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Improvement of properties of coating systems with cardanol modified epoxy primer

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Abstract
Ecological and economic issues in the new generation coating industries have led to the maximum utilization of naturally occurring renewable materials for polymer synthesis. This paper for the first time demonstrates the use of cardanol modified epoxy primer in three component coating systems and the findings of the change of resin on coating behaviour and therefore its application properties on concrete. The three component coating systems were prepared using cardanol modified virgin/pigmented epoxy and polyurethane. The coating properties of the systems were investigated for their physico-mechanical properties, chemical and corrosion resistance and the developed coating systems showed remarkable performance in terms of increase in tensile strength, stronger bonding with concrete and lowering of water vapour transmission.

Keywords: Coatings, epoxy, cardanol, primer, corrosion protection, properties enhancement.

1. Introduction

Epoxies have been used extensively owing to their excellent chemical and solvent resistance, good thermal and electrical properties, high strength and modulus, good adhesion property, and good processability. Epoxies are essential components for many composites, coatings, paints, lacquers, and for structural adhesives. Epoxies are extremely versatile but their use for high-performance applications is somewhat restricted because of their low impact strength and high rigidity. As a result research has been continuing even today to gain the greater understanding of associated oxirane chemistry and epoxy networks and on improving properties such as impact strength, toughness, flexibility, dielectric behaviour, high temperature applications, coefficient of thermal expansion and processability [1-13].

The worldwide demand for replacing petroleum derived raw materials with renewable plant based ones in the production of polymeric materials from the social and environmental concerns has been continuously increasing and has led to ever increasing use of plant based raw materials. Furthermore, these materials are sometimes cheaper than petrochemicals and reduce the overall cost. Sunflower, soybean, larch, cashew nut and linseed are some of renewable resources which have been used in pigmented formulation for use as functional coatings [14-23].

Epoxies generally comprise of a base component and a curing agent called hardener. The common base component is diglycidyl ether of bisphenol-A. The room temperature curing agents generally used to initiate the cross linking are either polyamines or polyamides [2, 3]. The need for high performance polymeric coatings having improved properties has led to the development of modified epoxy polymeric coatings by the interpenetrating polymer network mechanism [24-26].

Although extensive literature is reported on cardanol based epoxies and related systems in recent times but we could not find anything on cardanol modified epoxy primer based three coat systems [17, 18, 27, 29-32]. Hence, the study reported here was undertaken to develop new polymeric coating systems using cardanol modified epoxy primer suitable for aggressive conditions prevalent in fertilizers plants, chemical industries, thermal power plants, bridges etc. This paper shares the experimental data obtained from this long term study.

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Experimental

2.1 Materials

Epoxy and polyurethane resin were procured from local vendor M/s Krishna Conchem Products Private Limited, Mumbai and used as such. Cardanol modified epoxy resin for the present work was synthesized as per procedure reported elsewhere [6].

2.2 Experimental design and formulations

Coating systems namely A, B, C and D were developed using commercial and modified cardanol based coatings respectively with pigments micaceous iron oxide, blank fixe, calcite, magnesium silicate and titanium dioxide along with other additives and solvents (Table 1). Systems A and B are commercial epoxy primer based while C and D are modified ones.

Table 1: Compositions of coating systems

Coating Systems	Primer	Middle Coat	Top Coat
A	Epoxy	Pigmented epoxy	Pigmented epoxy
B	Epoxy	Pigmented epoxy	Polyurethane
C	Modified epoxy	Pigmented epoxy	Pigmented epoxy
D	Modified epoxy	Pigmented epoxy	Polyurethane

2.2.1 Preparation of test samples

Glass, steel and concrete panels of 150 mm × 100 mm size were prepared as per method given in IS: 101 Part 1/Sec. 3: 2001. Coating systems were applied on the thoroughly cleaned concrete, steel and glass panels using a paintbrush. The coated concrete panels were then used for the determination of resistance of coatings against various exposure conditions, steel panels were used for adhesion and flexibility and scratch resistance tests; and the glass panels were used to obtain free films for tensile and water vapour transmission tests. The coated panels were left in the laboratory for at least one week to ensure full drying and curing of the films. The edges of the concrete panels for immersion studies were then sealed with wax to prevent attack from the edges.

2.2.2 Evaluation of coating systems

Free film properties of the coating systems, such as tensile strength and water vapour transmission were measured as per ASTM D 2370-02 and ASTM D 1653-03. Bond strength was measured by the pull out method as per BS EN ISO 4624-2003 (BS 3900-E10-2007) using a DynaProceq adhesion tester, while scratch hardness and adhesion and flexibility were determined according to the method given in IS: 101 Part 5/Sec. 1 & 2-2001 and ASTM D 522-08 respectively. Visual examination of panels after immersion and humidity cabinet exposure was carried out as per ASTM D 714-02 [33-40]. Minimum of ten coating panels were prepared for each of above parameter studies and mean value along with standard deviation was calculated.

