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Silicone-Polyester Blended Coatings for Corrosion Protection

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ABSTRACT

Corrosion can be protected by the application of protective coatings developed by organic resins. Metal lose due to corrosion affects a country economic to a higher extent. Organic coating is the cheapest method to prevent corrosion. Silicone and polyester resins have good physical, mechanical and anticorrosive properties. They can be blended and made hybrid networks. Various concentrations of the two resins were mixed. The curing agent used in the study was polyisocyanate. The network of different functional groups between silicone and polyester resins was examined by FTIR spectroscopy. The crosslink formation between the resins was observed by the identification and analysis of NH bond, Si-O-Si, Si-O-C functional groups.The developed coating systems have got adhesion property which was evaluated by cross hatch test. Electrochemical Impedance Spectroscopy (EIS) was used to study the anticorrosion property of the systems by exposing the samples to 3% NaCl solution. EIS experimental results show that the coatings could protect the metal surface for the exposure to corrosive medium for more than 30 days.

Key words: Coating, corrosion, FTIR, EIS

INTRODUCTION

Corrosion is the destruction and deterioration of metals. The metals are damaged by the formation of unusable metal oxides by corrosion. The increase in the material cost gives an alarmic awareness to protect the existing metals used in industries, bridges, buildings and other places from the adverse effect of corrosion. Cathodic protection, alloying, metal coatings and organic coatings have been used in the past to protect the metal surface. There is a lot of improvement in the materials and methods to achieve perfect anticorrosive system. Organic coatings are the cheapest and easiest method for this purpose. Various types of organic resins (Erich, Laven, Pel, Huinink, & Kopinga, 2005; Gite, Mahulikar, & Hundiwale, 2010; Rossi, Deflorian, & Risatti, 2006) resins have been used for coating purposes in the past few decades. Among these, silicone resins have good resistance for corrosion in all kinds of environments and better thermal stability owing to their exclusive organic – inorganic hybrid molecular formation (Erich et al., 2005; Ramesh, Osman, & Arof, 2007; Rossi et al., 2006). Epoxy resin has good toughness, adhesion and chemical resistance, but, thermal and mechanical properties are not adequate for the applications in structural products (Rossi et al., 2006). Silicone resins have good compatibility with organic resins for modification. They have superior thermal properties such as higher thermo-oxidative stability. The important properties are good moisture resistance, partially ionic in nature, free rotation about bonds and good compressivity. Polyester resins have higher tensile and flexural strengths and can be cross-linked using different cross-linking agents, become quite resistant to softening and deformation at high temperatures. Once cross-linked, polyester resins become quite resistant to softening and deformation at high temperatures (Anand Prabu & Alagar, 2004; Perruchot, Watts, Lowe, & Beamson, 2003). The corrosion protection ability can be enhanced by blending more than one organic resin. The hybrid coating system can protect the surface more efficiently (Ramesh et al., 2007). In this work silicone (S2) and polyester (P1) resins were used for the coating formulations.

EXPERIMENTAL METHODS AND MATERIALS

Coating consists of binder, pigment, extenders and additives. In this study, the properties of binder system and the interaction of different resins used have been analyzed. S2 and P2 were taken in different compositions to prepare various binders. Polyisocyanate was used as a hardener. The resins and hardeners were blended in mechanical agitator for few minutes. Surface treated cold rolled steel panels were used as the substrate.

The developed binder system was then applied using brush and allowed to dry at room temperature. The physical property of the formed coating film was testified using cross hatch cutter and hence the adhesion of the coating to the substrate and the coating strength can be evaluated. All the tests were carried out following ASTM D3359 standards.Fourier transform-infrared spectroscopy (FTIR) is well established as an analytical technique for functional group analysis and to study the hydrogen bonding and phase separation behavior in polymers, since mid-infrared spectral changes in band intensity and frequency shifts are known criteria for the presence and strength of hydrogen bonds.

