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The production of a multi-walled carbon nanotube/hexamethylene diisocyanate nanocomposite coating on copper by electrophoretic deposition

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ABSTRACT

A multi-walled carbon nanotube (MWCNT)/hexamethylene diisocyanate (HDI) composite coating with excellent microstructural homogeneity was produced on copper substrate from aqueous suspensions using electrophoretic deposition (EPD). The concentrations of different additives were optimized to obtain stable suspensions of MWCNT. At the optimum EPD condition, a coating of thickness 170 μm was obtained at voltage of 30 V and deposition time of 3 min with well dispersed MWCNT in the polymer matrix. The deposit yield increased linearly with deposition time. The adhesive strength of the MWCNT/HDI composite coating was assessed qualitatively by peel test. The composite coated specimen showed greater resistance to corrosion in the chloride containing environment with inhibiting efficiency 96.65%. The mechanism for adhered coating is due to better wetting of HDI on copper substrate followed by acid-base reaction between metal hydroxide and polymeric resin. The potential application of the nanocomposite coatings could be protecting copper based metallic structure in marine environment.

1. Introduction

Carbon nanotubes (CNTs) are the most sought after materials for the scientific community of materials science throughout the world and are viewed as most ideal candidates for preparation of high performance polymer composite with unique mechanical and other physical properties [1–3]. The elastic modulus (stiffness) and tensile strength (strength) of CNT can be as high as 1 TPa and 200 GPa respectively, which is higher than the strongest steel at a fraction of the weight [4]. Therefore, CNT could be employed as very light, strong and tough fibers for composite structure [5]. There are number of reviews on the mechanical properties of CNT-polymer composite highlighting its importance and exciting potential applications [6–11]. The effective utilization of CNT for composite application primarily depends on homogeneous dispersion of CNT as filler throughout the polymer matrix. Aggregates act as defect sites and will seriously limit the mechanical performance apart from adversely effecting physical properties of the composite [3]. However, uniform dispersion of CNT in polymer matrix is restricted presumably due to (a) high surface energy which makes it difficult to suspend them in liquid but helps in formation of aggregates [12] (b), the high polarizability of the π-electrons of graphene sheets leads to powerful van der Waals attractive forces, and (c) axial geometry, which provides a large surface area of contact facilitating high attractive energy between CNT [13]. Therefore, a significant challenge critical for processing CNT for composite application is to form uniform dispersion of CNT within the polymer matrix, improve nanotube/matrix wetting, and enhance their mutual adhesion [14,15].

The overall aim of this investigation is to produce uniform deposits of multi-walled carbon nanotube (MWCNT) and polymer as thin film from its colloidal suspensions, by electrophoretic deposition (EPD). EPD is a colloidal forming technique where charged, colloidal particles in a stable suspension are deposited onto an oppositely charged substrate by the application of electric field [16]. It is commonly employed in processing of ceramics, coating, and composite [17–20]. EPD is very versatile, fast, and cost effective to produce coating of controlled microstructure on a wide range of substrates. The process can be applied, in general to any solid in particulate form with small particles (<30 μm) and to colloidal suspensions [21]. EPD is a very powerful tool for the ordered deposition of CNT and CNT-based nanostructures for a variety of applications, including (i) catalyst supports (ii) structural composites and coating (iii) gas sensor (iv) capacitor (v) biomedical scaffold (vi) electrode for fuel cells (vii) actuators and (viii) field emission devices, [19,21–24]. Most of the above research used organic solvents or mixture of organic solvent and resin to prepare composite [23,24]. Recently, Thomas et.al, [20] used aqueous EPD to obtain MWCNT coating of about 10 micron thickness at 40 V and 4 min deposition time. In majority of cases, EPD is reported to use organic/mixture of organic solvent as vehicle, which is not only hazardous but also polluting the environment and dangerous for sea species, when it is used in seawater. Research effort is being made to develop aqueous based EPD [20,25,26] to minimize the uses of organic solvent. Present investigation is an

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attempt in that direction, it not only involved aqueous processing but also used dispersant which is a natural polysaccharide of plant origin.

A major part of metallic constructions exposed to seawater and marine atmospheres are destroyed, due to the corrosion phenomena. Copper is one of the essential structural engineering materials widely used in chemical industry, pipelines for domestic and industrial utilities, heat conductors, heat exchangers, electronic industry, communication industry including seawater (marine environment) owning to its mechanical workability and other properties [27]. Under intense seawater/marine environment, the copper form thin layers of corrosion products, generally dark-brown to green-bluish colour, chemically known as copper hydroxide and copper carbonate, copper sulphate etc. depending upon exposure time, and presence of pollutants in the surrounding environment, which is technically also known as patina [28]. Copper ions being very sensitive to chloride ions, even presence of trace amount can cause corrosion at very significant rate in sea water and form unstable films of CuCl and soluble chloride complexes [27]. The conventional treatment approach is based on hydrophobic polymer paints coating or self assembled monolayer [27]; however, they have their own limitations, first and foremost is very short life span of coating and therefore, one has to go for coating very often, multistep, and tedious. Sometimes polymeric resin paints contains toxic substances like (chromium etc) which is very harmful to the environment. Nanostructure materials engineering extends the possibility of designing environmentally friendly anti-corrosion engineering 'smart' coatings which can last much longer compared to traditional coatings. CNT-reinforced polymer nanocomposite based protective coatings are attractive options for marine environment applications due to their excellent properties and unlimited possibilities of tailoring their chemical, physical and processing behavior to meet the requirement. CNT-reinforced nanocomposite coatings guard the substrate by providing a tough protective shield that can lock out destructive elements and keeping it resilient and durable for very longer period of time, which cannot be met by the traditional micrometer hydrophobic polymer/self-assembled monolayer coatings.

