

Anticorrosion Property of Vinylphosphonic acid-co-Diethylvinylphosphonate Copolymers Obtained by UV Curing

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Abstract

Copolymers of vinylphosphonic acid (VPA) with diethylvinylphosphonate (DEVP) at different molar ratio from 1:1 to 4:1 were synthesized by using ultraviolet light. The polymers are soluble in water. They are investigated as corrosion inhibitors for iron by using impedance spectroscopy. The best result regarding the anticorrosion property was obtained for copolymer VPA:DEVP 1:1, with an inhibition efficiency of 72%.

Introduction

Vinylphosphonic acid (VPA) homopolymer and its copolymers with various monomers have gained great importance in polymer chemistry due to their special properties given by the presence of phosphonic group [1]. For the beginning, these polymers were used in water treatment process as inhibitors of scale formation [2]. Nowadays, the major applications of copolymers of VPA with different monomers or grafted polyvinylphosphonic acid (PVPA) on other polymers or blends refers to polymer electrolytes membranes for fuel cells [3,4], ion exchange membranes [5], in medical field as component in products for bone reconstruction and tissue engineering [6] and as dental cement[7]. Poly(vinylphosphonic acid) (PVPA) can be synthesized via radical polymerization of vinylphosphonic acid in the presence of initiator [8]. Synthetic copolymers based on dialkylvinyl phosphonates (alkyl=methyl, ethyl, *iso*-propyl) have gained also applicative importance by the presence of phosphonate groups as flame-retardants [9] and anticorrosion agents [10].

The aim of this paper is to study the properties of copolymers of vinylphosphonic acid with diethylvinylphosphonate in aqueous solution as corrosion inhibitors.

The homopolymer of vinylphosphonic acid (VPA) and its copolymers with diethyl vinylphosphonate (DEVP) were prepared by radical polymerization at different molar ratios from 1:1 to 4:1, respectively, by using UV light. The use of UV light to polymerize is an attractive technique from environmental point of view. The photopolymerizable formulations are free of organic solvents, and has the advantages of low energy consumption, low temperature operation (room temperature) and the possibility to coat various substrates (wood, plastics, paper). The obtained polymers were investigated as inhibitors against corrosion for iron surface in neutral aqueous solutions by electrochemical impedance spectroscopy. From the literature data it is known that phosphonic acids and phosphonates, in general, inhibit steel corrosion in neutral and slightly alkaline solutions.[11]

Experimental

Vinylphosphonic acid (97%) (VPA) was purchased from Aldrich, diethylvinylphosphonate (DEVP) from Merck and photoinitiator Darocure 4265 from BASF.

The iron coins used for measurements against corrosion were previously polished with silicon carbide polishing paper until mirror-like surface was obtained. The iron surface was washed with distilled water and cleaned with ethanol in ultrasound bath.

The photopolymerizable formulations of VPA and VPA with DEVP at different molar ratios (1:1 to 4:1) containing photoinitiator at 3% w/w versus monomers were laid using film applicator (Zehnter) on PTFE plates and exposed to a medium pressure mercury lamp (400W,

Uvitron SUNRAY 400 SM, USA) to obtain cured films. The films were peeled out from PTFE plates and used for subsequent analyses.

Electrochemical experiments were performed by immersing the iron electrode into the 3% sodium chloride aqueous solution with and without PVPA and copolymers VPA:DEVP as corrosion inhibitors (VPA-DEVP 1:1, VPA-DEVP 2:1, VPA-DEVP 3:1 and VPA-DEVP 4:1) and the change of open circuit potential (OCP) was measured from the first moment of iron immersion in the first hour. The polymers were added in a quantity of 50 mg/200 ml solution. The polarization curves were obtained by scanning the potential of iron from -1200 to -200 mV at a scan rate of 1 mV/s. From the Tafel plots the corrosion potential (E_{corr}) and corrosion current density (J_{corr}) were extracted. Based on the J_{corr} values the inhibition efficiency (IE_p) was calculated using the Equation (1). All measurements were carried out at room temperature.

$$IE_p (\%) = [(J'_{\text{corr}} - J_{\text{corr}})/J'_{\text{corr}}] \times 100 \quad (1)$$

where: J_{corr} , J'_{corr} = corrosion current densities in the case of the solution containing inhibitors and the control solution, respectively.

