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Anti-corrosion characteristics of polyimide/h-boron nitride composite films with different polymer configurations

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ABSTRACT

Anti-corrosive polyimide/hexagonal boron nitride (PI/h-BN) composite films were prepared with different monomers to offer different polymer configurations: rigid and soft. In PI/h-BN composite films, different configurations of polymers show different crystallinity trends of the polymer matrix. In our study, the degree of crystallinity in rigid polymer decreases with the BN content; in flexible polymers it is independent of the BN content. It is worth noting that BN in different PI matrices can effectively enhance the protection of steel from corrosion. With a flexible PI matrix, the PI/h-BN coating exhibited better resistance to water vapor and better anti-corrosion. Only 5 wt.% of h-BN in the composite is enough to offer high anti-corrosion, a positive corrosion voltage.

1. Introduction

Polyimide (PI) shows good mechanical properties, such as low creep, low stress relaxation, high yield stress and high tensile strength [1–3]. Therefore, PI is a high performance polymer, lightweight, flexible, and resistant to heat, chemicals, and organic solvents [4–6]. Even though PI shows excellent chemical and thermal stability, water easily penetrates PI [5–7]. Water penetration reduces the protection of the PI coating barrier in anti-corrosion applications [8–10]. In order to decrease water penetration, many inorganic materials have been imported into the polymer matrix, such as silica [10,11], titanium oxide [12–14], clay [15–18] and graphene [19,20]. Generally, ceramic materials which are synthesized by the sol–gel method are spherical particles; however, spherical particles show worse barrier properties than 2-D flake materials in the polymer matrix on anti-corrosion applications. This is the reason why 2-D materials are widely used in anti-corrosion applications with polymer matrices [6,8,16–20].

Clay is a fine-grained soil that combines one or more clay minerals with traces of metal oxides. Usually, clay contains cations, which are quantified by the cation-exchange capacity (CEC). The CEC of clays used in anti-corrosion is about 100–120 meq/100 g [21–23]. Clay with high ion content in the polymer will enhance the ion conductivity of the anti-corrosive coating [23], which may reduce the stability and credibility of the anti-corrosion barrier, in turn, downgrading its anti-corrosion performance. A similar problem is also revealed in the graphene system. Graphene is an excellent electric conductor. Conductive graphene in the barrier layer may cause galvanic corrosion with other metals and/or reaction with another metal ion in the electrolyte. Boron nitride (BN) is a chemical compound with equal numbers of boron and nitrogen atoms. The hexagonal structure, as in graphene or carbon-related materials, is the most stable [24] packing of carbon atoms (belonging to group IV A). BN, compounds of boron and nitrogen atoms (groups III–V A), also have a stable hexagonal structure similar to graphene sheets. Because hexagonal boron nitride (h-BN) does not contain ions, it behaves as an excellent insulation. Therefore, we can expect that h-BN in a corrosion-protection coating may produce better anti-corrosion stability than clay and graphene. In addition, no previous study on BN in the polymer matrix has been reported for anti-corrosive applications. In this paper, we import h-BN to the PI matrix as a barrier layer, and evaluate its corrosion-protection characteristics with different PI matrices: rigid and soft. Dynamic mechanical analysis, X-ray diffraction (XRD), electrochemical measurements of Tafel plots, and the water vapor permeation test were undertaken to analyze the anti-corrosion related characteristics of the pristine PI matrix and the polyimide/hexagonal boron nitride (PI/h-BN) composite coating on steel.

2. Experimental

2.1. Materials

4,4′-Oxydianiline (ODA, 99.5%, Chriskev) and p-phenylenediamine (PDA, 99%, Aldrich) were vacuum-dried at 110 °C for 24 h prior to use. 3,3′,4,4′-Biphenyl tetracarboxylic dianhydride (BPDA, 99.5%, Chriskev) and 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) (IDPA, 97.5%, Chriskev) were purified by recrystallization using acetic anhydride (99.8%, Tedia). h-BN (Nanostructured and Amorphous Materials, Inc.) was vacuum-dried at 120 °C for 24 h to remove moisture. Molecular

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sieves (4 Å) were used to remove water from the solvent, N, N′-dimethylacetamide (DMAc, HPLC, Tedia).

2.2. Preparation of PI/h-BN composite films

The PI/h-BN composite films were synthesized using diamine (PDA, ODA), dianhydride (BPDA, IDPA) and h-BN. A stoichiometric amount of h-BN was dispersed in a given amount of DMAc with ultrasonication and mechanical stirring in a flask. Equimolars of diamine and dianhydride were slowly added to the above solution for polymerization. After all solid monomers had been dissolved in the solution the polymer precursor solution was kept at room temperature for 2 h. The resulting solution was cast on steel using a doctor blade and was then transformed into PI by chemical imidization at 150 °C for 1 h. The PI was synthesized by BPDA and PDA which is abridged to BP-PD; moreover, the PI is formed by IDPA and ODA named ID-OD. The chemical structures of BP-PD and ID-OD are shown in Scheme 1.

The pristine BPDA-PDA with symmetric configuration is a rigid polyimide and IDPA-ODA with kink configuration is a soft polyimide. The composite sample codes are denoted as BP-PD-x or ID-OD-x, where x represents the weight percentage of h-BN in each solid sample.

