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Synthesis, characterization, and corrosion protection properties of poly (*N*-(acryloyloxymethyl) benzotriazole-*co*-methyl methacrylate) on mild steel

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Abstract

The copolymers from different feed ratios of *N*-(acryloyloxymethyl) benzotriazole (AMBT) and methyl methacrylate (MMA) were synthesized using free radical solution polymerization technique and characterized using FT-IR and ^{13}C NMR spectroscopy. The thermal stability of the polymers was studied using theremogravimetrtic analysis (TGA). Potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) studies were carried out with mild steel specimens dip coated with different composition of copolymers. These electrochemical properties were observed in 0.1 M HCl medium. The polarization and impedance measurements showed different corrosion protection efficiency with change in composition of the copolymers. It was observed that the copolymer obtained from 1:1 mole ratio of AMBT and MMA exhibited better protection efficiency than other combinations.

Keywords: Acrylic copolymers; Benzotriazole derivatives; Corrosion protection; Benzotriazole copolymer; Impedance spectroscopy

1. Introduction

Generally acidic solutions are used as pickling agents for iron and steel, chemical cleaning of scale in metallurgy, acidizing in oil recovery, and other petrochemical processes. Chloride ions in acidic media are particularly aggressive and accelerate corrosion. The main problem of using mild steel in the acidic solution is uniform corrosion.

One of the means of combating corrosion in acidic environment is the application of corrosion inhibitors or coatings. Of the various types of protective coatings that are in use, organic polymer coatings play an important role in the prevention of corrosion on mild steel [1–5]. These coatings predominate in protection against corrosion by covering the metal surfaces. The corrosion protections by organic polymer coatings are remarkable in view of the fact that they are very thin. Funke et al. [6] reported that the organic coatings protected metals from corrosion by physicochemical, electrochemical, and adhesional mechanisms. Neto et al. [7] reported that the polymer film prepared by dip coating shows an increasing protection of metal substrate in acidic media.

Among the organic coatings, recently, the methacrylic polymer coatings have found wide applications in several industries [8–10]. Methacrylic coatings are fast setting adhesives, having high impact strength, capable of making excellent bonding with metals, show resistance to chemical fumes, alkalis, acids and exhibit high tolerance to contaminated surfaces [11]. They are widely used as binders in protective coatings because of their excellent durability [12]. The use of polymers in acrylic blends exhibited a new strategy for corrosion protection [13].

Contemporarily, numerous papers have been published on the inhibitive action of organic heterocyclic compounds containing nitrogen, sulfur, and oxygen on mild steel in acidic media [14–20]. Among the various heterocyclic compounds, the inhibitive action of benzotriazole and its derivatives on mild steel in acidic media have been reported by several authors [21–25].

Although there are a number of individual reports on the advantages of organic coatings and that of inhibitors, there

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are a very few reports outlining the tandem effect of an azo compound coupled with an acrylic polymer, in fighting corrosion of mild steel. Hence, in the present study, experiments were carried out in order to exploit the adhesive behavior of methacrylates and the inhibiting behavior of banzotriazole. Poly (*N*-acryloyloxymethyl benzotriazole-*co*-methyl methacrylate) (poly (AMBT-*co*-MMA) having different compositions were synthesized using different mole ratios of *N*-acryloyloxy methyl benzotriazole (AMBT) and methyl methacrylate (MMA) and dip coated on mild steel to increase the adhesion and corrosion resistance. The synthesized copolymers were characterized using FT-IR and ^{13}C NMR spectroscopy. The thermal stability of the copolymers was studied using theremogravimetrtic analysis (TGA). The electrochemical experiments such as potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) studies were carried out in 0.1 M HCl medium with mild steel dip coated with different compositions of the copolymers.

