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Synthesis of nano polyaniline and poly-*o*-anisidine and applications in alkyd paint formulation to enhance the corrosion resistivity of mild steel

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Abstract Protection of oxidizable metals against corrosion has now being intensively investigated, by applying or developing different methods such as coatings and conversion films; however, all reported methods involve environmentally hazardous materials. Conducting polymers have now been used as corrosion inhibitor coatings that are either chemically or electrochemically deposited on the metal substrate. The application of nanotechnology in the corrosion protection of metals has recently gained momentum. Environmental impact can also be improved by utilizing nanostructure particulates in coatings and eliminating the requirement of toxic solvents. We report here the synthesis of nanoparticles of polyaniline (PANI) and poly-*o*-anisidine (POA) using emulsion polymerization method in micellar solution of SDS and their anticorrosive property has been experimentally checked. The prepared nanoparticles have been characterized by FTIR and TEM. The nanoparticles of the synthesized polymers were dispersed in alkyd paint formulation for coatings on the metal surface (mild steel). The water absorption in the prepared coatings was also studied. The corrosion rate of polymeric film was determined by weight loss measurement and the surface morphology was examined by SEM. The nano PANI/Alkyd coatings showed considerable protection against corrosion than the POA/alkyd coatings.

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Introduction

Interest in studying conducting polymers as inhibitors of corrosion has increased notably in the last two decades.[1–6] These materials, for being polyconjugated systems having alternate simple and double bonds, possess considerable electron availability[7] which provide them with a rigid structure and a better capacity to be adsorbed on metallic surfaces.[8–10] As with other polymeric coatings, they act as a physical barrier, isolating the metal from the corrosive environment.

Moreover, because of the presence of polar groups, these materials can shift the potential of the substrate toward more positive values, which are located in the passive zone.[11] The conducting polymers synthesized from aniline have been shown to be the best candidates to be used as protectors of corrosion, in addition to their other interesting physical, chemical, electrochemical, optical, and mechanical properties.

Most of the effective corrosion-resistant paint formulations that are popular in industries are based on chromic compounds, which need to be replaced with alternative materials such as polyaniline (PANI) and poly-*o*-anisidine (POA). Previous workers in this field have proposed a new approach to corrosion prevention based on the formation of an electronic barrier of metallic surface, and hence we thought of investigating the use of conducting polymer as corrosion-resistant coating. PANI is one of the most common conductive polymers used as a coating and has been intensively investigated.[12–14] The design and production of PANI-based coating systems with commercial viability require paint formulations with a minimum possible agglomeration of intrinsic conducting polymer (ICP), well-dispersed nanoparticles (70–100 nm) of uniform size and superior adhesion,[15] as well as the prolonged protective performance under different corrosive conditions.[1,16] The development of conducting polymeric nanoparticles-based corrosion inhibitors with self-cleaning properties, discoloration resistance, and high scratch as well as wear resistance is expected to cause a major revolution in the world of corrosion.

The PANI-based paint formulation consists of predispersed and highly concentrated PANI (3–5 wt%) in different binder matrices such as alkyd, polyurethane, acrylic, and epoxy.[5,13] These formulations, however, do not fulfill all chemical, physical, and technical requirements of corrosion protective coatings.[12] It has been reported that the PANI primer itself does not work properly under all widely varying practical applications.[13–15] The technique proposed by the NASA/Los Alamos group[17] is not practical for the general coatings industry because it fails in terms of adhesion and reproducibility and lacks better performance compared with high-performance coating systems.

In the present study, the corrosion-protective performance of nano PANI/alkyd coatings has been investigated on mild steel (MS), and the results are compared with nano POA/alkyd coatings with a similar loading of the conducting polymers (0.5–1.5%).

Materials

The materials used in the experimental study include soya alkyd and cobalt octoate (Poonam Paints, MIDC, Jalgaon, India), xylene (Merck, India), sodium dodecylsulfate (SDS) (Loba Chemicals, Mumbai, India), and ammonium persulfate (APS) (Sd fine chemicals Ltd., Mumbai, India). Aniline and *o*-anisidine monomers (Sd fine chemicals Ltd., Mumbai, India) were double-distilled under vacuum prior to use.

