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Synthesis and Characterization of Anticorrosive Acrylic Silicone Hybrid Resins

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Abstract

New Acrylic-Silicone hybrid resins for corrosion protective coatings were developed by emulsion co-polymerization of methyl methacrylate (MMA), butyl acrylate (BA), styrene with methacryloxypropyl trymethoxysilane (MATS) and octamethylcyclotetra siloxane at 80-850C in the presence of Ammonium per sulphate (APS) as the initiator. Resulting polymers were characterized by using Fourier transformed infra red spectroscopy (FTIR) and particle size analyzer. The obtained polymers had high solid content and were used in emulsion paints as binder. The coatings were prepared and there anticorrosion behaviour was discussed with varying silicone content. The experimental results show that these polymers supply very useful properties such as high anticorrossivity UV light stability, washing and coating with highest silicone content exhibited the maximum corrosion resistance property. Remarkable improvements in film properties were seen.

Keywords: Hybrid resins, Emulsion polymerization, Acrylic, Silicone, Corrosion protective coatings.

Introduction

Surface preparation is becoming a major concern of industrialists in attempt to corrosion protection of materials. Industrial maintenance paints, formulated for interior and exterior applications, are used as means to control corrosion. When coatings are exposed to the

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outdoors, synthesized resins, the main components of coatings, are oxidized by such things as sunlight, heat, water, oxygen, and air-polluting materials. Therefore, weatherability, especially for coatings, is defined as the property of being resistant to gloss loss and chalk, which are highly affected by UV [1, 2]. Corrosion, whether in atmosphere, underwater, or underground is caused by completion of an electrochemical cell which allows for the flow of electricity from one part of the surface of the metal to another. Corrosion means the breaking down of essential properties in a material due to chemical reactions with its surroundings [3]. In the most common use of the word, this means a loss of electrons of metals reacting with water and oxygen. Weakening of iron due to oxidation of the iron atoms is a well-known example of electrochemical corrosion. This is commonly known as rust. This type of damage usually affects metallic materials, and typically produces oxide(s) and/or salt(s) of the original metal. Corrosion also includes the dissolution of ceramic materials and can refer to discoloration and weakening of polymers by the sun's ultraviolet light. Plating, painting, and the application of enamel are the most common anti-corrosion treatments.

The corrosion resistant coatings act as a physical barrier layer to isolate the surface of metal from corrosive environment. Typical advantages of organic systems are they are mechanically flexible and tough, but have poor abrasion and thermal resistance. Conversely, inorganic systems have excellent abrasion resistance and high density, but are brittle and require high processing temperature [4-6]. Hybridization technique is in use these days. This technique offers the advantages of each component, used for hybridization contributing its individual benefits to overall system [7]. Inorganic-organic hybrid materials are well known to combine the properties of inorganic phase with that of organic polymers. In addition, inorganic/organic hybrid coatings provide better adhesion than pure organic coatings, because the inorganic component of the precursors can easily react with metal substrates by the surface hydroxylation. The adhesion properties of coatings are crucial for durability of corrosion protection. In the present scenario, low VOC (volatile organic compound) coatings have become prime concern of the paint industries. Thus, from the industrial point of view, water based sol-gel precursors have numerous advantages over the corresponding non-aqueous medium, including substantial VOCs (volatile organic compound), reduction, and ease of handling. Therefore, our main objective is to introduce organic inorganic hybrid resins for coating systems to enhance the flexibility of the films as well as to obtain highly dense coatings on metal surfaces to improve the corrosion resistance ability. As silicone shows good anticorrosion behavior [8] and Acrylic improves other properties of the coatings [9, 10]. We used these two resins for organic inorganic hybrid resin preparation. In this context, our present work describes the preparation of the acrylic silicone hybrid resins for corrosion protective coatings using different monomer contents. The anti-corrosion behavior of the developed coatings was studied.

Experimental

Material

Monomers Butyl Acrylate (BA), Methyl Methacrylate (MMA) and Styrene were purchased from Aldrich and freed from inhibitor by shaking with 10% NaOH, washing with water and drying over Na2SO4, then distilled under reduced pressure before use and stored at -150C to avoid thermal polymerization. Octamethyle cyclotetra siloxane (alfa), 3-methcryloxypropyl trimethoxy silane (MATS, alfa), Ammonium per sulfate (APS, fluka), dodecyl benzene sulfonic acid (DBSA, alfa) used as polymerization catalyst and surfactant and sodium dodecylbenzene sulfonate (SDBS, Aldrich)used as surfactant , were used as received

Preparation of reagents

Acids: The acids were diluted by taking the required quantity of water and acids on a volume basis to achieve the desired concentration. The following concentrations of various acids were used, Acetic acid (5%, 15%), and Hydrochloric acid (5%, 10%).

