

Performance of polymer blends on phosphated steel substrate

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Received 13 November 2003; accepted 15 March 2004

Abstract

Polymer blends are used to protect mild steel structures from corrosive environment. Multi-coat protective coating systems are substituted by single coat polymer blend, which will protect the surface equally for long duration when compared to the multi-coat system. In our studies, we have prepared three polymer blends, viz. silicone–acrylic, silicone–titanate and epoxy–acrylic blends. These polymer blends are applied over sandblasted as well as phosphated mild steel panels by brush. The mechanical properties like hardness and adhesion of these blends are measured and found that nearly 2 Vickers Pyramid Number (VPN) has been increased for phosphate surface. The accelerated salt spray chamber exposure also confirms that the phosphate gives additional protection to the steel substrate. The electrochemical impedance spectroscopy measurements are carried out periodically for all the three blends for 7 days. The impedance observation of acrylic silicone and silicone titanate blends on phosphate surface gives resistance values above $10^6 \Omega \text{ cm}^2$ after 7 days, whereas the same blends on sand blasted surface exerted resistance values below $10^6 \Omega \text{ cm}^2$ after the same duration, the epoxy acrylic blends are found to give resistance values above $10^9 \Omega \text{ cm}^2$ irrespective of the surface modification. Thus, this study concludes that the polymer blends of organic to organic binders protect the phosphate steel surface for longer duration than that of the blend composed of organic and inorganic system.

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Keywords: Polymer blend; Sand blasted; Phosphate; Hardness; Impedance measurement

1. Introduction

Nowadays polymer blends and polymer alloys are replacing multicoat systems to protect mild steel structures from corrosive atmosphere. Polymer blend comprises of two or more different characteristic polymers mixed together to get a homogeneous or heterogeneous phase binder, which will protect the steel structures for long duration depending upon the constituents present in the blend. It helps to enhance the mechanical properties like toughness, abrasion resistance, etc. and to reduce the permeability of gases and corrosive liquids in addition to the reduction of cost and labour [1,2]. Epoxy polyamide coatings are well known for adhesion and corrosion resistance properties in neutral environment [3]. This resin is used as a binder in primer, undercoat and top-coat formulations. Silicone formulations are mainly used to protect the surface from high temperature areas [4]. Acrylic coatings are well known for their better impermeability to water and used as a decorative coating formulation. A good

organic coating system fails quickly on under-prepared surface. Surface preparation like wire brushing, pickling and abrasive blast cleaning methods do not fulfill all the requirements for cleaning the surface prior to painting. Chemically treated phosphate surface generally impart better adhesion to the surface for organic coating system [5]. In our studies, we have prepared three polymer blends, viz. silicone–acrylic, silicone–titanate and epoxy–acrylic, and the performance of these coatings on sand blasted as well as phosphated steel surfaces is compared in aggressive chemical environments.

2. Experimental

Three different types of polymer blends have been prepared as follows:

- (a) *Silicone–Acrylic blend:* In this formulation, low molecular weight silicone polymer blended with high molecular weight acrylic polymer. The resultant inorganic to organic polymer blend is diluted with xylene–butyl

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Table 1
Mechanical properties of polymer blend on sand blasted and phosphate steel surface

No.	Test	Silicone–Titanate blend		Silicone–Acrylic blend		Epoxy–Acrylic blend	
		Sand blasted surface	Phosphated surface	Sand blasted surface	Phosphated surface	Sand blasted surface	Phosphated surface
1	Thickness per coat	30	34	30	35	32	37
2	Vicker's hardness (VPN)	4.9	6.9	3.8	4.2	3.6	4.2
3	Scratch hardness (kg)	2.1	2.3	1.4	1.9	1.7	1.9
4	Salt sprays (h)	168	180	168	180	240	252

acetate solvent mixture to get brushable consistency and applied over sandblasted as well as phosphated mild steel surface.

- (b) *Silicone–Titanate blend*: This inorganic to inorganic polymer has been prepared by mixing high percentage of silicone polymer with low percentage of titanate polymer and diluted with xylene and butanol solvents, then applied over sandblasted as well as phosphated steel surfaces.
- (c) *Epoxy–Acrylic blend*: This organic to organic blend has been prepared by mixing high molecular weight acrylic polymer with low molecular epoxy resin. This component is diluted with xylene, butyl cellosolve and methyl isobutyl ketone solvent mixture. Another component used is diluted polyamide as hardener. These two components are mixed together and applied over the sandblasted as well as phosphated mild steel surfaces.