2.2.3 Immersion test

The chemical resistance behaviour of the coating systems was studied by an immersion test at room temperature ($23\pm5\ ^0$C), in which a minimum of three coated concrete panels were placed vertically in different reagents such as water, 5% sodium chloride, 20% hydrochloric acid solution, 30% potassium hydroxide solution, saturated solution of urea, triple phosphate (NPK) and diammonium phosphate for 400 days so as to compare the performance of these systems. For this purpose, the panels were taken out at regular intervals, washed with water and visually examined for the film integrity, overall appearance and any coating failure.

Results of coatings degradation were represented on a scale of 0-10 for blisters, 10 being no blister; and frequency of blisters was shown by letters F for few, M for medium, MD for medium dense and D for dense.

2.2.4 Humidity Cabinet test

The concrete panels coated with different coatings were kept in a Sheen humidity cabinet maintained at 100% relative humidity and $45\pm5\ ^0$C temperature as per IS: 101 Part 6/Sec. 1: 2001. Observations were recorded at regular intervals for any visible sign of deterioration of coatings during the 400 days of exposure as described above.

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2. Results & discussion

The presence of hydroxyl (-OH) and carboxyl (-COOH) functional groups along with aliphatic unsaturation in the cardanol modified epoxy primer offers the possibility for many chemical reactions and the long alkyl side chains provide flexibility because of an internal plasticization effect (See Figure 1). Presence of side chain also provided high cross-linking density to the modified epoxy primer facilitating the formation of strong network structure and hence resulting in good mechanical characteristics and better chemical and corrosion resistance.
The results of the tensile strength and water vapour transmission of the free films; and the bond strength, flexibility and scratch hardness are given in Tables 2 and 3, respectively. Chemical resistance results are given in Tables 4 and 5 while humidity cabinet test results are given in Table 6.

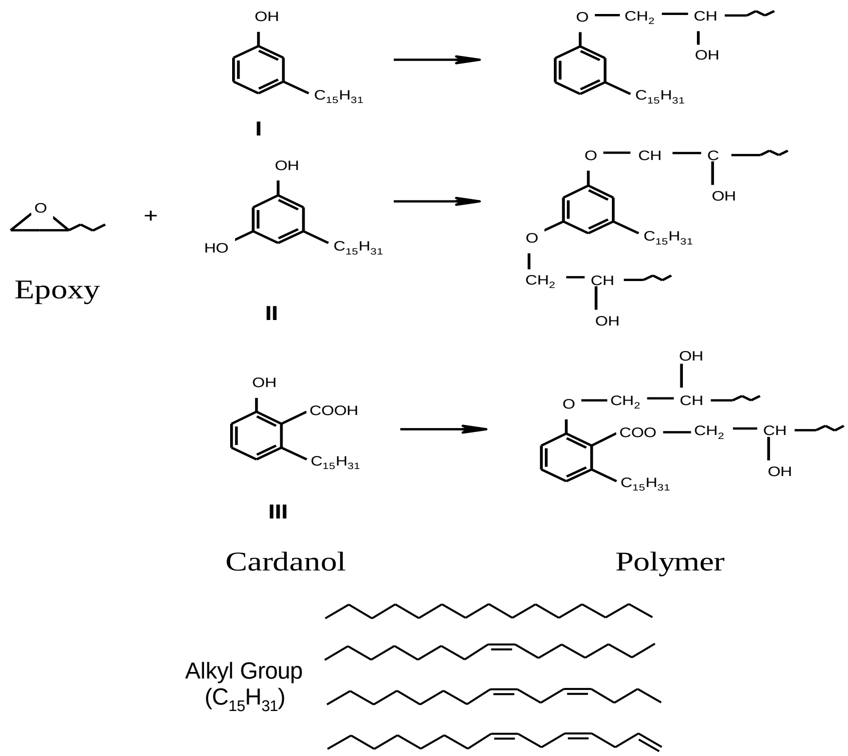

Figure 1: Reaction of epoxy with cardanol [21]

Table 2: Free film properties

Coating Systems	Tensile strength (N/mm^2)		Water vapour transmission (mg/cm^2-24 h)	
	Mean	SD	Mean	SD
A	23.0	1.50	0.6	1.00
B	10.3	1.10	1.8	0.98
C	18.0*	1.80	0.5	1.55
D	19.0	0.98	1.1	0.80

* Brittle films & hence lower values.

3.1 Physico- mechanical properties of the coating systems

Physical properties of the coating systems like drying time, coverage and film thickness are determined as per ASTM D 1005-13 and D 1640-03 test methods. It can be noted that the panels were coated with a thickness as per standards so as the dry film thickness of primer being 50±10 µm, middle coat 100±10 µmand top coats was 50±10 µm with total being 200±10 µm for three coat systems. The touch dry time for different coatings varied from 8-10 hours, while hard dry time varied between 3-7 days. The covering capacity of the coatings varies from 4.5-7.0 m^2/l.

Water vapour transmission of coating systems as per ASTM D 1653-03 are in the range 0.6-1.8 as compared to cardanol modified epoxy primer based coating systems which have lower values in the range of 0.5-1.1 mg/cm^2-24 h. (Mean of ten samples with less than 2% standard deviation in all cases).

