Corrosion Property Analysis of Coating Formulated Using Acrylic Polyol and Silicone Resin Hybrid Systems

S.K.M. Jamari[a] , K. Ramesh[b], B. Vengadaesvaran[c], S.Ramesh[d], S.R. Rau[e] and A.K. Arof[f].

Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

[a]uchiha_ctk@siswa.um.edu.my, [b]rameshkasi@um.edu.my, [c]venga@um.edu.my, [d]rameshtsubra@gmail.com, [e]rao3535@siswa.um.edu.my, [f]akarof@um.edu.my

Abstract. Coating systems consist of acrylic polyol resin and silicone intermediate resins were tested for their corrosion resistance properties. The corrosion protection property of the coating was evaluated by using Electrochemical Impedance Spectroscopy (EIS) which showed that system with 70 % of acrylic has the highest corrosion resistance. The maximum value of corrosion resistance obtained was found to be $1.40 \times 10^9 \, \Omega$ on the 30th day for the 70 % of acrylic sample. The glass transition temperature (T_g) obtained using the Differential Scanning Calorimetry (DSC) were in the range of 23 °C to 65 °C. It showed that all samples are suitable for decorative paints, general industrial coatings and floor care coatings. The functional groups and also the cross-linking between the organic resins were analyzed using Fourier Transform Infra-Red Spectroscopy.

Introduction

Petrochemical, chemical, construction and marine projects are adversely affected by the enormous lost due to corrosion. This will cause the increase in the cost of raw materials, finished products and property market. Therefore immediate steps need to be taken to prevent corrosion and protect valuable metal substrates. Among the methods of corrosion protection, organic coating has wide range of applications since it often possesses good electrochemical and adhesion properties [1]. Using multi component coating system will have some advantages to achieve higher affectivity. A hybrid of acrylic polyol and silicone intermediate resin was used in this research in order to obtain a good coating system that can withstand physical damage and has good corrosion protection properties.

Silicone resin was used because of its good chemical and weathering resistance, very high heat resistance, good tear strengths and it can withstand thermal shocks. It is also capable of bonding with other materials of various natures, in which it can modify the molecular structure of polymers to make new formulations that can improve the adhesion of the coating [2]. These characteristics would aid acrylic resin to further increase its coating system properties. Acrylate resin has several advantages over other resins in terms of gloss retention, hydrolysis stabilization, high weathering and embrittlement resistance, exterior durability and relatively modest cost [3,4]. However, acrylic needs to have a curing agent since it cannot crosslink itself without the help of hardener. This is where polyisocyanate (NCO) plays its role as the hardener [3].

Experimental

Samples preparation. All resins were obtained from Bayer Material Science (acrylic polyol resin – Desmophen A365 BA/X with 2.9 % of OH content; polyisocyanate – Desmodur N3390 with 19.6 % of NCO content, Germany) and Wacker Silicone (Silanol Functional Phenyl Silicone intermediate resin – Silres IC836 with 3-4.5 % of OH content, Germany). The silicone resin was first dissolved in xylene. The hybrid blend of binder system was prepared by varying the weight percentage of silicone and acrylic resin components are shown in 'Table 1'. The binder systems were prepared up to 60 % of silicone and 40 % of acrylic since beyond the range the binders could not be suitable for coating. This could be dissolved with excess solvent but to avoid higher amount of the VOC (volatile organic component) the compositions were prepared within the ratios. These systems were then mixed with polyisocyanate (NCO) that acted as hardener with suitable ratio [5].

Table 1: Blending ratio of silicone-acrylic resins

Acrylic polyol	Silicone	Code
100%	0%	A100-S0
90%	10%	A90-S10
80%	20%	A80-S20
70%	30%	A70-S30
60%	40%	A60-S40
50%	50%	A50-S50
40%	60%	A40-S60

The cold rolled mild steel panels were cleaned with solvents to degrease the steel panels and the surfaces of the panels were sand-blasted with 60 grit aluminium oxide media at 414 kPa pressure. All samples were applied on these panels by using spray coating method. Conventional spray method is one of the most efficient methods of applying coating system to a substrate. This method relies on compressed air to break the coating into tiny droplets that are carried to the substrate surface. It gives a smoother and more uniform surface than applying by using brush or roller. One of the steps when using spray coating method is to let the air flow first before started to shoot the coating mixtures. This can be used to blow off dust from the surface of the substrate indirectly. However, if the air pressure applied is too high, it can lead to overspray and bounce back of the coating since some of the coating droplets may not reach the substrate [4]. The coated panels were left to cure in room temperature for a week before they were tested for their corrosion properties. The dry film thickness of the samples was measured by Elcometer 456 (Elcometer Instruments Ltd, Manchester, UK) thickness tester.

