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Impedance response of nanocomposite coatings comprising of polyvinyl butyral and Haydale's plasma processed graphene

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ABSTRACT

In this research, the electrochemical impedance spectroscopy study was conducted on graphene/polyvinyl butyral nanocomposite coatings. Functionalized graphene used in this study was produced by Haydale's plasma modification process involved different gasses or their mixer such as argon, fluorine, and oxygen. The presence of porous bounded Warburg and Gerischer diffusion elements in the model circuits indicate that coatings behave as electrolyte diffusion limited or porous electrode that improves the mass transport resistance by trapping the electrolyte solution in the coating. Capacitive-resistive behavior at intermediate to lower frequencies range in phase angles also confirms the blocking behavior towards corrosive species. Small-angle x-ray scattering study shows that coatings have surface fractels structure of intermediate roughness to a smoother surface for composites coatings indicating improved dispersion of graphene in resin, which resulted enhanced barrier properties.

1. Introduction

Among nonmetallic coatings, polymers are widely used on metallic surfaces as passive physical barrier (coatings or films) to the corrosive species. Incorporation of barrier fillers in coatings provide tortuous/longer diffusional paths for the corrosive solution due to the high aspect ratio, platelike or layered structure e.g. carbon nanotubes, clay etc. and slowdown the corrosion process to a manageable rate [1]. The development of single-layer graphene from graphite, has given rise to its broad use as reinforcement for polymer matrix. The barrier nature of graphene owing to the layered structure can be used to slow down the penetration of corrosion promoting species through organic coatings as reported earlier [2]. Further, the barrier properties of composites depend on many factors such as; I) Nanoscale level dispersion and distribution of fillers, II) Interfacial compatibility of polymer and filler phases, III) polarity match between the filler surface and the polymer chains. The full advantage of nano-fillers can only be achieved by considering factors above that could lead to uniform transfer of chemical, physical and mechanical properties of filler to host polymer matrix [3–6].

Recently, Haydale Ltd. introduced dry plasma process for functionalized graphene production as an alternative to graphene produced or functionalized from wet chemistry. Williams et. al patented and reported many advantages of GP produced from Haydale' process such as improved exfoliation, enhanced dispersion and compatibility with host matrix owing to selective surface groups and undamaged crystalline structure [7,8].

Recenlty, Chaudhry at el. prepared composites coatings of thermally reduced graphene with polyvinyl butyral on carbon steel. Electrochemical techniques showed superior barrier properties for shorter period of time at very high concentration of graphene. This study also suggested that functionalized graphene can reduce the amount of graphene required to improve the coating properties. Along with the barrier nature of polymeric coatings, the high insulating nature of polymers also prevents external flow between anodic and cathodic areas. The presence of very high percentage of gaphene in coatings can also deteriorate the physicochemical properties of coatings rapidly for longer periods of time due to excellent conductivity of the graphene [2]. Many studies showed that modification of graphene on the basis of wet chemistry and complex processes can improve the disperiosn in main matrix used for coating. Yuan et al. modified the graphene oxide surface with p-phenylenediamine modified graphene oxide and p-phenylenediamine/4-vinylbenzoic acid using twostep process. Polystyrene/graphene nano-composites showed improved anti-corrosion properties with the incorporation of 2 wt.% of modified reduced graphene due to excellent interaction and dispersion of

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graphene in polymer matrix [9]. Similarly, nanocomposite of silane and pernigraniline modified graphene showed superior barrier properties when incorporated in polymer matrix [10,11]. Another researcher modified the GO with TiO_2 through complex process and showed that modification improved the exfoliation and dispersion [12].

This study deals with the comparison of barrier properties of nanocomposites prepared from Haydale's graphene and thermally reduced graphene oxide (U-GP). Haydale's process is an enviromentally friendly dry plasma process contrary to wet chemistry and produce functionalized graphene with various groups. We used four kinds of graphene i.e. U-GP and Haydale's processed graphene nanoplatelets produced using three types of process gasses i.e. Fluorine (F-GP), Oxygen (O-GP), and Argon (A-GP).

2. Experimental procedure

M-GP (commercial name HDPlas™) was used as purchased from graphene supermarket, USA with planer size 0.3–5 µm and platelets thickness < 50 nm. U-GP (A-12, graphene supermarket, USA) thickness < 3 nm and planer size 2–8 µm were used for comparison. Polyvinyl butyral (PVB) with trade name Butvar B-98 (molecular weight 40,000–70,000) were purchased from Sigma Aldrich. PVB had 18–20% hydroxyl content, and 80% butyral content. GP amount was kept constant i.e. 3 wt.% of Resin (Butvar B-98) (5 g Resin/50 ml methanol) for all the composites. Model coatings were prepared by bath sonication of GP for 4 h in 50 ml methanol followed by 48 h of mixing with PVB in closely tight glass flask. Carbon steel samples were polished staring from 60 to 600 grit sand paper. Using dip coater, carbon steel substrates were coated with PVB-GP dispersion by immersion and withdraw speed of 50 and 200 mm/min respectively. Samples were immersed in solution for 1 min. Two coats were applied for each sample in similar manner with an interval of 15 min. Further, the samples were dried at room temperature for 3 days followed by baking in air circulating oven at 175 °C for 2 h to generate final coating with thickness in the range of 270 ± 3 µm. Four carbon steel samples were prepared for each PVB and composite coatings. A flat cell assembly (Fig. 1) with working volume of 350 ml consisting of carbon steel coupon as the working electrode (WE) with expose area 2.6 cm^2, graphite plate as counter electrode (CE) having dimensions of 25 × 25 × 5 mm with expose area 2.6 cm^2, and a silver/silver chloride electrode as reference electrode (RE), were used for the electrochemical measurements. The open circuit potential of steel samples was recorded against Ag/AgCl electrode as reference electrode for 1 and 12 h. After the completion of each step, EIS was measured. Impedance measurements were performed vs. (E_{OCP}) after 1 and 12 h from the time of immersion. The frequency sweep was performed from 10^5 to 10^{-2} Hz at 10 mV AC amplitude.