Table 3: Properties after application

Coating Systems	Bond* Strength (N/mm^2)		Adhesion** & Flexibility (3.18 mm dia Mandrel)	Dry & Wet Abrasion* (1000 Strokes)	Scratch** Hardness (1500 g weight)
	Mean	SD			
A	3.2	0.99	Pass	Pass	Pass
B	3.7	0.91	Pass	Pass	Pass
C	5.6	0.70	Pass	Pass	Pass
D	6.0	0.68	Pass	Pass	Pass

*Coated concrete panels were used.
** Coated steel panels were used.

3.2 Properties of the coating systems after application on the substrate

For adhesion and flexibility test, the coated steel panels were subjected to bending using a cylindrical Mandrel bending tester and passed the test for 3.2 mm dia Mandrel. The coating films showed no signs of damage, detachment or cracking after the test indicating good flexibility and about 28% elongation as per ASTM D 522-08. However following the procedure of ASTM D 2370-02 using two ton Shimadzu Universal Testing Machine (UTM), it was found that the tensile strength decreased for cardanol modified epoxy primer based coating systems but is still significant; reason being thick and the brittle nature of free films making them very difficult to mount on UTM for carrying out tensile test (Table 2 & 3). Tensile strengths shown in Table 2 were mean of ten sampleswith less than 2% standard deviation in all cases.

All the coated steel panels passed the scratch hardness test when tested using a weight of 1500 g and dry and wet abrasion cycles up to 1000 strokes on concrete panels showing good abrasion resistance. Also water vapour transmission decreased by 20% for cardanol modified epoxy primer based coating systems indicating better barrier properties.

Bond strength of the cardanol modified epoxy primer based coating systems are in the range of 5.6-6.0 N/mm^2 as compared to corresponding epoxy which is in the range 3.2-3.7 N/mm^2, i.e. the bond strength for the modified resin is 85% higher indicating appreciable increase in bond strength for the cardanol modified epoxy primer based coating systems. Bond strengths recorded were mean of ten sampleswith less than 1% standard deviation.

Table 4: Chemical resistance tests (400 days immersion results)

Coating SystemsImmersion medium	A	B	C	D
Water	10	10	10	8M
Sodium chloride (5%) solution	8F	10	10	10
Saturated urea solution	10	10	10	10
Saturated diammonium phosphate solution	8F	10	10	10
Saturated NPK solution	10	10	10	10
Hydrochloric acid (20%) *	8F	10	10	8F
Potassium hydroxide (30%) solution	10	10	10	10

* Panels started to disintegrate & hence removed after 300 d.

3.3 Chemical resistance tests

Coating systems A, B and C showed no sign of coating disintegration even after 400 days immersion in water while system D showed only small blisters throughout the panels. Similarly when the coated panels were immersed in a 5% sodium chloride solution for 400 days, panels coated with system B, C and D were not affected while system A showed signs of mild swelling due to debonding of coating. In 20% hydrochloric acid solution immersion tests, few small blisters were seen in coating system A and D but all the panels started to disintegrate badly after 300 days and hence were removed and test was stopped.

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In saturated urea and NPK solution immersion tests, all the panels remain unaffected after 400 days. In saturated diammonium phosphate solution immersion tests, panels coated with system B, C and D were not affected while system A showed few small blisters only. Similarly in 30% potassium hydroxide solution immersion test, all the coated panels remain unaffected after 400 days. On the basis of the above results, it can be inferred that the performance of the cardanol modified epoxy primer based coating systems is far better than the corresponding virgin epoxy based coating systems.

Table 5: Panels after 400 days immersion

Coating Systems	A	B	C	D
Control (Without immersion)				
Water	No Change	No Change	No Change	
Sodium chloride (5%) solution		No Change	No Change	No Change
Saturated urea solution	No Change	No Change	No Change	No Change
Saturated diammonium phosphate solution		No Change	No Change	No Change
Saturated NPK solution	No Change	No Change	No Change	No Change

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Hydrochloric acid (20%) *		No Change	No Change	
Potassium hydroxide (30%) solution	No Change	No Change	No Change	No Change
Humidity Cabinet		No Change	No Change	No Change

* Panels started to disintegrate & hence removed after 300 d.

Table 6: Humidity cabinet test (Temperature: 45 ± 5^{0}C, Humidity: 100%, Exposure time: 400 days)

Coating Systems	Observations
A	8F
B	10
C	10
D	10

3.4 Humidity cabinet test

In this test, panels showed no sign of failure up to 180 days of exposure. After 400 days, panels coated with system A showed small blisters throughout the panels. Hence, it can be concluded that the anticorrosive behaviour of the cardanol modified epoxy primer based coating systems is superior to corresponding virgin epoxy based coating systems.

Conclusions

The results of the present study clearly showed that the cardanol modified epoxy primer based coating systems when applied on concrete were found to be better with respect to resistance to salt, alkali, acids and fertilizers as well as adhesion, hardness, bending and flexibility. This means that the use of cardanol modified epoxy primer have enhanced the performance of the coating system. Hence it can be concluded that cardanol modified epoxy primer based coating systems can be used in different weather conditions and under aggressive conditions; and such coating systems could be an excellent choice in the future for the coating industry.

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