Electrochemical Impedance Spectroscopy (EIS). EIS has been extensively used to study the performance of polymer coating on metal substrate. From the spectra, the important elements in

the circuit can be found and the coating behavior such as water uptake delamination of coating, initiation and propagation of corrosion at the metal coating interface can be explained. McIntyre and Pham (1996) have explained the method to find these elements such as the coating/pore resistance (R_c or R_p), solution resistance (R_s), coating capacitance (C_c) and the double-layer capacitance (C_{dl}) of a delaminated coated metal obtained from Bode plot [6]. Dhoke and Khanna (2012) have provided a clear explanation of how these elements work in a coating system under EIS [7]. EIS analysis was performed as a function of time (days) with the exposure of 3.5 % NaCl solution at open circuit potential. The coated metal plate served as the working electrode. Standard saturated calomel electrodeand platinum electrode were used as reference and counter electrode respectively. The inner diameter of polyvinyl chloride tube used is 3.1 cm (tested area is 15.1 cm^2) bound to a coated panel with an araldite adhesive. The inner 15.1 cm^2 specimen surface was exposed to a 3.5 % NaCl solution at ambient condition. This electrochemical cell placed in a Faraday's Cage to reduce current noise picked up by the working electrode and EIS measurements were performed using a Gamry PC14G300 potentiostat and Echem Analyst Version 5.6 analyzer. The frequency was in the range of 300 kHz to 10 mHz and the amplitude of the signal was 10 mV. The Bode plot has been used to obtain the coating resistance (R_c) and coating capacitance (C_c) of the samples [8-11]. EIS can be used to determine the adhesion properties of the coating to the substrate by obtaining data from log Z versus Log ω. Capacitance measurements can be used to estimate the relative electrolyte uptake rates by the coatings and the rates of delamination of the coating from the metal substrate.

Differential Scanning Calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the samples according to ASTM D7426 equivalent to ISO 11357–2. B. Vengadaesvaran et al. (2010) obtained glass transition temperature of phenyl silicone-acrylic polyol ranging from 34 °C to 89 °C in his study [8]. A METTLER TORLEDO DSC822^e (Mettler-Toledo Inc., Polaris Parkway, Columbus OH 43240) was used to study the T_g values of the samples. 5.0±0.2 mg of each sample was taken in aluminum crucibles in an inert atmosphere. The comparison between the references of pure silicone resin and acrylic polyol resin cured with polyisocyanate were also taken into account. The DSC temperature program ran dynamically under nitrogen condition with a flow rate of 50 mL/min.

Fourier Transform Infrared (FTIR) spectroscopy is the helpful tool for the identifications and characterization functional groups in chemicals as well as the cross-linking between them can be determined by using FTIR. The FTIR analysis for all the samples was carried out in the range of 4000 cm-1 to 400 cm-1 with 4 cm-1 spectral resolution

Results and Discussion

Electrochemical Impedance Spectroscopy. The corrosion protection ability of the coating was examined in terms of the coating resistance and the capacitance using impedance measurements. 'Fig. 1' shows the effect of silicone and acrylic composition on coating resistance for a 30-day of exposure to electrolyte solution. From the graph, it is understood that A70-S30 has a very high coating resistance. The coating resistance values were found to be in the range of 10^9 Ω for the whole period of exposure. The coatings formed by the binders A60-S40 and A80-S20 also have very high resistances where this can be described as good performing zone since both of the systems have coating resistance higher than 10^6 Ω [11]. The resistance value of A90-S10 coating was 2.4 x 10^8 Ω on the 20th day then it dropped to 4.6 x 10^5 Ω on the 25th day. A similar pattern

can also be observed for A40-S60 sample as it dropped rapidly from 1.1 x 10^8 Ω on the 10th day to 3.8 x 10^4 Ω on the 15th day. This may be because of the coating would allow more electrolytes to penetrate and the corrosion started at the interface. A50-S50 binder system behaved stable throughout the time of exposure. A small drop in coating resistance was observed on the 15th day which may be attributed by the initiation of corrosion and the corrosion product might have blocked the pore afterwards. A100-S0 coating system showed poor performance in this study which has the coating resistance in the range of 10^6 Ω initially and dropped to 10^5 Ω.