General procedure for preparation of PANI and POA nanoparticles[18]

In total, 0.49 g (0.0021 m) of APS was dissolved in 10 mL of 0.1 M HCl solution and added drop wise into a mixture containing 0.40 g (0.0043 m) of aniline or 0.52 g (0.0043 m) of *o*-anisidine and 9.80 g (0.034 m) of SDS in 100 mL of 0.1 M HCl solution at 1.0 mL/min rate. The molar ratio of monomer(s) to APS was kept as 2.0 throughout the experiment, and the total volume of mixture after the addition of initiator (APS) was 110 mL. Since the Krafft point of SDS is around 16°C, the polymerization was performed at 20 ± 0.1°C with the mechanical stirring of 500 rpm in two-neck round bottom flask mounted in a thermostat for 12 h. The dark green precipitate of polymer nanoparticles (PANI or POA) was filtered and washed several times with methanol and then dried in a vacuum oven at 60°C and 5 mm of pressure for 72 h.

Synthesis of PANI/alkyd and POA/alkyd coatings

The synthesized PANI and POA were used for the preparation of PANI/alkyd and POA/alkyd coatings. The PANI/alkyd and POA/alkyd coatings were prepared separately by dispersing 0.5, 1.0, and 1.5 wt% of polymer(s) (PANI and POA) in 10 wt% solution of alkyd in xylene.

Characterization

PANI/alkyd coatings and POA/alkyd coatings were applied by film applicator on all sides of mild steel strips (70 × 30 × 1 mm) having thickness ≈60 μm (mild steel is a steel containing carbon percentage of 0.16–0.29). The determination of specular gloss at 60° was performed with a gloss meter (G 1060; Khushboo Scientific, Mumbai, India), while scratch hardness and impact resistance properties were measured with instruments from Khushboo Scientific, Mumbai, India (430 PII, ASTM D2794). The morphology of the resulting polymeric films was examined by scanning electron microscope (SEM) [JEOL JSM-6360A SEM]. Corrosion tests were performed in water, acid (5 wt% HCl), alkali (5 wt% NaOH), and NaCl (3.5 wt%) solutions by placing the steel strips in dip glass dishes and dipping the coated samples in the test media until the coatings showed deterioration and development of cracks. The protective behavior of the polymeric films against the dissolution of mild steel (MS) was evaluated by calculating the corrosion rate (V_p) for each one of the samples. The calculation of corrosion rate (V_p) was done using the following expression[8,12]:

$$V_\mathrm{p} = \frac{\Delta g}{Atd}$$

where Δg is the weight loss in grams for each sample, A is the exposed area of the sample in cm^2, t is the time of exposition in years, and d is the density of the metallic species in g/cm^3.

The weight loss was measured after carefully washing the samples with distilled water to remove the deposited corrosion product, and dried in a vacuum oven at 60°C to remove moisture from the samples.

Results and discussion

IR spectroscopy study

The IR spectra of the two samples, PANI and POA, are exhibited in Fig. 1. We note the prominent absorption peaks for polyaniline (curve a) at 829, 1165, 1460, and 1585 cm^{-1} assignable to out-of-plane C–H bond, aromatic C–N–C bond, aromatic C=C bond,[8] and nitrogen bond between benzoid and quinoid rings, respectively. However, POA (curve b) showed the same absorption bands, but having two additional bands at 1118 and 1257 cm^{-1}. These could be assigned to vibrations of the C–O–C bonds of the ether group[19] and aromatic C–O,[20] respectively. Also, the vibrational frequencies for both the samples are summarized in Table 1.

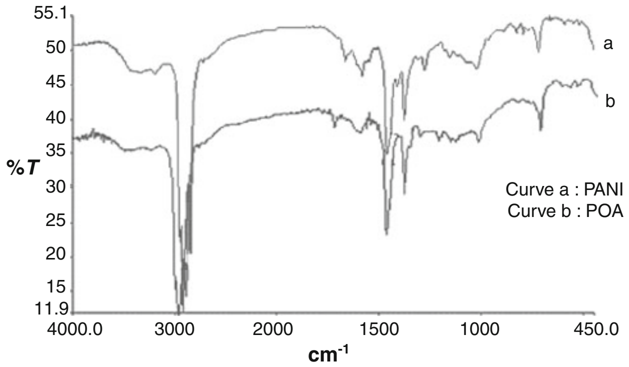

Fig. 1: IR spectrum of PANI (curve a) and POA (curve b)

Table 1: IR absorptions of PANI and POA

Functional groups	IR absorptions (cm^{-1})	
	PANI	POA
Benzoid and quinoid rings	1585	1586
C=C aromatic	1460	1460
Aromatic amine	1377	1377
C–O aromatic	–	1257
C–O–C ether	–	1118
C–N–C	1165	1123
C–H out of plane	829	850

TEM analysis

Transmission electron microscope images of the PANI and POA are shown in Fig. 2. It is observed from the images that the PANI (Fig. 2a) nanoparticles were spherical and globular, with particle size in the range of 30–50 nm, whereas POA (Fig. 2b) nanoparticles were found to be rod-shaped and having width of 15–20 nm and length of 40–50 nm.

