



Influence of boron incorporation on poly(phenyldiammine) nanostructures: Novel, well-defined and highly conducting nanospheres dispersed smart corrosion protective epoxy coatings



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ABSTRACT

The work reports the synthesis of nano Poly(borophenyldiammine) PBPDA: a novel nanoconducting polymer via easy, scalable and eco-friendly green approach. The method is template less and surfactant less, ensuing PBPDA nanospheres of uniform size c.a. 120–130 nm of high solubility, conductivity, surface area, crystallinity and well-defined shape. More interestingly, PBPDA nanoparticles dispersed epoxy nanocomposites were prepared using DMSO, as an alternative non-toxic solvent, considering the extreme present urgency for clean environment. Our findings revealed that coatings exhibited outstanding anti-corrosive properties as compared to other conducting polymer based coatings, which is corroborated to B in PDA, which acted as a filler, cross linker and modifier.

Introduction

With the recent development, in the nanoscience and nanotechnology fields, the dependence of material properties on fillers has become a focal point of significant interest. In view of this, conducting polymers (CPs) such as Polyaniline [1], Polypyrrol [2] and Polythiophene [3–7] have emerged as, fascinating nanofillers. Further, these CPs and their hybrids, have attracted great interest because of their exclusive properties emerging from the combination of organic and inorganic hybrid (OIH) materials [8–11]. They display enhanced optical, mechanical, magnetic and corrosion resistant properties [12]. These composites have been widely used in various fields such as military equipment's, safety protective garments, automotive, aerospace, electronics and optical devices [12,13]. Further, it has been observed that the valuable properties of the OIH materials are mainly dependent upon the properties of constituents, volume fraction of components, shape & arrangement of fillers and interfacial interaction between matrix with fillers [14,15]. Literature reports, intriguing area of their application in coatings and paints [16] arenas as inhibiting pigments, anti-bacterial as well as anti-fungal materials [17]. However, considering the drive initiated by coating chemists to formulate these OIH CPs, but still it is in cradle stage. Few reports have appeared on hybrid CPs (Al_2O_3 [18], SiO_2 , [19] ZnO , [20,21] Fe_3O_4 [22–25] etc.) to be used as corrosion protective materials. The promising strategy for the development of these next-generation OIH materials, as per our previous findings, is doping with hetero-atoms (e.g. N, S, P or B)

[26–29]. Hetero-atom [30] doping is an efficient way to modulate properties of CPs for their engineering applications. Considering this lead, shortcomings have to be removed which are associated with CPs and for enhancement of their properties, the introduction of Boron in CPs as a dopant, was proposed. Furthermore, doping with Boron and its Chemistry along with its applications has not been reported till date. In this communication, we envisioned to perform the green synthesis following four principles of green chemistry and analysing effect of B doping on Poly(o-phenyldiammine). [31] The epoxy dispersed nanocomposite was formulated using DMSO as green solvent reducing VOCs and PBPDA as a non-toxic anti-corrosive pigment in protective coating materials. As per our present knowledge and expertise in this field, the synthesis and application studies of Boron doped PDA (PBPDA) have never been investigated before.

Fig. 1 shows FT-IR spectrum of PBPDA which showed the presence of an intense NH stretching vibration (ν_{str}) at 3278 cm^{-1} . The C=N (ν_{str}) and C=C (ν_{str}) stretching modes for the quinoid (Q) and benzenoid (B) rings, which appeared at 1505 cm^{-1} and 1675 cm^{-1} respectively. The peak at 1244 cm^{-1} was assigned to the C–N stretching mode for the benzenoid rings, and peak at 1480 cm^{-1} showed C–O aromatic peak with benzene ring. The C–H bending vibration formed during protonation was confirmed.

by the presence of peaks at 1112 cm^{-1} and for C–O–C ether linkage at 1115 cm^{-1} . The band at 750 cm^{-1} revealed the presence of 1, 4 substitutions of NH_2 group at 1st position another group at 2nd position with respect to benzene ring respectively (Schemes 1 and 2 shows