Results and discussion

The OCP curves for iron electrode in 3% NaCl solution containing (1) 0.0 (control solution), (2) PVPA, (3) VPA-DEVP 1:1, (4) VPA-DEVP 2:1, (5) VPA-DEVP 3:1: and (6) VPA-DEVP 4:1 as inhibitors of corrosion are shown in Figure 1.

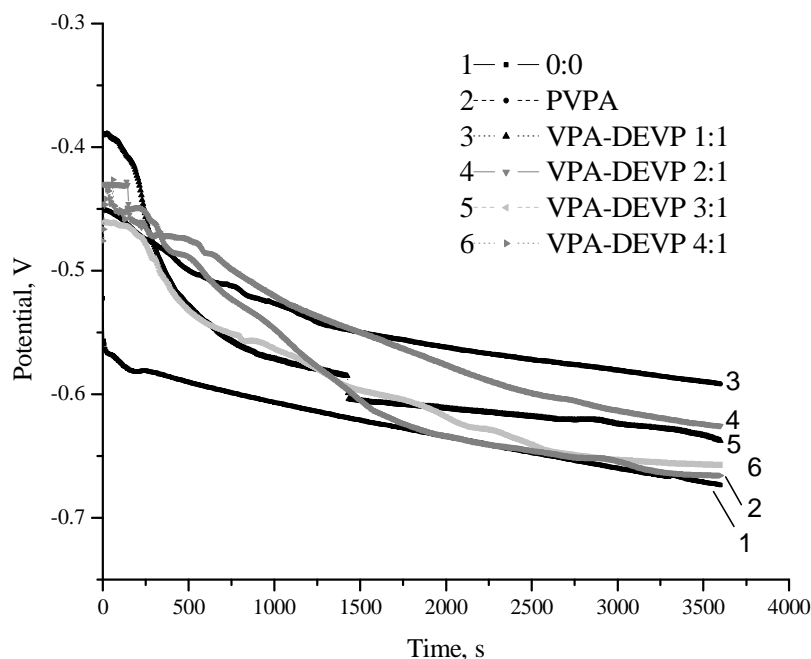


Figure 1. OCP curves for iron electrode in 3% NaCl solution containing (1) 0.0, (2) PVPA, (3) VPA-DEVP 1:1, (4) VPA-DEVP 2:1, (5) VPA-DEVP 3:1: and (6) VPA-DEVP 4:1

In the presence of polymers in solution, it can be observed that in the first minutes the potential decreased due to dissolution of iron ions from the surface and oxide formation.

Also, on the surface of electrode it forms a protective layer by the reaction between iron oxide and phosphonic acid and/or phosphonate groups [12]. Therefore, the potential shifted towards the less negative values in time (plots 2-6) and its tendency is to remain almost constant. It

means that the polymer has attached to the surface of iron and in all cases the presence of polymers has prevented the corrosion. The best values of OCP were observed for copolymer VPA:DEVP 1:1 which contains the highest number of phosphonate groups, and could facilitate faster the formation of adherent layer on the metal surface by phosphonate groups. The potentiodynamic polarization curves of iron electrode in 3% NaCl solution in absence and presence of inhibitors are shown in Figure 2.