These coated mild steel specimens are allowed to dry for 7 days and subjected to the following mechanical tests. The thickness of the polymer blends on sandblasted as well as phosphated surface has been measured by using a micrometer and the results are given in Table 1. Similarly the Vickers Hardness is measured by using LECO DM 400 Micro hardness tester and the result is expressed in Vickers Pyramid Number (VPN). The scratch hardness has been measured as per the British specification BS3900 and the values are given in Table 1. The coated panels are also exposed in the salt spray chamber and conducted the experiment as per the ASTM Specification B117 and the results are given in Table 1.

3. Electrochemical impedance measurements

Impedance measurements are made at open circuit potential using EG&G Model 6310 AC impedance system with a three electrode configuration. The impedance measurements in all cases have been carried out over a frequency range of 10 KHz–0.1 Hz using 10 mV peak-to-peak sinusoidal voltage. A computerized Bode plot was used to analyse the experimental data. The electrochemical tests have been carried out in aerated 3% NaCl solution. The surface area of the coated panels exposed to the electrolyte is 1 cm².

A three-electrode cell setup was formed by fixing a glass tube on to the surface of coated panels (working electrode) and filling it with the NaCl solution as electrolyte. A high

surface area Pt mesh and saturated calomel electrode have been used as counter and reference, respectively. The measurements are carried out after the intervals of 1 h; 1, 5 and 7 days of duration.

4. Surface morphology

The surface morphology studies of sand blasted and phosphated steel surfaces were carried out using SEM Model HITACHI S3000H.

5. Results and discussion

The physical properties of the coatings on mild steel substrate are given in Table 1. The table shows that the thickness of the polymer blends is almost uniform and also indicates that the thickness of phosphate layer is nearly 5 μm . The hardness measurements show that the phosphated surface offers better hardness to the polymer blend on the steel surface than the sandblasted surface. Further, the Vickers Pyramid Number for Silicone–Titanate blend, silicone–acrylic blend and epoxy–acrylic blend on sand blasted surface are 4.9, 3.8 and 3.6, respectively. This result indicates that the inorganic polymer blend offers better hardness than the organic polymer blends. The inorganic polymer resists the intent due to the hard setting of the polymer blend, whereas the organic polymer blends give better flexibility and elongation. Similar behavior has been observed in scratch hardness measurements also.

The performance of the polymer blends on sand blasted as well as phosphated surface in salt spray exposure is given in Table 1. Regular examination of the panels during salt spray exposure showed that corrosion spots appeared on the coating over sand blasted surface much earlier than that over the phosphated surface thereby indicating better performance of the coating over phosphated surface. Further, the epoxy–acrylic blend coated panels with stand the salt spray test for longer duration than the other two blends as there is a possibility of the inorganic polymer blend coating having micro-pores in higher order than that of the organic polymer blended systems.

Figs. 1 and 2 show the Bode impedance plots of silicone–titanate polymer blends on sand blasted and phos-

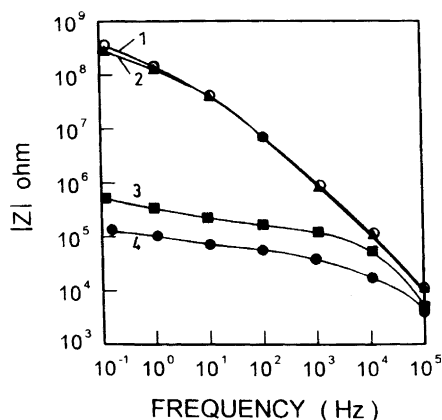


Fig. 1. Bode plot of Silicone–Titanate blend on sand blasted steel surface in 3% NaCl solution for different durations: (1) 1 h; (2) 1 day; (3) 5 days and (4) 7 days.

phated steel surface in 3% sodium chloride solution for different durations, respectively. It is seen from the figures that the polymer blend exerted high resistance in the order of $10^8 \Omega \text{ cm}^2$ at the beginning for both surfaces. But the resistance is slightly higher on the phosphate surface. Sudden fall in the resistance has been noticed after fifth and seventh days of the polymer blend in sodium chloride solution. This behaviour of the polymer blend indicates that initially the polymer blend is well intact on the steel surface and acts as a good insulating barrier in the chloride electrolyte medium. Then the sudden fall in the resistance denotes that the polymer blend allows the diffusion of the electrolyte into it that and the corrosion process takes place [5].