'Fig. 2' shows the coating capacitance of the binder systems. A70-S30 system has lower conductivity whereas A40-S60 has the highest conductivity. The coating capacitance is inversely proportional to coating resistance.
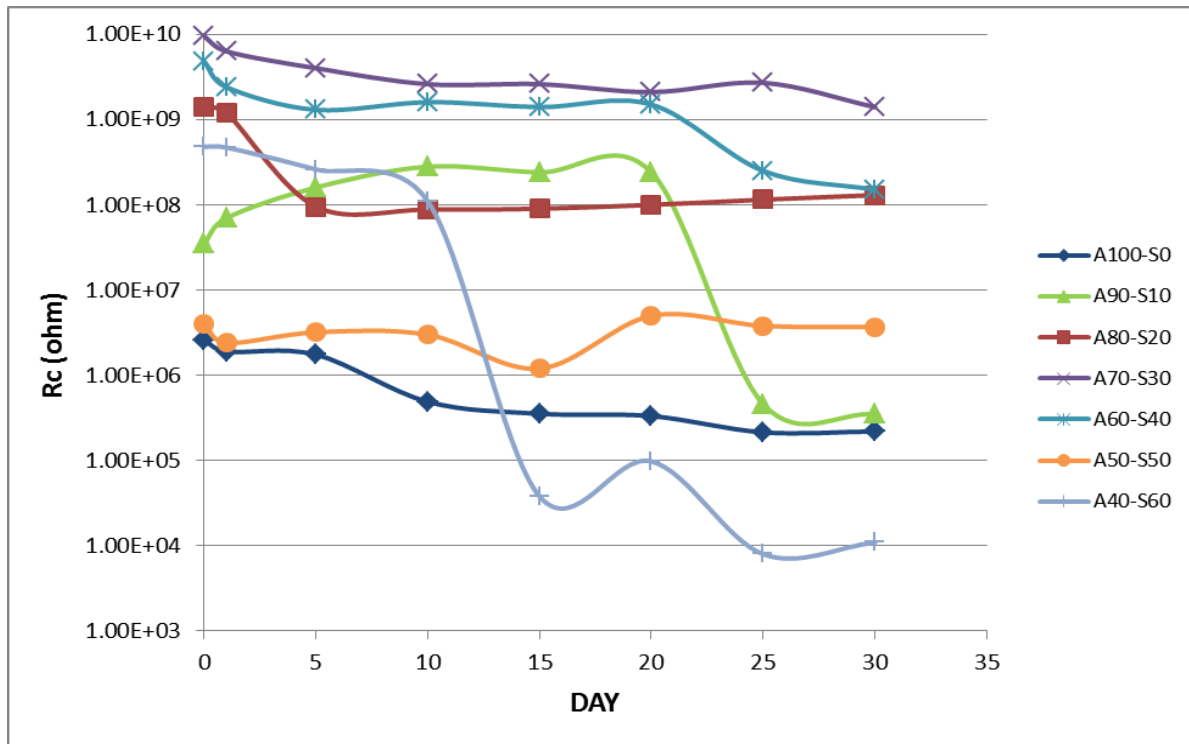

Figure 1: Plot of coating resistance (R_c) versus time of immersion.

The coating capacitance increases with time of immersion and this increment leads to the second time-constant indicating that new parameter, Cdl would appear.

Differential Scanning Calorimetry. The Tg values for pure silicone and polyisocyanate obtained are 76.78 °C and 101.22 °C respectively. The polyisocyanate used has very high Tg value and this explains the brittleness of the film formed by this curing agent. A40-S60 recorded high glass transition temperature as 63.69 °C and this confirmed that the brittleness of the sample due to the existence of more silicone resin in the blending system compared to acrylic polyol resin. Thus, it is not suitable for industries with high impact environments [9]. Samples with lower silicone percentage have Tg values below 50 °C (A70-S30, A90-S10 and A100-S0) are suitable for general industrial coatings and decorative coatings [9]. The A70-S30 sample possesses Tg value around 40 °C which is suitable for general industrial applications. From the EIS results can