2. Experimental details

2.1. Materials

The mild steel samples embedded in a polymer setting had an area of exposure of 1 cm^2. These specimens were mechanically polished using different grades of emery paper. They were subsequently washed with double distilled water, degreased with methanol, and then dried at room temperature. The aggressive solutions used were made from AR grade HCl. Appropriate concentration of the acid was prepared using double distilled water.

Table 1
Mole ratio of AMBT and MMA in the copolymer

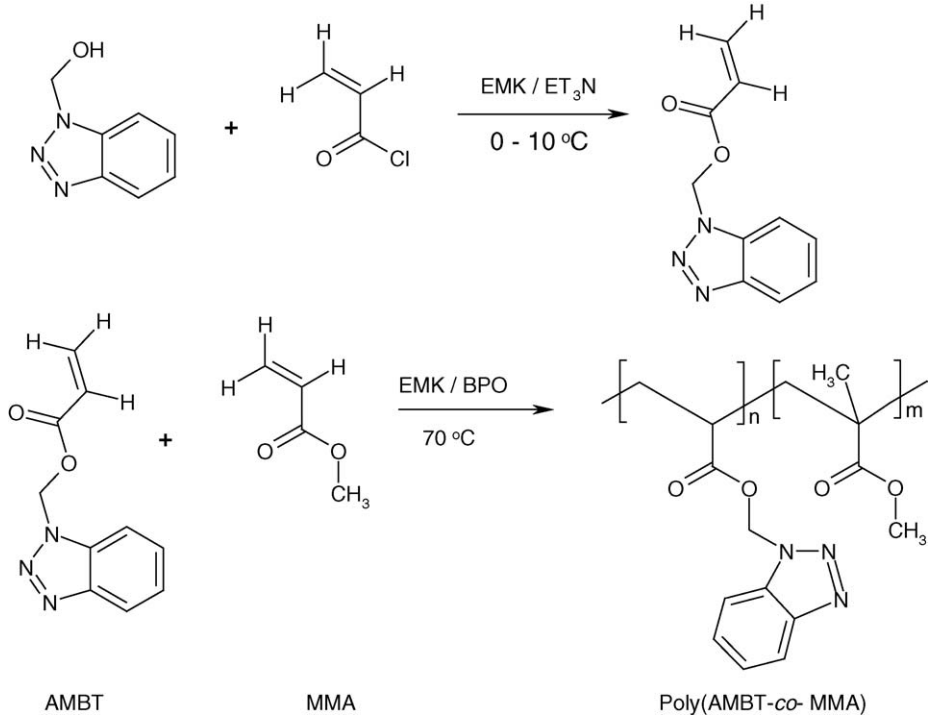
S. no	Compound name	AMBT (%)	MMA (%)
1	Copolymer 1	10	90
2	Copolymer 2	20	80
3	Copolymer 3	50	50
4	Copolymer 4	90	10

2.2. Synthesis of various composition of poly (AMBT-co-MMA)

In the first stage, *N*-hydroxymethyl benzotriazole was synthesized according to a previously reported procedure [26]. In the second stage, *N*-acryloyloxy methyl benzotriazole (AMBT) was synthesized by reacting *N*-hydroxymethyl benzotriazole (8.1 g, 0.04 mol) with acryloyl chloride (4.0 g, 0.044 mol) in ethyl methyl ketone (EMK) (300 ml) in the presence of triethylamine (4.4 g, 0.044 mol). In the third stage, the copolymer, poly (AMBT-*co*-MMA) having different composition was synthesized by free radical solution copolymerization of the monomers AMBT and MMA at different mole ratios using benzoyl peroxide (BPO) as initiator in EMK solvent. The molar feed ratio of the monomers is shown in Table 1. A schematic representation of the synthesis is shown in Scheme 1.

2.3. Measurements

FT-IR spectrum of the copolymer 3 was recorded on Perkin Elmer FT-IR spectrophotometer with KBr pressed pellet. ^{13}C NMR spectrum of the copolymer 3 was obtained from Hitachi



Scheme 1.