Fig. 3 shows the Bode plot of silicone–acrylic polymer blend on sand blasted and phosphated steel surface in 3% sodium chloride solution for different durations. It is seen from the figure that the resistance produced by the polymer blend on sand blasted surface in initial, first and fifth days are 3×10^5 , 2×10^5 and $6 \times 10^3 \Omega \text{ cm}^2$, respectively, and whereas the same polymer blend on phosphate steel surface have resistance values in the order of 4×10^6 , 3.5×10^6

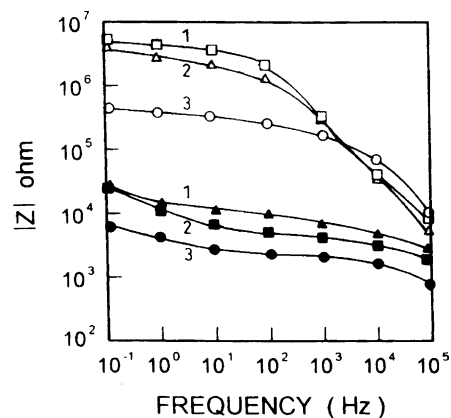


Fig. 3. Bode plot of Silicone–Acrylate blend on sand blasted and phosphated steel surface in 3% NaCl solution for different durations: (1) 1 h; (2) 1 day and (3) 5 days.

and $2 \times 10^4 \Omega \text{ cm}^2$ for initial, first and fifth days of duration, respectively. These results show that the resistance values are stable up to five days duration and so the polymer blends adhere well on the sand blasted as well as phosphated steel surface. But the resistance produced by the polymer blend on phosphated surface is much more than the same blend on sand blasted surface. This result indicates that the phosphate conversion layer is responsible for this higher resistance due to the formation of strong bonding between this layer and the polymer blend.

Figs. 4 and 5 show the Bode plot of epoxy–acrylic polymer blend on sand blasted and phosphated steel surface in 3% sodium chloride solution for different durations. It is seen from these figures that the polymer blends produce high resistance even after 30 days of duration, irrespective of the surface. After 30 days, the resistance offered by the polymer blend on sand blasted as well as phosphated surface is in the order of $10^9 \Omega \text{ cm}^2$, which shows that the coating is highly impermeable to water/chloride ions.

Figs. 6 and 7 show the SEM characteristics on sandblasted and phosphated steel surface. It is observed from the figures

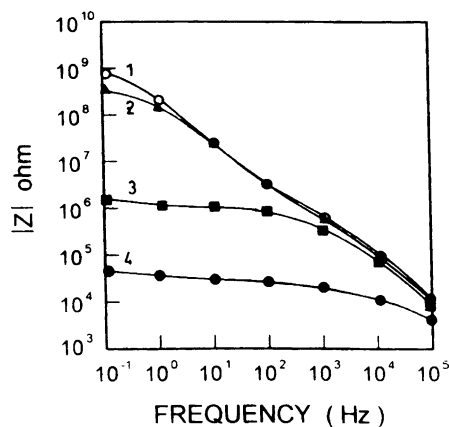


Fig. 2. Bode plot of Silicone–Titanate blend on phosphated steel surface in 3% NaCl solution for different durations: (1) 1 h; (2) 1 day; (3) 5 days and (4) 7 days.

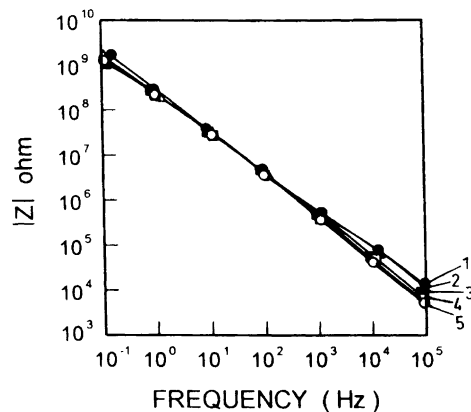


Fig. 4. Bode plot of Epoxy–Acrylate blend on sand blasted steel surface in 3% NaCl solution for different durations: (1) 1 h; (2) 1 day; (3) 5 days; (4) 7 days and (5) 30 days.