Alkalies: Sodium hydroxide was dissolved in water to make solutions of 5% and 10% concentration on a weight per volume basis. Two concentrations of 10% and 20% of ammonium hydroxide were taken by diluting with water on a volume basis. Panels were immersed in these chemicals at an ambient temperature for 24 hours.

Polymerization procedure

Preparation of seed latex: The seed nuclei are small and colloidally stable in the polymerizing medium that can grow to give the final latex particles. The polymerization was carried out using DBSA. A selected amount of water, siloxane and DBSA +SDBS (2-4% of the monomer ,dissolved in 10 g of water) were successively charged to a four necked round bottomed flask equipped with a stirrer, reflux condenser, thermometer pocket and a dropping funnel, and stirred. The polymerization was started once the flask was introduced into an oil bath of controlled temperature. Then MATS was added and temp. was maintained at 80±10 C.

Seeded emulsion polymerization of acrylic monomer: A selected amount of seed latex and water were charged to the reactor. Then appropriate amount of Hydroxyethyle cellulose,

$NaHCO_3$ and initiator solution (APS 0-2g dissolved in 5 g of water) were introduced into the reactor and the monomer mixture (BA, MMA, and Styrene) was added drop wise to the medium. Polymerization was continued for 6 hours and temperature was maintained at 80±10 C

Characterization of Synthesized Polymers

Synthesized polymers were characterized by spectral analysis and particle size analysis. Samples were coded as acrylic resin – PA, hybrid polymer with silicone content 5% – HA, 10% – HB, 15% – HC.

Spectral analysis: Spectral analysis of synthesized polymer was done by using IR spectroscopy. The IR spectra of prepared hybrid polymers were obtained by using FTIR spectrometer. KBr pellets of sample were subjected to analysis at 20 scans (figure 1-4).

Particle size analysis: Particle size analysis was done by Particle sizing systems, Inc. Santa Barbara, Calif., USA (figure 5).

Coating formulation and film preparation

An emulsion paint was prepared as per the formula given in table 1 [11]. The films were applied on to the sand blasted steel panels (mechanical properties) and glass panels (chemical properties) with the help of a film applicator. All efforts were made to maintain a uniform film thickness of 50 micron for the characterization of general chemical resistance and mechanical properties. The cured films were stored for three days under ambient atmospheric conditions before testing.

Table 1 Emulsion paint formulation

Compound	Functional	Amount %	Amount (g)
Water	Solvent	28	279.5
Sodium benzoate	Softening agent	0.19	1.9
Tagofomax	Antifoaming	0.36	3.58
Hydroxyethyle cellulose	Thickening agent	0.6	6

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Ammonia solution 25%	pH adjustment	0.16	1.6
Titanium dioxide	Opacifying white pigment	11.64	116.2
Aluminium Silicate	Extender	2.54	25.4
Talk (325mesh)	Extender	5.45	54.5
Calcium Carbonate	Extender	31.98	319.8
Formaldehyde	Antibactericide	0.2	2.0
Ethylene glycol	Co-Solvent,antifreeze	1.07	10.7
Butyl glycol	Colescence agent	0.93	9.3
Mineral spirits	Leveling agent	0.93	9.3
DisperseA	Dispersing agent	0.39	3.9
Dioctylphthalate	Softening agent	0.5	5.0
Acrylic silicone hybrid resin	Binder	15.06	150.6

Characterization of film properties

For corrosion resistance point of view, resins were evaluated by humidity test (table 2) and salt spray test (table 3). Coated panels were evaluated for there chemical resistance properties like water resistance (table 4), acid resistance (table 5) and alkali resistance (table 6), and mechanical properties like adhesion, gloss, etc (table 7).

Corrosion resistance properties: Corrosion resistance properties were tested by using salt spray cabinet. The parameter for the humidity test are – temperature cycle of 42-48-42°C of 1 hour each at relative humidity of 100%, and for salt spray test- 5%(w/w) solution of NaCl at a temperature range of 33.3-36.1°C as per ASTM B 117. Results of accelerated corrosion resistance according to ASTM rating are given in table 2 and 3.