Water uptake studies of the coating

Figure 3 shows the water uptake of 0.5% PANI/alkyd, 0.5% POA/alkyd, and pure alkyd coatings. The paint formulation was applied over 5 × 7.5 cm glass plates by means of brush and allowed to cure for 7 days at ambient temperature. These coated glass panels were weighed and immersed in a 500 cm^3 beaker containing 400 cm^3 of distilled water. The panels were reweighed at regular time intervals of 25 h, after removing the surface water by means of a filter paper. The weight gain was measured up to 10 days, with an accuracy of the weight measurement of ±0.1 mg. In our study, a very little water absorption was observed in both PANI

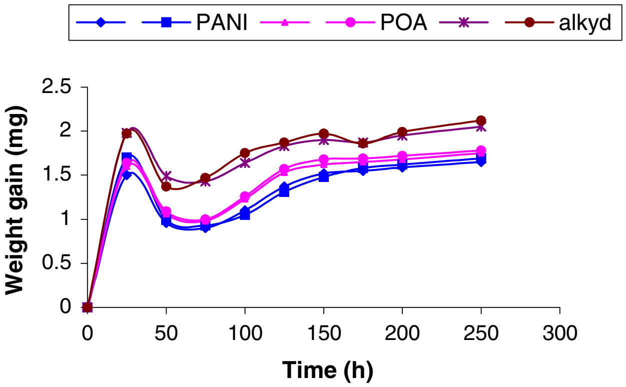

Fig. 3: Water uptake of 0.5% PANI/alkyd and 0.5% POA/alkyd coating. The size of the symbols represents the error limits

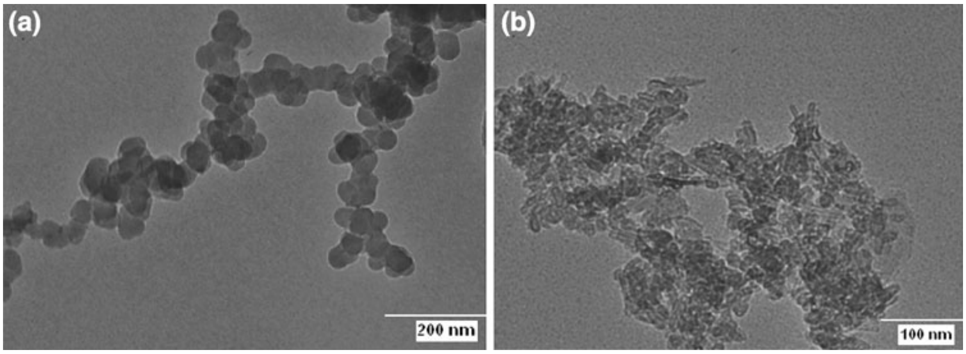

Fig. 2: TEM micrographs of PANI nanoparticles (a) and POA nanoparticles (b)

and POA coatings (Fig. 3), in comparison with pure alkyd coating. All measurements were carried out in duplicate and the average data are reported and presented in Fig. 3.

Physico-mechanical properties

The physico-mechanical distinctiveness of PANI/alkyd and POA/alkyd coatings are summarized in Table 2. The scratch hardness of both coatings was found to be synergistically increased as compared to pristine alkyd coating. Scratch hardness of both coatings was increased from 0.5 to 1 wt% and again decreased for 1.5 wt% due to the increased loading of nanoparticles in alkyd. The overall scratch hardness of PANI was found to be more than POA, because in the case of aniline, amino group and the aromatic ring are in the same plane, and this coplanar orientation with respect to the metallic surface confers to PANI a greater capacity to form more homogeneous film and this may be imparting better adhesion to the metal substrate.[9,10,12] While in the case of POA, scratch hardness was comparatively less, because of methoxy group at ortho position that created the steric hindrance with amino group, and hence affecting planarity of the POA and causing disturbance in distribution of particles compared to PANI. Furthermore, the difference between the scratch hardness of PANI and POA at similar loading was also due to the differences in structural characteristics and particle size of the conducting polymers.