FTIR spectrum was recorded in the absorbance mode using a Perkin Elmer spectrometer. KBr method was used for the measurements. For all spectra recorded in a range 400 - 4000 cm^{-1} was carried out at a resolution of 4.0 cm^{-1}.

RESULTS AND DISCUSSION

The samples were coated with the developed coatings. They were allowed to dry for a week before the characteristic analyses. FTIR spectroscopy was used to study the crosslinking of the resins. To identify the crosslinking, it is necessary to determine the Si-O-C bond which could be formed due to silicone and polyester combination. In silicone and polyester resins, there is no such bond. When the hardener cures the silicone-polyester binary resin, an NH – bond will be formed. Hence there should be no NCO band but NH vibration band should be observed in the FTIR spectrum.

This should be noticed in the spectra of the binder samples prepared. The important peaks of silicone resins such as Si-C, Si-O, $Si-CH_3$ and Si-O-Si exist between 950 to 1200 cm^{-1}. The peaks are very closer to each other. In fact, an overlapping of peaks was observed in this range by (Anand Prabu & Alagar, 2004). Figures 1 shows the IR spectra for the S2P2 binder systems. OH band is available at 3519 cm^{-1} for the 100 wt% P2 system. The addition of S2 resin to the P2 resin has shifted the peak in the range of 3407 to 3436 $cm^{-1}$for different compositions of the blends as given in Table 1.

Table.1 OH functional group

OH Functional Group	Peak Value
S2	3397.65
P2	3519.26
S2P2	3407 to 3436

The 845 cm^{-1} band in the pure S2 may have shifted to 910cm^{-1} as the polyester content is increased from 20 wt% to 80 wt%. It is to be noted that there is a band at 826 cm^{-1} in the pure P2 spectrum. Hence the shift in these bands and the difference in the shape of the spectrum of the blends indicate the formation of Si – O – C bands. NH stretching band appear between 1523 to 1536 cm^{-1} and shows the occurrence of crosslinking between the isocyante hardener and the organic resins. It is supported by the disappearance of NCO peak (Anand Prabu & Alagar, 2004). The peak values assigned for C=O and C=C are 1725 cm^{-1} and 1590 to 1640 cm^{-1} respectively. For the pure S2 resin these peaks are available at 1714 $cm^{-1}$and 1594 cm^{-1}. For P2 system, they appear at 1724 and 1608 cm^{-1}. For the S2P2 binder systems, the peaks have been changed 1726 and 1638 cm^{-1} respectively. Hence the shift in these bands and the difference in the shape of the spectrum of the blends indicate the formation of Si – O – C bands.