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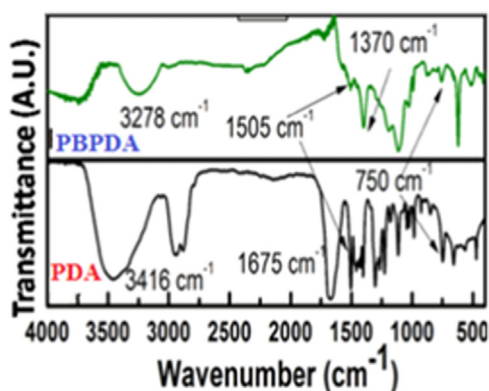


Fig. 1. FT-IR spectra of (A) PBPDA (green) and (B) PDA nanoparticles (black).

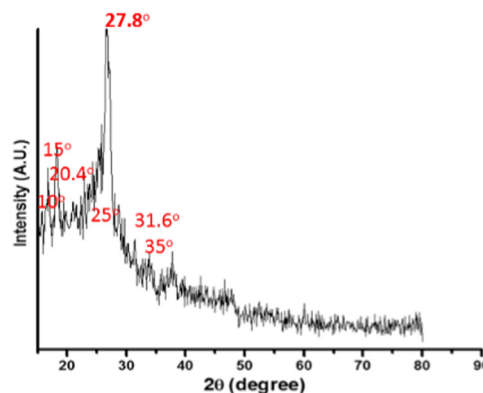
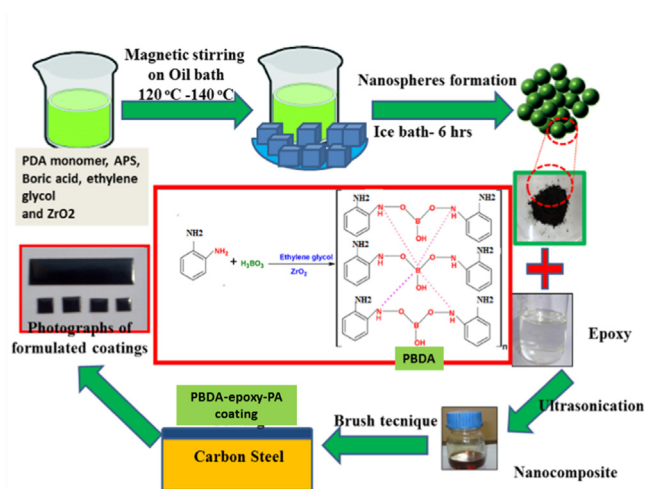
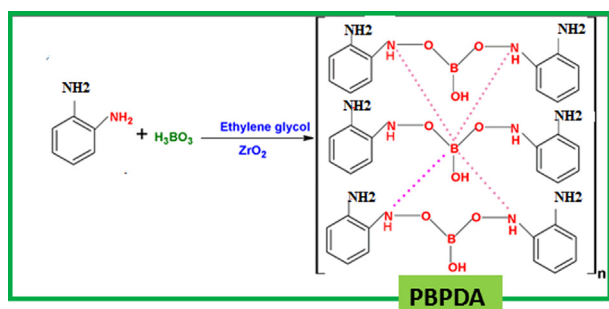


Fig. 2. X-ray diffraction pattern of PBPDA nanoparticles.



Scheme 1. Mechanism of formation of PBPDA nanospheres and their epoxy-PA based nanocomposite coatings on CS substrate (Details procedure of synthesis of PDA, PBPA and nanocomposite coatings are given in ESI).



Scheme 2. Reaction scheme of formation of PBPDA nanospheres.

formation and mechanism). The additional bands appeared at 1370 cm^{-1} and 645 cm^{-1} which clearly depicted the -B-O and -B-N- stretching and bending peaks, evidently confirms the successful doping of boron. This showed that -B- interacted with PDA backbone due to its electron deficient nature, it withdraws electrons towards itself causing these extra peaks as compared to neat PDA. FT-IR spectrum of PDA had all characteristic peaks as PBPDA except presence of -B-O- and -B-N- characteristic peaks present.