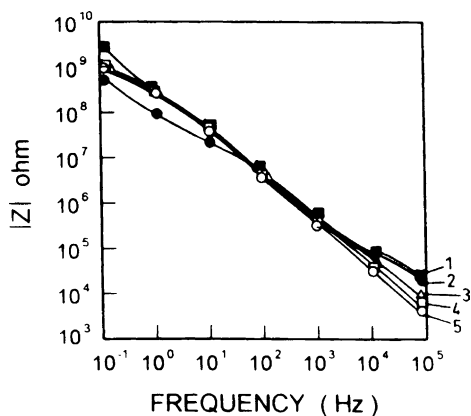


Fig. 5. Bode plot of Epoxy-Acrylate blend on phosphated steel surface in 3% NaCl solution for different durations: (1) 1 h; (2) 1 day; (3) 5 days; (4) 7 days and (5) 30 days.

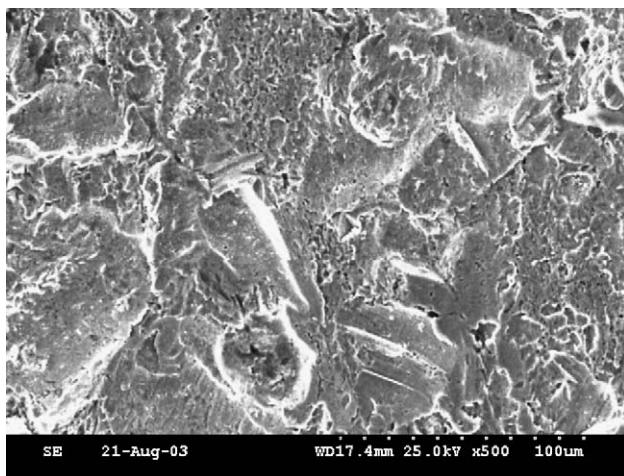


Fig. 6. Sand blasted steel surface.

that the reaction of zinc phosphate over the grain boundary area of the steel is more, and hence, the coating is thicker on these area compared to interior of the grains. It appears that some of the mid grains surface have not at all reacted with zinc phosphate.

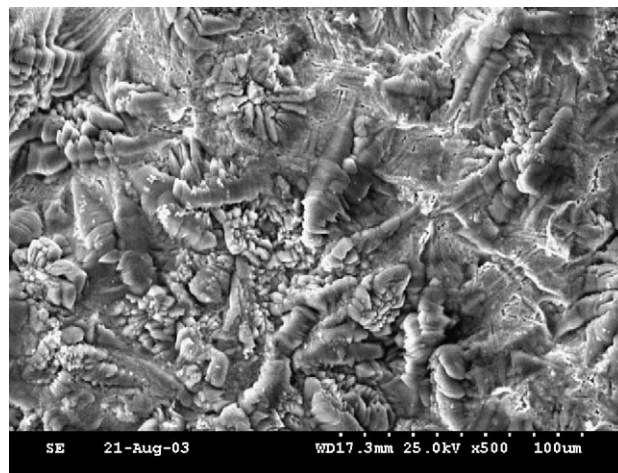


Fig. 7. Phosphated steel surface.

6. Conclusion

This study reveals that the Silicone-Titanate polymer blend possesses better hardness than the Silicone-Acrylic and Epoxy-Acrylic polymer blends irrespective of the nature of the surface. The phosphated surface always gives excellent hardness and anchoring to the polymer blends on steel surface. The salt spray and impedance measurement indicate that the Epoxy-Acrylic polymer blend system is more suitable than the other two systems as far as protection from chloride environment is concerned.

References

- [1] L.A. Utracki, Polymer alloys and blends, Hansen York, NY, 1989.
- [2] L.E. Nielson, Mechanical properties of polymers and composites, vol. 2, Marcel Dekker, New York, NY, 1974, p. 379.
- [3] N.S. Moss, J. Oil Color Chem. Assoc. 71 (12) (1988) 415.
- [4] L. Mathivanan, M. Selvaraj, S. Syed Azim, K. Balakrishnan, Prog. Org. Coat. 28 (1996) 113.
- [5] B.S. Skerry, D.A. Eden, Prog. Org. Coat. 15 (1987) 269.