The specific aim of the present work is to fabricate MWCNT/hexamethylene diisocyanate (HDI) composite coating by EPD from aqueous suspensions for possible potential application in stringent marine environment to protect copper based structure from oxidation and further corrosion. In this study HDI has been reported as polymeric matrix for the first time. The influence of dispersant and polymeric resin on improving the adhesive strength of the MWCNT/HDI composite coating on copper substrate will be examined. The most plausible mechanism of coatings by combination of MWCNT and polymeric resin (HDI) on copper substrate has been proposed.

2. Experimental

2.1. Materials

MWCNT was purchased from Sigma-Aldrich Chemie, GmbH, Steinheim, Germany, with diameter range of 110–170 nm and average length 5–9 μm as reported by the supplier (Fig. 1). The Scanning electron microscopy (SEM) image of pristine MWCNT showed large number of cross-linking and entanglements. The entanglement could be broken to large extent by addition of dispersant. Fig. 2 shows well dispersed MWCNT in presence of dispersant Gum Arabic (GA). GA used as dispersant is a highly branched polysaccharide and is known for its dispersion property. HDI is an organic polymeric resin generally used in special applications such as enamel coating which are resistant to abrasion and degradation from UV light. The as received MWCNT was further characterized by the Raman spectroscopy (Fig. 2). The D-band (1353 cm^{-1}), G-band (1575 cm^{-1}) and D'-band, the second order overtone of D-band (2696 cm^{-1}), confirms the typical characteristics of multiwall carbon nanotube.

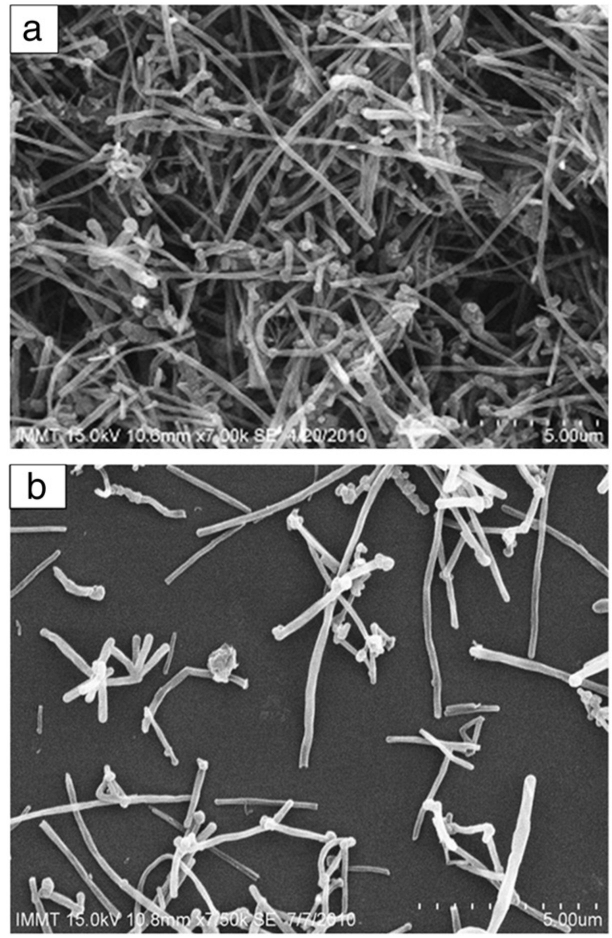

Fig. 1. a. SEM image of as received pristine MWCNT with very large number of cross-linking and entanglement. b. SEM micrograph of well dispersed MWCNT in presence of dispersant GA.

2.2. Preparation of MWCNT/HDI suspension for EPD

Preparation of well dispersed suspension, free from agglomerates, is a prerequisite for obtaining uniform, homogeneous and crack free deposit by EPD. 0.1 wt.% of MWCNT suspension was prepared in aqueous solution by adding pre-optimized quantities of GA and HDI, combination (600 mg/g) and (0.27 mg/g) respectively. Dispersant is

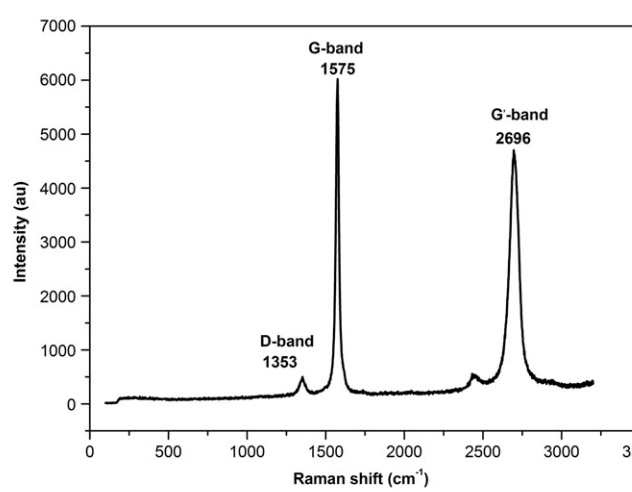

Fig. 2. Raman spectra of multi-walled carbon nanotube.