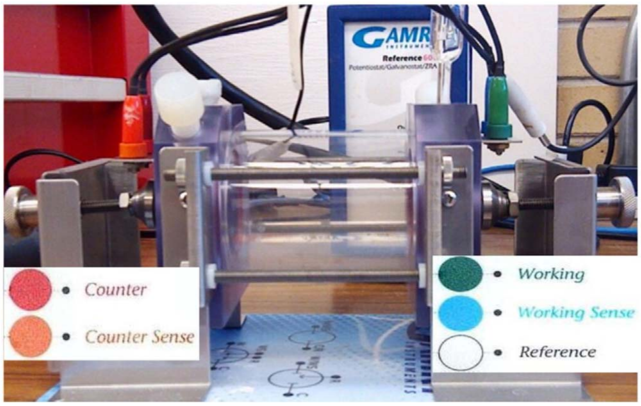

Fig. 1. Electrochemical flat cell Setup.

3. Results and discussion

Thermogravimetric analysis (TGA) (Fig. 2a) of the PVB resin over temperature range of 20–800 °C reveals the thermal degradation of different compounds. The weight loss (9%) due to the dehydration of copolymer can be observed up to 370 °C. The major degradation peak around 406 °C was due to the thermal degradation (89%) of PVB which remains till 460 °C, releasing products such as butanal, C4- hydrocarbons followed by degradation of cyclic and crosslinked compounds [2,13]. Similarly, Fig. 2b shows the DSC thermograms of PVB during isothermal heating. First heating clearly indicates the presence of sharp peak at 63 °C indicating glass transition temperature (T_g). After isothermal heating at 200 °C for 2 h, second heating indicates disappearance of sharp peak and shows a small hump in the thermogram at 70 °C. This behavior was unlike to the previous reports where thermal treatment showed that T_g shifted to 170 °C. It was reported that the self-crosslinking of PVB was taking place owing to the interaction of $-OH$ or acetate groups on adjacent PVB chains which may results reactions between functional groups leading the bridge bonds [2,14]. Fig. 3(a–b) show the structure and infrared spectroscopy spectra and analysis of assigned peaks. The spectrum of heat treated resin does not show any new peak indicating absence of new bonds owing to cross-linking. These results are in agreement with the previous reports where heat treatment produced changes in PVB structure measured by hardening of sample [2,15].

The microstructure of polymers can be analyzed using scattering methods, such as small angle x-ray scattering (SAXS) [16]. The structural features at various length scales (length scale $\sim 2\pi/q$) in polymers and nanocomposites are probed by the scattering vector (q). Also, the power-law decaying exponent ($\log(I) \sim \log(q)^{-\alpha}$) at lower q values explains the size of the scattering objects or fractals. In a report by Malekani et al. [17], α was directly related to the fractal dimensions, D_f. Specifically, mass fractals exhibited an $\alpha \le 3$ (a substance whose surface and mass are both characterized by the fractal properties). The α is directly related to the mass fractal dimensions, D_m. The surface fractals are formed for $3 \le \alpha \le 4$, and the surface fractal dimension, Ds, can be calculated as follows: $\alpha \equiv 6 - D_s$ where $3 < (6 - D_s) \le 4$ [17,18].

SAXS patterns (Fig. 4) from the free-standing thin films of PVB and its nanocomposites with various types of GP at 3 wt.% loading were investigated. Neat PVB exhibited an $\alpha \sim 3.2$ (not shown here), which remained unchanged after the crosslinking reaction. An $\alpha > 3$, in this case, showed the presence of surface fractals, which might be associated with the crystallinity of PVB and its molecular architecture. The addition of GP, in all cases, increases the α value. Incorporating U-GP in PVB slightly increased α, which further increased to 3.6 for both F-GP, and A-GP nanocomposites, and $\alpha = 3.5$ was observed for O-GP/PVB nanocomposites. Very close values of α in M-GP nanocomposite systems shows the nearly similar dispersion of M-GP in all cases. The surface fractal size$\equiv 2\pi/\Delta q_{(\text{R-squred}\rightarrow 0.99)}$ and Dimension $\equiv 6 - \alpha$ was found as: PVB (~20.4 nm, 2.8), U-GP (~17.4 nm, 2.7), O-GP (~12 nm, 2.5), F-GP (~10.8, 2.4), A-GP (~10.7, 2.4) indicates that graphene produced from Haydale's process produced better dispersion in the resin. D_s can be used to find the degree of roughness and irregularities where D_s between $2 \le D_s \ge 3$, the value of 2 and 3 indicate highly smooth and disordered surface respectively [19–21].

A survey scan of GP was done using x-ray photoelectron spectroscopy (XPS), (Figure-2-ESI) showed different C/O atomic ratio as; U-GP, 62/1: A-GP, 10/1: O-GP, 11/1: and for F-GP, 14/1 and C/F is 133/1. These results show that Haydale's graphene contain higher C/O ratio in the form of different groups such as epoxy, hydroxyl, carboxylic acids and alcohols which can result in the better dispersion [22–24]. TEM (Fig. 5) of overlapping M-GP nanosheets shows different morphological features from that of U-GP with lateral size ranging in micrometers. FT-IR (Table 2-ESI) does not hint any new peak in all the cases except some slight shifting of wave numbers of some peaks may be indicating