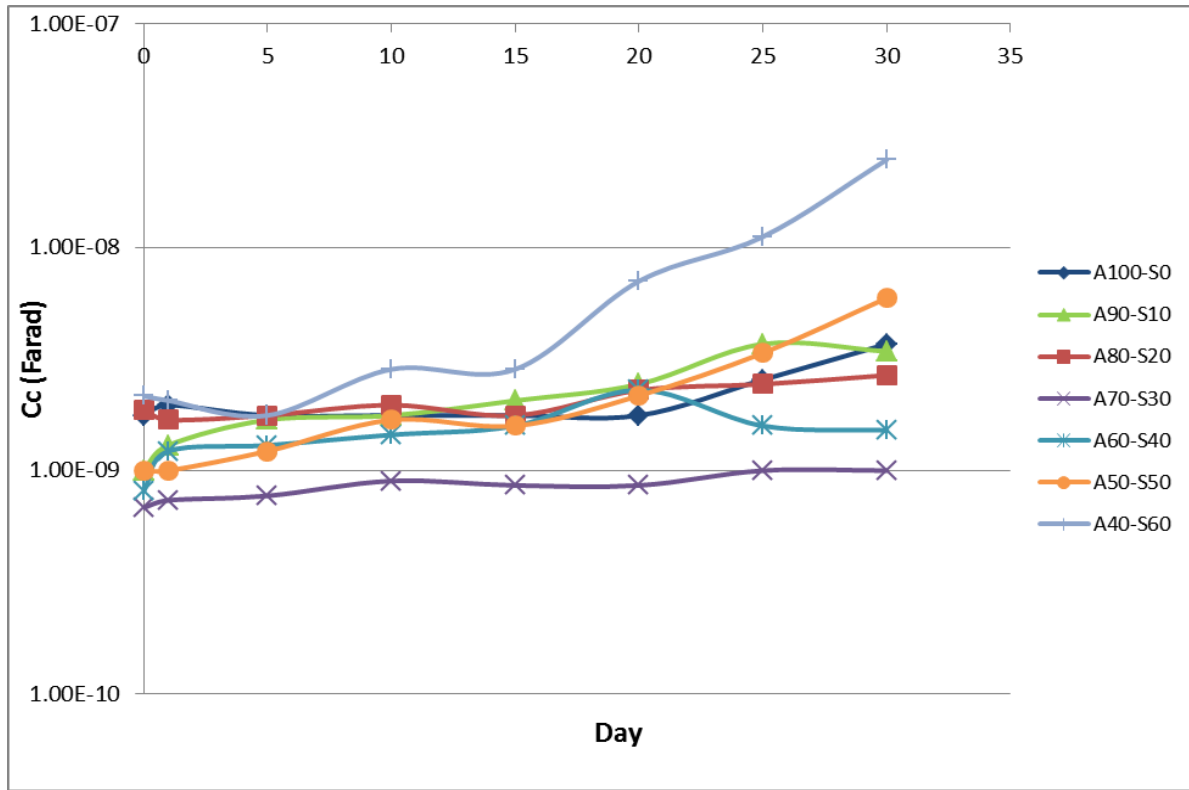be concluded that this composition can withstand corrosive environment for longer period of time.

Figure 2: Plot of coating capacitance (C_c) versus time of immersion

From FTIR results the crosslinking between resins was observed. The shift in the peaks at 680 cm^{-1} and 732 cm^{-1} has been observed when the silicone concentration increased which would increase impact resistance of the coatings [12-14]. A new peak has been observed in the binder systems at 1550 cm^{-1} that indicates the formation of NH bond which may be the resultant product of cross-linking between the resins and the curing agent since there is no such peak in the spectra of pure polyisocyanate.

From the results from EIS, DSC and FTIR, it is understood that the crosslinking has been obtained and hence the properties of the coatings enhanced.

Conclusion

Different compositions of binder coatings were developed using silicone and acrylic polyol resins. The important properties were evaluated using different analytical methods. The coatings have good mechanical and thermal properties. Electrochemical studies showed that A70-S30 binder system has higher coating resistance for a period of 30 days of exposure to 3.5 % NaCl solution. It could be understood that the coating systems can prevent the substrate very well from corrosive environment when they are used as external coatings. DSC clearly depicts that the increase in glass transition temperature with the increase in silicone resin content. This implies

that the network density increases until an optimum composition of A70-S30 is reached at which the corrosion resistance properties been enhanced which was further supported by EIS results.

Acknowledgements

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