The gross structural analysis of PBPDA (Fig. 2) by XRD spectrum revealed the presence of characteristic peaks of PDA. In particular, peaks in the 2θ range of 20–35° reflected the presence of doped PANI, whereas the peak at $2\theta = 31.6^\circ$ corresponds to (101) planes of PBPDA [27]. The analysis of B doped PDA samples confirmed the doping of B in

PDA, (JPCDS No. 35-1365, 73-2158), the formation of primitive lattice due to incorporation of B within the PDA lattice. The presence of peaks (Fig. 2) at 10°, 15°, 20.4° and 25° showed the formation of partial crystalline structure of the PBPDA polymer. Two characteristic peaks centered at $2\theta = 20.4^\circ$ and 25° can be ascribed to the presence of the periodicity along the parallel and perpendicular plane to PDA conjugation chains, respectively [29].

Notably, a peak at 27.8° was observed, which is found to be indicative of the presence of B moiety in the system. The TEM micrograph of PBPDA (Fig. 3a) revealed the formation of a well-defined spherical nanospheres which lead to the formation of a network in the whole arena. SEM studies of PBPDA were in concordance with TEM results (Fig. 3b) showing nanoparticles c.a. 90–110 nm size. The presence of homogeneously distributed PBPA nanoparticles in PBPDA/epoxy was clearly seen in micrograph of 3.0% PBPDA/epoxy formulation. Thus, evidently showing how excellent dispersion was achieved after coating preparations, which we have confirmed by TEM (Fig. 3c) and SEM studies of prepared coatings. These nanospheres lead to the formation of a network in the whole arena. SEM studies of PBPDA were in concordance with TEM results showing the presence of nanospheres of well-defined geometrical morphology. Incorporation, of B moiety was examined by EDX analysis, which clearly confirmed the presence of C, N, H and B atoms in nanospheres (Fig. 3d).

The conductivity value of pristine PDA was found to be 5.02×10^{-3} S/cm and which was significantly increased after boron doping in case of PBPDA. It was found to be 1.8 S/cm, which is corroborated to the presence of B in PDA chains, which exhibited an excellent dispersion and superior charge transport between polymer chains and lead to rise in conductivity values up to 10^3 times i.e. (5.02×10^{-3} S/cm from 1.8 S/cm). Moreover, B seems to be an interesting p type dopant as well, whose diffusion induces an easy transport across the chains, which acted as an acceptor. The uniformly dispersed B dopant made effectively as conducting bridges between the polymer chains of PDA.

BET analysis of PBPDA nanospheres confirmed the porous nature and higher surface area of these nanoparticles. The average surface area of nanoparticles was found to be 281.300 m^2/g and pore volume 0.2550 cc/g and pore radius 15.921 Å. The porous nature of nanoparticles has suggested that these particles have a potential for their applications in the field of adsorption, catalysis reactions.

The Potentio-dynamic polarization curve of PBPDA-epoxy nanocomposite coated CS in 7 wt % NaCl environment (Fig. 4) revealed that the I_{corr} value significantly decreased from 89.13 $\mu\text{A}/\text{cm}^2$ (bare CS) to 37.4 nA/cm^2 (PDA-epoxy) and E_{corr} value increased from -613.8 mV (bare) CS to -174.6 mV (PDA coated CS) [32,33]. However, in case of PBPDA dispersed nanocomposite coatings, E_{corr} value increased from -174.6 mV (PDA-epoxy) to +103.2 mV (PBPDA-epoxy), simultaneously I_{corr} value decreased from 37.4 nA/cm^2 for PDA-epoxy to 342 nA/cm^2 (PBPDA-epoxy coated CS) Likewise, the polarization resistance (R_p) value of PBPDA-epoxy increased with respect to PDA-epoxy [27]. The

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