POLYMERS OF VINYLPHOSPHONIC ACID WITH DIALKYLVINYL PHOSPHONATES AND THEIR ANTICORROSION PROPERTY

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Introduction

Importance:

Functional synthetic copolymers based on vinylphosphonic acid (VPA) with different monomers have gained great importance in polymer chemistry due to their special properties given by the presence of phosphonic groups. Vinylphosphonic acid homopolymer (PVPA) and its copolymers have found applications in various domains: water treatment processes, control steel corrosion, adhesives for metallic surfaces, polymer electrolytes membranes for fuel cells, ion exchange membranes, in the composition of products for bone reconstruction and tissue engineering in medical field and dental cement.

Aim

The aim of this paper is to study the properties in aqueous solution of copolymers of vinylphosphonic acid with dimethylvinylphosphonate and investigate the possibility to apply these copolymers in surface protection against corrosion.

Experimental

The photopolymerizable formulations of VPA and VPA with DMVP 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 sodium chloride aqueous solution with and without PVPA and copolymers VPA:DMVP and the change of open circuit potential (OCP) was measured in the first hour.

Results and discussion

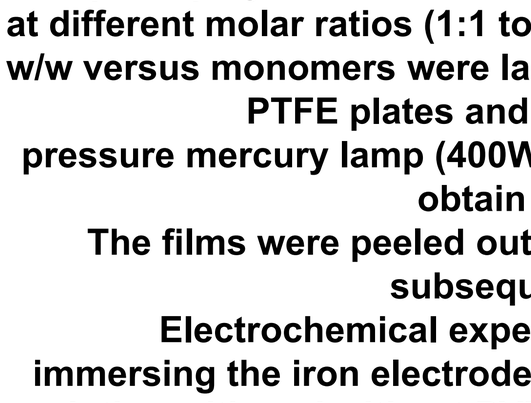

Figure 1. The structures of the monomers and (co)polymers

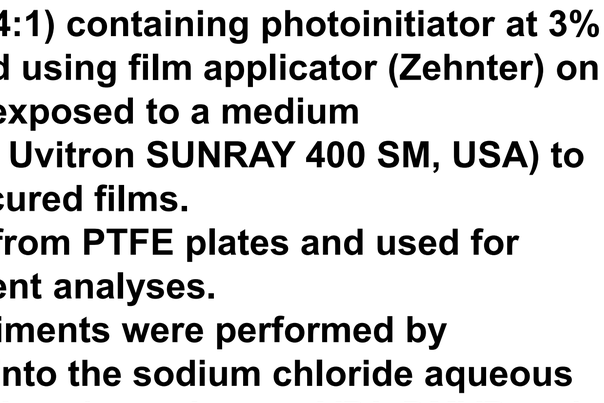

Figure 2. ATR-IR spectra of VPA monomer and VPA:DMVP 3:1 copolymer.

Electrochemical impedance measurement (EIS)

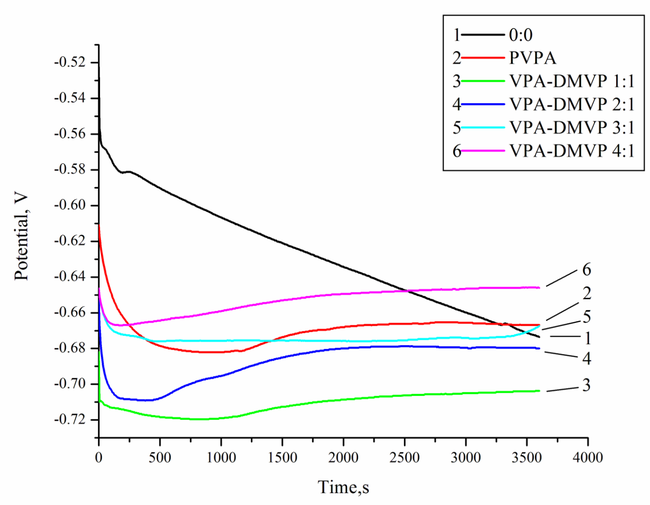

Figure 3. OCP curves for iron electrode in 3% NaCl solution containing
(1) 0.0,
(2) PVPA,
(3) VPA-DMVP 1:1,
(4) VPA-DMVP 2:1,
(5) VPA-DMVP 3:1: and
(6) VPA-DMVP 4:1