Chemical resistance properties

The chemical resistance tests like water, acid and alkali, were performed on coating systems prepared as mentioned earlier. All panels were cured at ambient temperature before subject to test. Coated panels were sealed from three sides by using molten wax before dipping in various chemicals and after that coated films were exposed to the action of acids, alkalies and water.

Mechanical properties

Hardness: This property deals with the resistance of a material to indentation of scratching. The hardness of a coating material is generally tested by scratch hardness test which is done by scratch hardness tester (ASTM D 5178, Sheen instruments limited England).The panels were loaded with different weights until a clear scratch showing the bare metal surface was seen.

Adhesion: The percentage adhesion was determined by using crosshatch adhesion tester (ASTM D 3359, Sheen instruments limited, England).

Flexibility: The flexibility of the coated films was determined by bending the panels to 1800 using a ¼ inch mandrel (Sheen instruments limited England).

Gloss: The gloss of the films coated on the panels was determined by glossometer (Sheen Instruments limited England).

Gloss retention: Gloss retention properties of the coating prepared were examined by wetherometer. The paint films were exposed to alternate cycles of UV radiations for 4 hrs at 50°C and condensation for 4 hrs at 45°C. The cycles were repeated and the coating was observed for gloss retention. Results of gloss retention tests are shown in figure 6.

Results and discussion

Spectral analysis

The characterization was done by IR analysis. IR spectrum was used to confirm the reactive groups in monomers and to confirm that all silanol groups have reacted. Theoretically all silanoles should react and final polymer should not have any silanol group present. The silanol group is characterized by a peak at 892cm-1. When all silanol have reacted, ideally there will be no peak at 892 cm^{-1}. The peak at 1456 cm^{-1} was attributed to the $Si-CH_3$, whereas the band of 844 - 846 cm^{-1} and peak at 1074 cm^{-1} was due to the stretching

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vibrations of $Si-O-CH_3$ and Si-O respectively. The peaks at 2959, 1734 and 1146 cm^{-1} resulted from the C-H and C=O and C-O stretching vibrations. The IR spectra of acrylic polymer is shown in figure 1 while figures 2, 3 and 4 are IR spectra of the hybrid polymer with silicone content 5, 10, and 15% respectively.

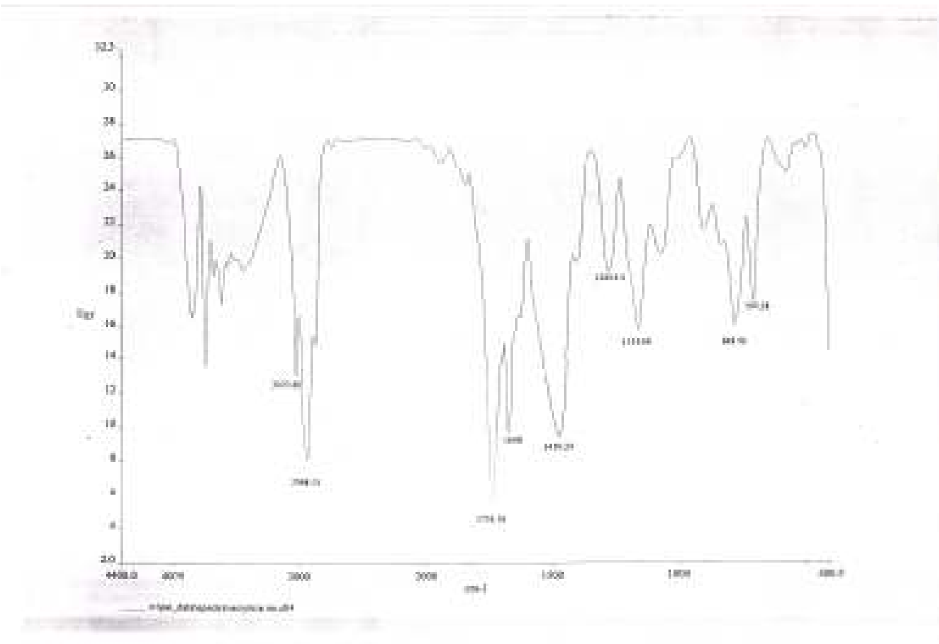

Figure 1: IR spectrum of acrylic polymer PA.