The impact resistance of the PANI/alkyd coatings was found to be higher than the POA/alkyd coatings, and in both cases it was increased with increasing loading from 0.5 to 1 wt% and then remained constant at 1.5 wt% loading of polymers. The gloss values of PANI and POA in alkyd coating decrease with increase in the percent composition of conducting polymers due to the increase in opacity of the coatings.

Morphology

We represent the results of SEM analysis in Fig. 4. The SEM micrograph of 1.0 wt% PANI/alkyd and POA/alkyd coatings before corrosion (Figs. 4a and 4c) and after corrosion of coatings (Figs. 4b and 4d) are being exhibited. The SEM micrograph of 1.0 wt% PANI/alkyd coating reveals the good quality uniform dispersion of nanoparticles of polymers in the coating, also showing appropriate adhesion of film on the MS substrate. The SEM micrograph of 1.0 wt% PANI/alkyd coated MS specimen shows the corroded part of mild steel (Fig. 4b). The development of small cracks on the coating after the corrosion test in 5% HCl for 720 h can be noted, whereas in 1.0 wt% POA/alkyd the coating exhibits very poor performance in the same corrosive media kept for similar duration. Highly deep cracks, with loss of coating, can be clearly seen in Fig. 4d.

Corrosion rate analysis of PANI/alkyd and POA/alkyd coatings

In this study, PANI/alkyd, POA/alkyd, and pure alkyd coatings were placed in different corrosive media for 720 h, in which the pure alkyd coating was found to be dissolved completely within 10–12 h. The corrosion rate of PANI/alkyd and POA/alkyd coatings was monitored for 720 h and both coatings showed no visual deterioration or dissolution during this period. It was found that the sample of the alkyd-coated mild steel (MS) had a higher corrosion rate (V_p), while the rate of corrosion decreased slowly as the percentage of PANI and POA in alkyd coatings increased, and it was due to the formation of passive oxide layer on the metal substrate. The PANI and POA materials are polyconjugated systems having alternate simple and double bonds, possessing a considerable electron availability, which provide them the rigid structure and better capacity to adsorb on the metal surface.[8,12] In overall study, it was found that PANI/alkyd coatings showed better corrosion resistivity than POA/alkyd coatings (Figs. 5a–5c). Because PANI enhances the electrostatic interaction between coating and the metal substrate and forms the superior oxide layer, which adheres as a uniform layer on the metal substrate and that prevent the penetration of corrosive ions in the coatings.

Table 2: Physico-mechanical properties of PANI and POA in wt% in alkyd coating

Percent composition of PANI and POA in alkyd coating (wt%)	Drying time (h)		Scratch hardness (kg)	Impact resistance (kg/cm^2)	Flexibility	Gloss
	Dry to touch	Dry to hard				
Alkyd	0.50	84	0.4	63.7	Fail	89
0.5 PANI/alkyd	0.25	70	2.5	68.2	Pass	86
1 PANI/alkyd	0.25	48	3.2	72.8	Pass	83
1.5 PANI/alkyd	0.16	48	3.0	72.8	Pass	76
0.5 POA/alkyd	0.25	72	2.2	65.9	Pass	81
1 POA/alkyd	0.25	48	2.8	70.4	Pass	78
1.5 POA/alkyd	0.10	48	2.5	70.4	Pass	72