2.3. Measurements

A dynamic mechanical analyzer (DMA, TA Instruments, DMA 2980) was employed to determine the storage modulus (E′) and glass transition temperature (Tg) of pristine PI and composite films. Thermal gravimetric analysis (TGA, TA Instruments, Q500) was employed to determine the thermal stability of composite films. The crystalline characteristics were identified using XRD (Bruker, D2 Phaser). Electrochemical measurements of Tafel plots of coated steel 304 electrodes were taken with an electrochemical workstation (Jiehan 5600). The water vapor transmission rate (WVTR) of the composite films was measured with a permeation test system (Mocon, Permatran-W 3/61).

3. Results and discussion

The crystallinity difference between pristine PI and PI/h-BN composite films has been directly identified by XRD. Fig. 1 shows the XRD patterns of the symmetric-configuration BP-PD series and kink-configuration ID-OD series. The pristine BP-PD film in Fig. 1(a) exhibits two peaks of 2θ in the region of 12–26°, which identifies the pristine BP-PD a semi-crystalline polyimide, while the pristine ID-OD film in Fig. 1(b) displays a broad curve without peaks, which confirms that the ID-OD is an amorphous polymer. The symmetric configuration of the BP-PD shows a higher tendency for crystallization than the kink configuration of ID-OD. With h-BN in the BP-PD polyimide, the crystalline peak height of the matrix in Fig. 1(a) decreases with the h-BN weight fraction increasing. The higher h-BN fractions lead to lower peak heights of the contributed PI, meaning that h-BN hinders the packing of rigid chains and in turn reduces the crystallization of the PI matrix. On the other hand, the XRD patterns of ID-OD-x films are similar to that of pristine ID-OD film, because the pristine PI is amorphous.

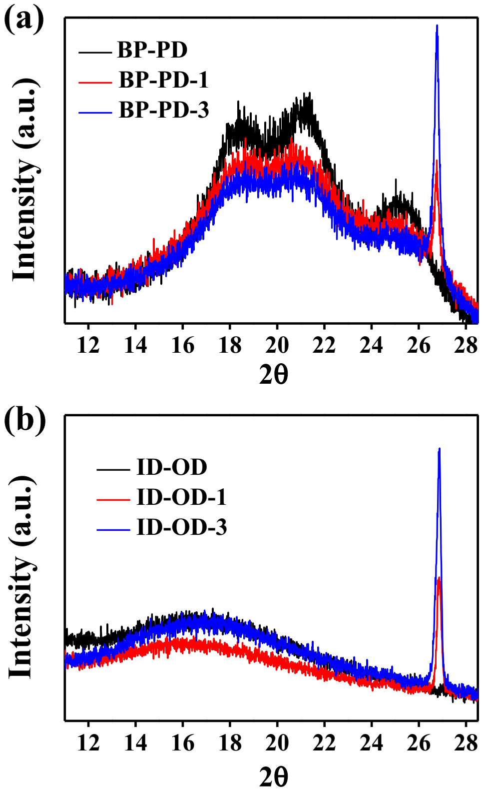
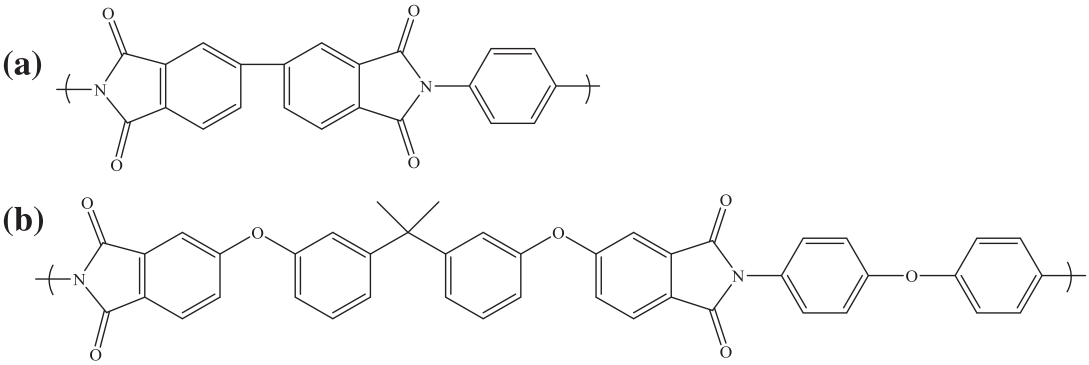


Fig. 1. XRD patterns of pristine PI and PI/h-BN composite films for (a) the BP-PD series and (b) the ID-OD series.

The storage moduli (E′) of PI and PI/h-BN composite films determined by DMA are displayed in Fig. 2. Because BP-PD is a semi-crystalline polymer and ID-OD an amorphous polymer, the former has a higher modulus than the latter. At temperatures no higher than 150 °C, both series of PI and PI-h-BN composites have the same trend of BN effects on the modulus. The modulus increases with the BN fraction. But there are differences in both series at higher temperatures. The rigid BP-PD and BP-PD-x in Fig. 2(a) keep their moduli above 1500 MPa below 250 °C while ID-OD and ID-OD-x downgrade their moduli at 220 °C. BP-PD shows higher modulus than BP-PD-1 and BP-PD-3, the reason is that BP-PD is a semi-crystal polymer, the modulus of crystal polymer should be higher than amorphous one. According to above reason, importing BN into BP-PD caused a reduction in polymer



Scheme 1. The chemical structures of (a) BP-PD and (b) ID-OD.