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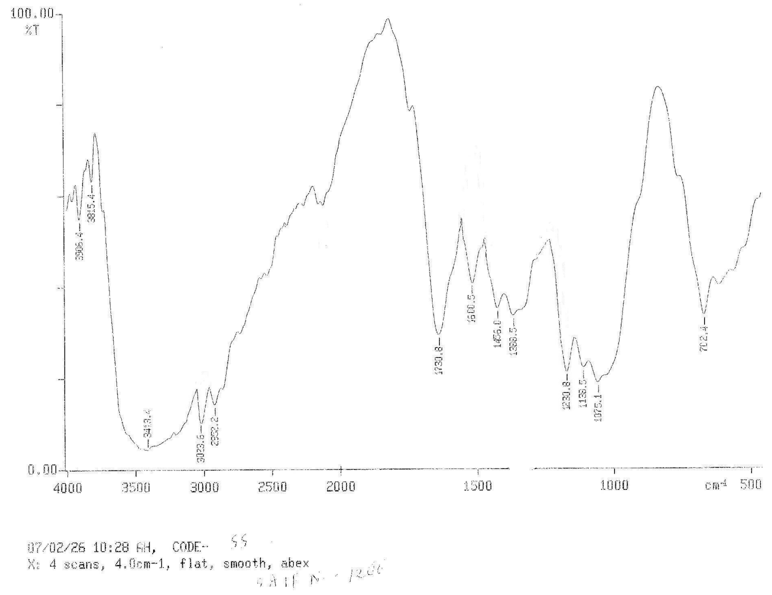

Figure 2: IR spectrum of hybrid HA.

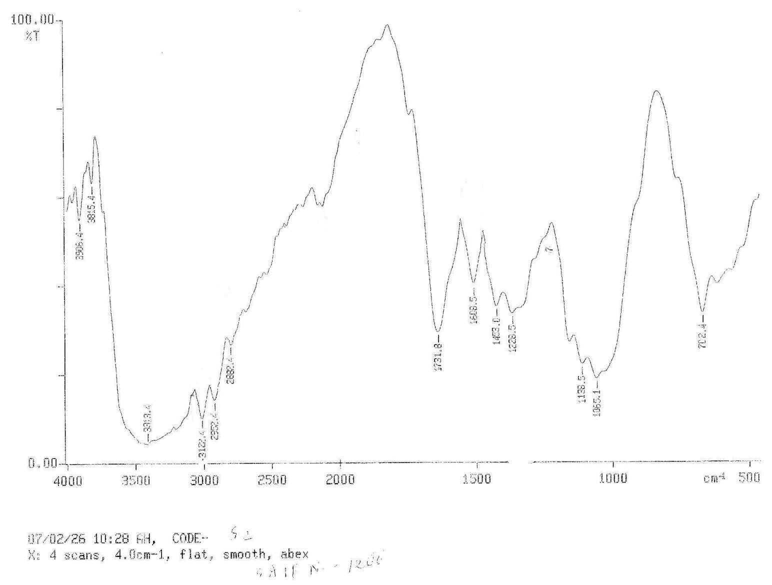

Figure 3: IR spectrum of hybrid HB.