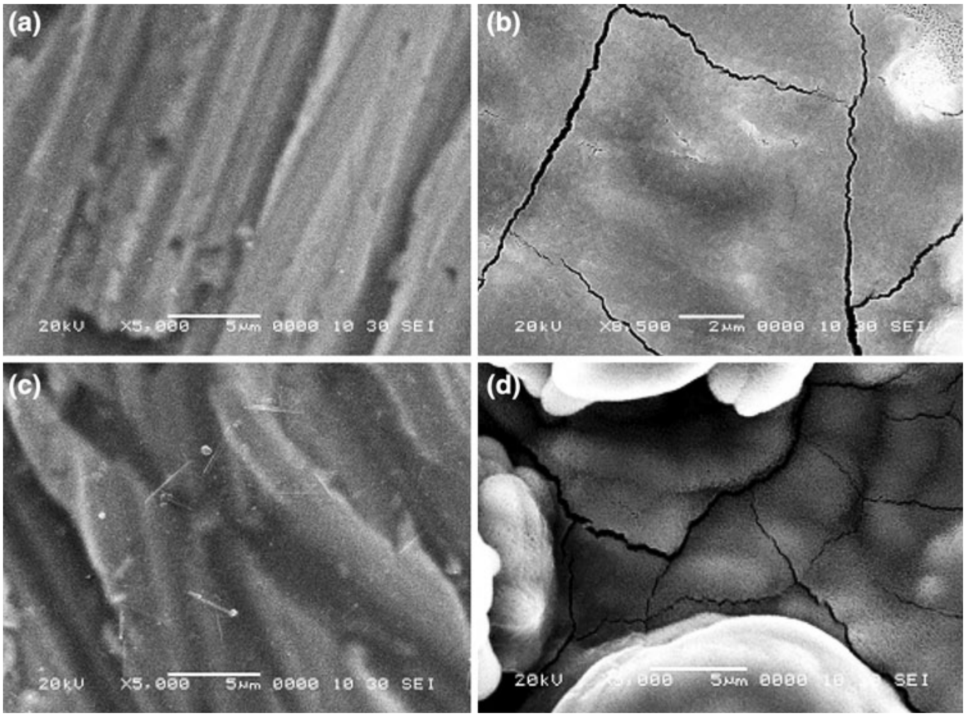

Fig. 4: SEM micrographs of (a) 1% PANI/alkyd coated MS specimen, (b) 1% PANI/alkyd coated MS specimen dipped in 5% HCl (720 h), (c) 1% POA/alkyd coated MS specimen, and (d) 1% POA/alkyd coated MS specimen dipped in 5% HCl (720 h)

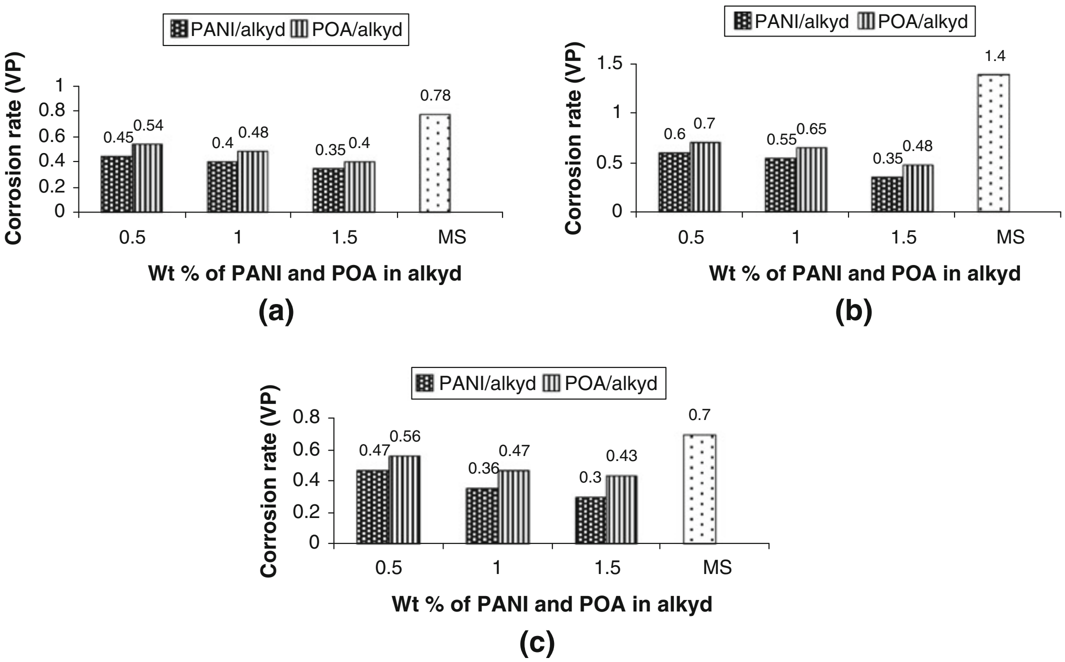

Fig. 5: Corrosion rate of PANI/alkyd, POA/alkyd, and MS coatings in (a) 5% HCl, (b) 5% NaOH, and (c) 3.5% NaCl

Conclusion

The dispersion of PANI nanoparticles in alkyd resulted in better physico-mechanical properties as compared to dispersion of POA nanoparticles in alkyd paint formulation. The dispersion of a small amount (0.5–1 wt%) of PANI and POA remarkably enhanced the scratch hardness and impact resistance performance. Dispersion of PANI/alkyd coating showed better corrosion resistivity of mild steel in comparison with

POA/alkyd coatings in all corrosive media such as 5% HCl, 5% NaOH, and 3.5% NaCl. The present investigation proved that PANI nanoparticles were better corrosion inhibitors in alkyd paint formulation to protect the mild steel against corrosion.

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