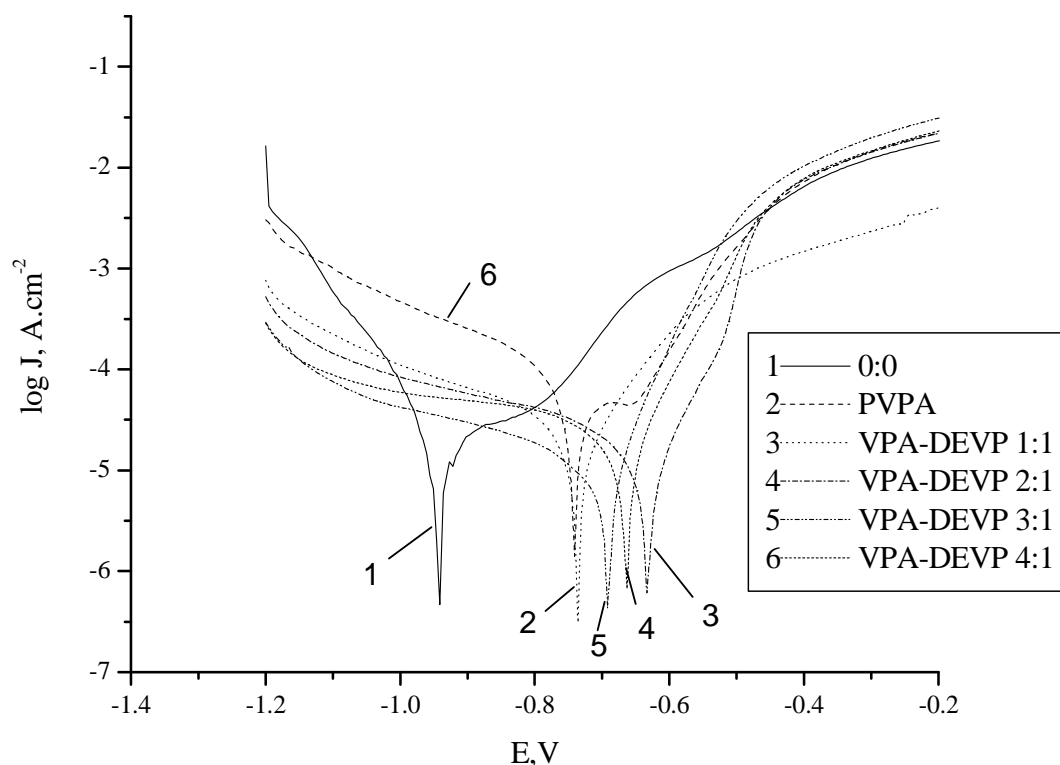


Figure 2. Potentiodynamic polarization curves of iron immersed in NaCl solutions for control solution (1) 0.0 and containing (2) PVPA, (3) VPA-DMVP 1:1, (4) VPA-DMVP 2:1, (5) VPA-DMVP 3:1 and (6) VPA-DMVP 4:1 as inhibitors of corrosion

Table 2. Corrosion parameters of iron immersed in 3% NaCl solution in the absence and in the presence of inhibitors obtained by potentiodynamic polarization studies.

Sample	J_{corr} , A/cm^2	E_{corr} , V	R_{corr} , mm/year	IE_p %
0:0	3.34E-05	-0.942	0.134	-
PVPA	1.58E-05	-0.736	0.119	52.75
VPA:DMVP 1:1	9.07E-06	-0.628	0.0795	72.88
VPA:DMVP 2:1	9.76E-06	-0.685	0.0592	70.82
VPA:DMVP 3:1	1.04E-05	-0.661	0.0907	69.02
VPA:DMVP 4:1	1.18E-05	-0.728	0.159	64.71

The values of the corrosion parameters: corrosion current density J_{corr} ($A\ cm^{-2}$), corrosion potential E_{corr} (V), rate of corrosion R_{corr} (mm/year) and inhibition efficiency of the polymers IE_p are listed in Table 1. The inhibition efficiency was calculated with Equation 1. The corrosion current density (J_{corr}) in case of the control solution is $3.34 \times 10^{-5}\ A\ cm^{-2}$. In the presence of the inhibitors the decrease in corrosion current and corrosion rate are observed. The significant reduction in J_{corr} and R_{corr} values were observed in the case of

VPA:DMVP 1:1 and 2:1 polymers, which present also good inhibition efficiency. These copolymers have the better ability to anchor to the iron surface and form a more uniform and less porous film.

Conclusion

The using of UV light to obtain copolymers from vinylphosphonic acid (VPA) and diethylvinylphosphonate (DEVP) was advantageous because DEVP itself does not polymerize by UV light exposure, homopolymer of DEVP is not soluble in water but by copolymerization with VPA were obtained copolymers soluble in water.

Homopolymer of vinylphosphonic acid (PVPA) and copolymers of vinylphosphonic acid (VPA) with diethylvinylphosphonate (DEVP) at different molar ratio from 1:1 to 4:1, respectively, were obtained by polymerization using UV light in the presence of photoinitiator. The polymers were tested as corrosion inhibitors for iron in NaCl aqueous solution and their presence in solution decreased the corrosion current density that means the formation of protective film on iron surface. The presence of phosphonate groups from diethylvinylphosphonate in polymers enhanced the anticorrosion property in comparison with homopolymer of vinylphosphonic acid.

Acknowledgments

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