➢The potential of iron in sodium chloride solution in the absence of polymers (plot 1) shifted toward the negative direction during the time of immersion due to the dissolution of iron ions by the attack of chloride ions. This decreasing tendency will be followed even after one hour because the corrosion will continue.
➢In the presence of polymers, it can be observed that in the first minutes the potential decreased due to dissolution of iron ions from the surface and oxide formation. While on the surface of electrode it forms a protective layer by the reaction between iron oxide and phosphonic acid and/or phosphonate groups, the potential shifted towards less negative values in time (plots 2-6) and it has the tendency to remain constant. It means that the polymer has attached to the surface of iron and in all cases the presence of polymers shifted the OCP values (the absolute and the steady state potential) to the more positive direction and the corrosion was prevented.

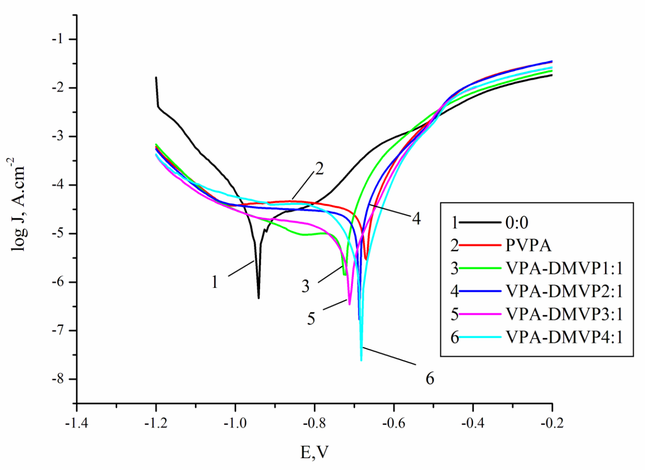

Figure 4. Potentiodynamic polarization curves of iron immersed in NaCl solutions for control solution
(1) 0.0 and containing
(2) PVPA,
(3) VPA-DMVP 1:1,
(4) VPA-DMVP 2:1,
(5) VPA-DMVP 3:1: and
(6) VPA-DMVP 4:1
as inhibitors of corrosion

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

Sample No.	Polymer	Jcorr [A/cm^2]	Ecorr [V]	Rcorr [mm/year]	IEp [%]
2	PVPA	3.340E-5	-0.885	0.4640	36.91
3	VPA:DMVP 1:1	2.862E-5	-0.704	0.2509	45.94
4	VPA:DMVP 2:1	1.149E-5	-0.736	0.1007	78.30
5	VPA:DMVP 3:1	1.05E-5	-0.699	0.0922	80.17
6	VPA:DMVP 4:1	8.734E-6	-0.681	0.1745	83.50

➢The values of the corrosion parameters: corrosion current density Jcorr (A/cm^2), corrosion potential Ecorr (V), rate of corrosion Rcorr (mm/year) and inhibition efficiency of the polymers IEp are listed in Table II. The inhibition efficiency was calculated with equation

$$IEp\ (\%) = [(J'corr - Jcorr)/J'corr] \times 100$$

➢The Tafel potential (Ecorr) in the case of the control solution is –0.942 mV versus saturated calomel electrode. In case of all inhibitors considered for polarization studies the Ecorr is shifted to more anodic values.

Conclusions

•Homopolymer of vinylphosphonic acid (PVPA) and copolymers of vinylphosphonic acid (VPA) with dimethylvinylphosphonate (DMVP) at different molar ratio from 1:1 to 4:1, respectively, were obtained by radical polymerization using UV light and photoinitiator.
•The polymers were tested as corrosion inhibitors for iron and their presence in aqueous solution decreased the corrosion current density by the formation of protective film on iron surface. The presence of phosphonate groups from dimethylvinylphosphonate in copolymers was beneficial and at a molar ratio VPA:DMVP 4:1 and 3:1 enhanced the anticorrosion property in comparison with homopolymer of vinylphosphonic acid.

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