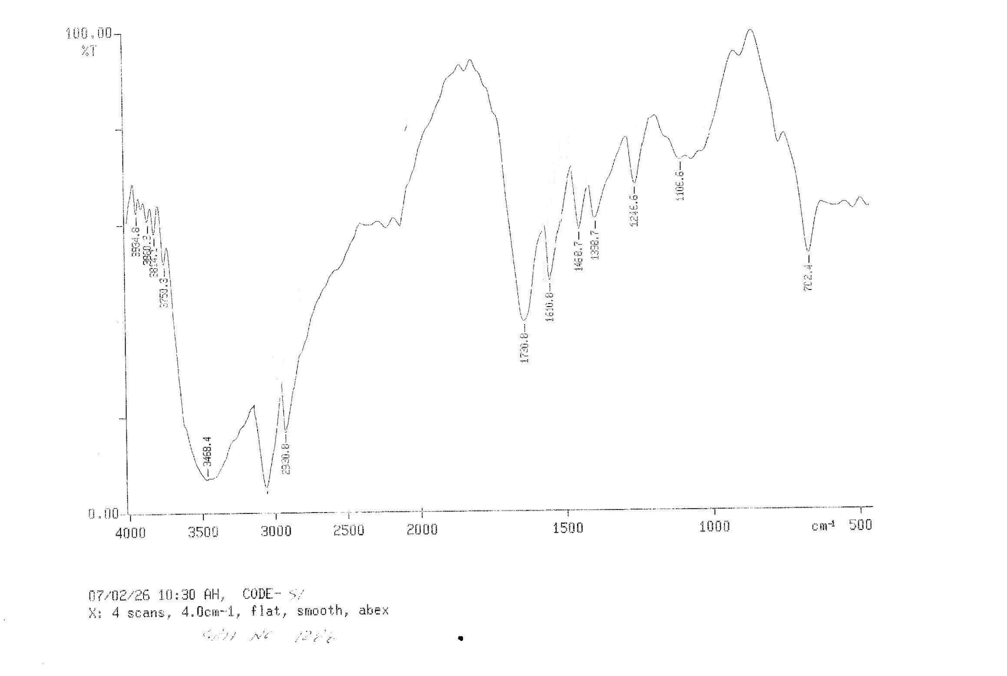

Figure 4: IR spectrum of hybrid HC.

Particle Size Analysis

From particle size graphs, figure 5, we can see that acrylic polymer is having a larger particle size than the hybrid polymer with different silicone content. The finer particles of hybrid provide better film integrity and packing, resulting better chemical and physical properties.

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Figure 5: Particle size graph, top left-sample PA, top right-sample HA, bottom left-sample HB, bottom right- sample HC.

Corrosion resistance properties of hybrid films

From the results, given in table 2 and 3, it can be seen that incorporation of siloxane moity in the backbone of acrylic resins has helped to develop a coating with improved humidity and salt spray resistance. The resistance properties of prepared coating increases with the increase of the silicone content in hybrid resin.

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Table 2 Salt spray test

No.	Parameter	PA	HA	HB	HC
1	Scratch corrosion				
	-24 hours	10	10	10	10
	-72 hours	9	10	10	10
	-196 hours	8	8	9	10
2	Blistering around scratch				
	-24 hours	10	10	10	10
	-72 hours	9	10	10	10
	-196 hours	8	9	10	10
3	General blistering				
	-24 hours	10	10	10	10
	-72 hours	9	10	10	10
	-196 hours	7	9	10	10

Table 3 Humidity test

No.	Parameter	PA	HA	HB	HC
1	Scratch corrosion				
	-24 hours	10	10	10	10
	-72 hours	9	10	10	10

	-196 hours -300hours -500 hours	8 8 4	8 6 5	9 8 7	10 9 7
2	Blistering around scratch -24 hours -72 hours -196 hours -300hours -500 hours	10 9 8 6 5	10 10 9 7 6	10 10 10 8 8	10 10 10 9 7
3	General blistering -24 hours -72 hours -196 hours-300hours -500 hours	10 10 9 8 7	10 10 10 9 8	10 10 10 10 9	10 10 10 10 9

Chemical resistance properties of hybrid films

Water resistance: The resistance of the hybrid films against deionized water and sea water is shown in table 4. It was found that the water (deionised and sea) resistance of the film increases with the increase in silicone percentage.

Table 4 water resistance of hybrid films

Sample	Deionized water	Sea water
PA	Z	Z
HA	X	Y
HB	X	X
HC	X	X

When dipped for 2 weeks, X= unaffected, Y= slightly affected, Z=affected

Acid resistance: The acid resistance of hybrid films is shown in table 5. The acid resistance increases with the increases in silicone content.

Table 5 Acid resistance of hybrid films

sample	Acetic acid		Hydrochloric acid	
	5% (v/v)	15% (v/v)	5% (v/v)	10% (v/v)
PA	G	P	G	P
HA	G	G	G	P
HB	E	E	E	E
HC	E	E	E	E

When dipped for 24 hrs, E=Excellent, G=Good, P=Poor

Alkali resistance: Resistance to alkali of hybrid films is shown in table 6. Alkali resistance of all the films, pure acrylic to acrylic silicone hybrids were found satisfactory.