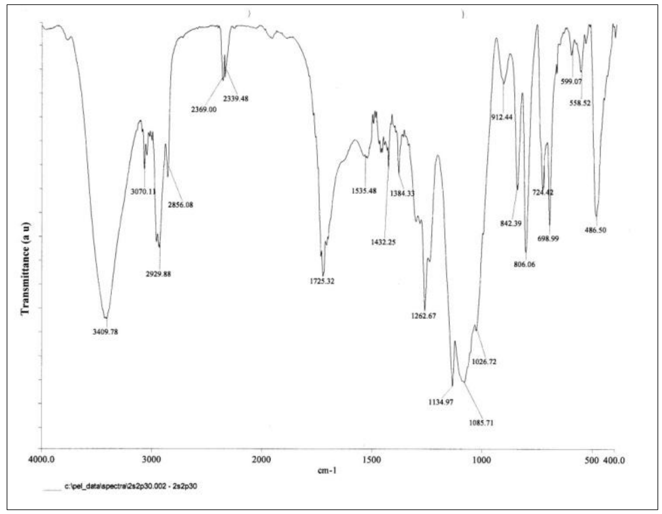

Figure1: FTIR Spectra of S270P230 system

Cross hatch test results show that the S2 concentrations between 30-60% are classified in 4B categories. Binders developed by 50% and 40% S2have 5B characteristics. From the results as shown in Table 2, it is observed that most of the coating systems have good adhesion power. Addition of silicone to the polyester resin has increased the network density, which helped to increase the adhesion power. The carboxylic and hydroxyl functional groups in silicone and polyester interacted with the hydroxides on the substrate surface to ensure adhesion of the resins to the substrate [8]. However, according to (Packham, 1996), crosslinkings not only occur between the resin molecules and the hydroxides of the substrate surface but also between themselves. When S2 and P2 resins react/crosslink, Si-O-C bonds will form, which provides good strength for the coatings. The coatings having 20% polyester resin possibly may have lesser Si-O-C bonds and hence have lower adhesion power.

Table. 2 Cross Hatch Cutter Equivalent Results

Composition	S2P2
20 : 80	3B
30 : 70	4B
40 : 60	5B
50 : 50	5B
60 : 40	4B
70 : 30	3B
80 : 20	2B

EIS studies were carried out by exposing the samples to 3% NaCl solution. Initially the resistance values of the binder systems did not reduce significantly. This is because initially the coating film was still strong and did not allow water molecules to enter or penetrate to the substrate. Once the ions begin to enter the coating, resistance decreased (Lazarevic, Mi kovic-Stankovic, Kacarevic-Popovic, & Drazic, 2005). During the course of exposure, the values of coating resistance was in the range of 10^9 - 10^7 Ω for a high performing coating system (Mills & Schaefer, 2010). The binder systems consisting of 40% P2 with S2 resin showed higher resistance for the 30 days of immersion. 20% and 80% of all the three systems concentrations have lower values. Figure 2 shows the corrosion resistance values for S2P2 system.

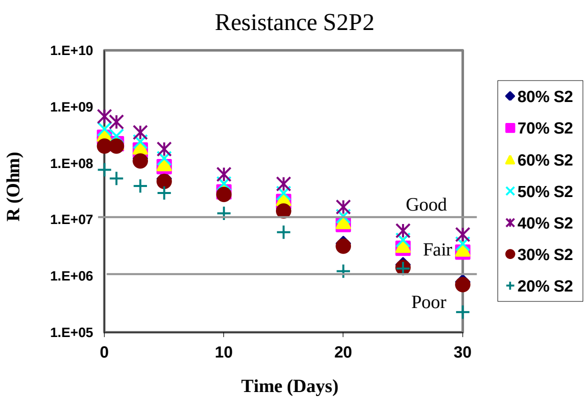

Figure.2 Corrosion Resistance Values of S2P2 system for 30 days.

The initial penetration of electrolyte into the interface of the coating and substrate would have caused the formation of corrosion product and this would have extended to other areas and reduce the adhesion of the coating with the substrate and hence the resistance values decreased further (Doherty & Sykes, 2004; Hinderliter, Croll, Tallman, Su, & Bierwagen, 2006).The transport mechanism of electrolyte solution to the interface of the coating and the substrate may have occurred by means of Ficks' diffusion. The driving force was the concentration difference at the interface. The diffusion of electrolyte to the interface enabled the molecules to disrupt the polar interaction between the coating and the metal substrate which had resulted in good adhesion (Kolek, 1997).

CONCLUSION

A study was conducted to analyse the corrosion protection ability of the organic resin blends. Silicone and polyester resins were used to develop the binder systems. The coatings with 40 to 60% polyester resins showed good adhesion power. Various concentrations of the two resins were mixed. The curing agent used in the study was polyisocyanate. The network of different functional groups between silicone and polyester resins was examined by FTIR spectroscopy. The crosslink formation between the resins was observed by the identification and analysis of NH bond, Si-O-Si, Si-O-C functional groups. The developed coating systems have got adhesion property which was evaluated by cross hatch test. Electrochemical Impedance Spectroscopy (EIS) was used to study the anticorrosion property of the systems by exposing the samples to 3% NaCl solution. EIS experimental results show that the coatings could protect the metal surface for the exposure to corrosive medium for more than 30 days.

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