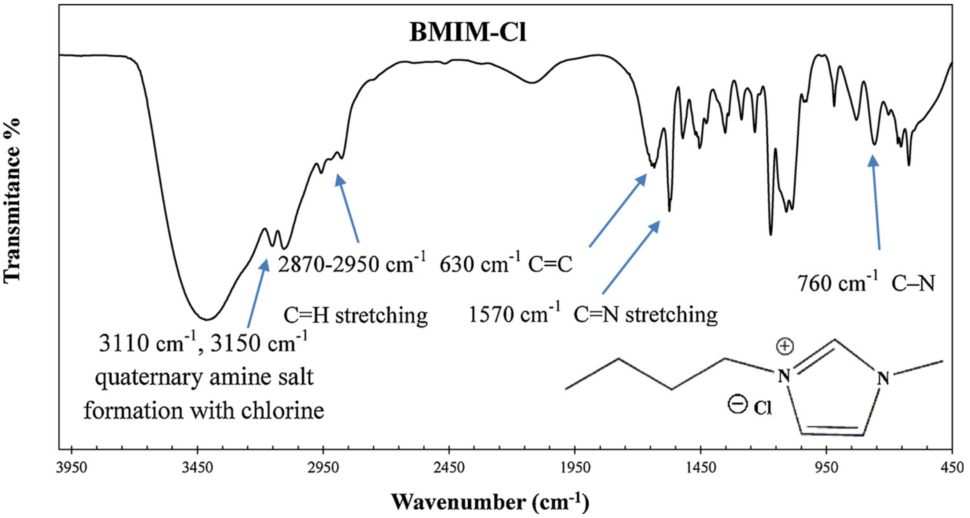

Fig. 1. The chemical structure and FT-IR spectra of BMIM-Cl.

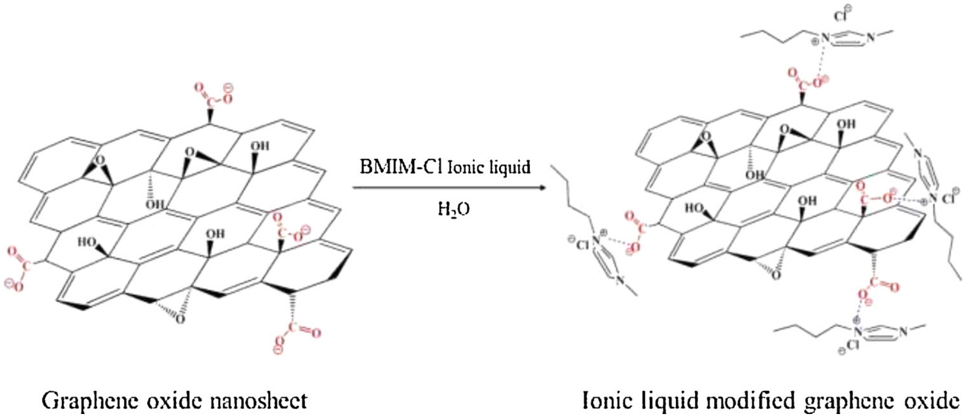

Fig. 2. The schematic of interaction between BMIM and GO.

previous reports [15,19–22]. It has been shown that the presence of many oxygen containing functional groups, i.e carbonyl, carboxylic, epoxide and hydroxyl, on the GO surface makes it incompatible with non-polar solvents and therefore the organic polymers. So, the GO nanosheets extremely tend to aggregation in the epoxy matrix, because of van der Waals interactions, declining the coating properties [23,24].

In order to increase the dispersion properties of GO sheets in the epoxy resin many different kinds of methods have been used, including covalent and non-covalent functionalization of GO sheets with organic and/or inorganic compounds. Covalent functionalization is a method that has led to good results, but it has been limited because of the presence of toxic solvents, difficult and long steps in process [25–27]. However, the non-covalent method based on surfactant has many advantages in this regard. Lotya et al. [28] prepared graphene dispersions, stabilized them in water by a surfactant at concentrations up to 0.3 mg/mL. Smith et al. [29] dispersed graphene in water, stabilized by a range of 12 ionic and non-ionic surfactants. They found that the graphene can be properly dispersed with the aid of a range of surfactants at low surfactant concentration. Jun Wan et al. [30] showed the improvement of graphene dispersion in the epoxy coating via a facile surfactant-assisted process and found that the surfactant treatment of graphene is an effective method to improve the dispersion stability in water. Sung et al. [31] prepared non-covalently functionalized GFs (*f* -GFs) with 1-pyrenebutyric acid (PBA), that are highly soluble in various solvents and used them in epoxy resin. The results indicate that incorporation of f-GFs into the epoxy resin improved the thermal conductivity and mechanical properties at 10 wt% and 1 wt% of particles, respectively.

Ionic liquids (IL) are organic salts with unique properties such as low melting point (below 100 °C) non-flammability, air and moisture stability and high conductivity [32,33]. Low vapor pressure is one of the most interesting characteristics of ILs which makes them as non-toxic substance. Kangkang et al. [34] investigated the IL surfactants in an ultrasonic-assisted extraction followed by HPLC analysis. Pourghasemi et al. [35] studied the corrosion inhibition effectiveness of 1,4-di [1-methylene-3-methyl imidazolium bromide]- benzene as an ionic liquid on mild steel in 1 M H_2SO_4. Wang et al. [36] prepared an epoxy nanocomposite reinforced with carbon nanotubes stabilized by ionic liquid and found significant improvement in the physical and mechanical properties due to the strong interfacial bonding between the carbon nanotubes and the polymer matrix. Wang et al. [37] applied a non-covalent modified graphene oxide by methacryloxyethyltrimethyl ammonium chloride (DMC), a kind of ionic liquid and used it in a poly (vinyl alcohol) (PVA) matrix. They showed considerable enhancement in the mechanical properties and remarkable improvement in thermal stability of the composite at low loading of nanoparticles. Kui et al. [38] modified GO sheets by sod Benzeneas ium borohydride and imidazolium ionic liquids (Imi-ILs) containing two vinyl-benzyl groups and introduced them into the poly (methyl methacrylate) (PMMA). They found that the functionalized graphene sheets uniformly dispersed in the PMMA matrix and increased the storage modulus (58.3%) and glass transition temperature (19.2 °C) at 2.08 vol.% loading. High electrical conductivity was also achieved at graphene loading levels beyond 1 vol % (ca. 2.55 Sm^{-1}) with a low percolation threshold (0.25 vol.%) for the composites. Wen-Shi et al. [39] applied a non-covalently modified