Table 6 Alkali resistance of hybrid films

Sample	Sodium hydroxide		Ammonium hydroxide	
	5% (w/v)	10%(w/v)	10% (v/v)	20% (v/v)
PA	E	E	E	E
HA	E	E	E	E
HB	E	E	E	E
HC	E	E	E	E

When dipped for 24 hrs, E=Excellent, G=Good, P=Poor

Mechanical properties of hybrid films

The mechanical properties of the prepared coating system are given in table 7. It can be seen by the data given in table that the scratch hardness of the film remains same in all the three compositions, it shows that the silicone content have no effect on the hardness property of the resin. Data from the adhesion test shows that silicone content has a great influence on the adhesion property of the polymer, as increasing silicone content increases the adhesion. The flexibility test data shows a considerable improvement in performance, and gloss also improves as the silicone content increases. Thus it is seen that hybrid resin performs better in terms of flexibility, adhesion and gloss and glass retention, whereas hardness of system remains unaltered as silicone content in the hybrid resin increases.

Table 7 Mechanical properties of hybrid films

No.	Parameters	PA	HA	HB	HC
1	Hardness	1800 g passes	1800 g passes	1800 g passes	1800 g passes
2	Adhesion (no. of squares retained)				
a.	Wood	25	62	78	92
b.	Aluminum	5	35	92	99

c.	Mild steel	9	73	100	100
3	Flexibility	1/4" passes	1/4" passes	1/6" passes	1/8" passes
4	Gloss at 60̊	90	92	94	95
5	Viscosity FCB4(secs)	82	75	69	73

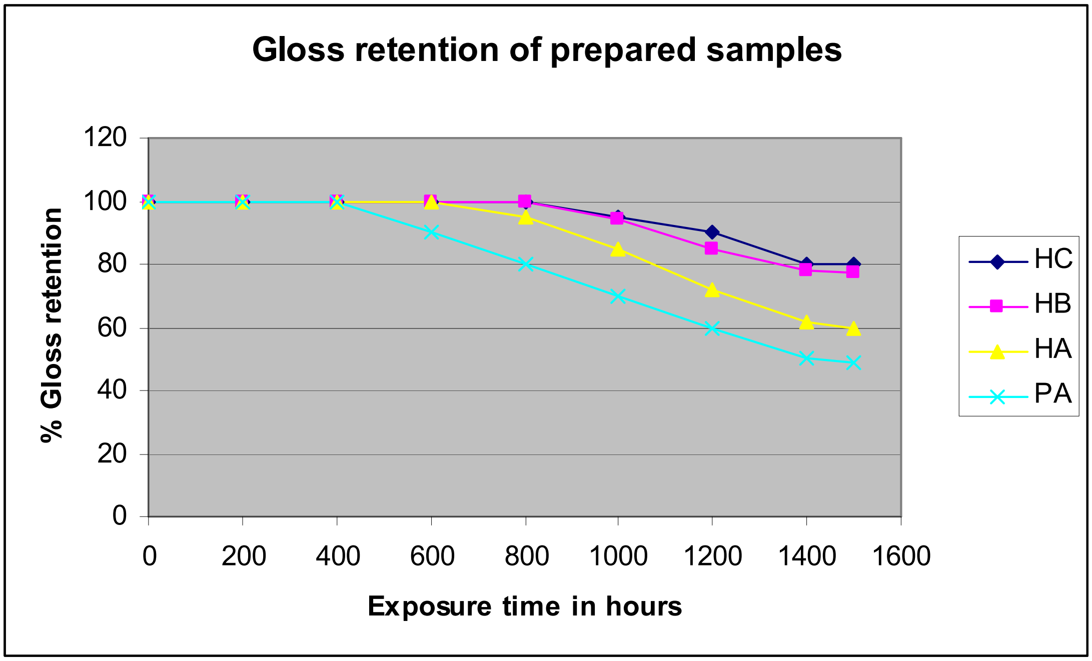

Figure 6: Gloss retention performance of prepared samples

Conclusion

Hybrid resin of acrylic and silicone is synthesized in aqueous media by emulsion polymerization, leading to lower VOC as compared to conventional systems. From the performance data, it is seen that increase in silicone content improves corrosion resistance and chemical resistance properties of the coating and other mechanical properties were improved by acrylic resin content. It proofs that in a hybrid system we can improve the properties of the system by adding two component and good properties increases as the content of one component increases and other properties are not affected. So these resins can be used in coatings where corrosion resistant paints are required because of good corrosion resistance, adhesion, flexibility, gloss and resistance to various chemicals, and we can improve the performance by increasing silicone content in the hybrid resin of Acrylic and Silicone.

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