CHEMICAL RESISTANT ELASTOMER-MODIFIED EPOXY SILOXANE SURFACER

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Abstract: A new, elastomer-modified epoxy siloxane surfacer offers advantages for pulp and paper plants, chemical process industries, secondary containment applications and other industries where outstanding chemical resistance is required. The chemistry, application characteristic and performances properties of the new surfacer are reviewed and compared to traditional materials used in these applications.

Introduction

With state and government regulation becoming more stringent, the coating industry is looking for alternate technologies to improve or upgrade coating formulation. Epoxy coatings have been used for industrial and marine applications to protect steels and concrete from corrosive and chemical environments, because they provide the excellent corrosion protection, excellent adhesion to various substrates, high mechanical strength and the good chemical resistance properties.

Concrete is a common construction material used in chemical environments. However concrete is subject to cracking and permeable to liquids and gases. Chemical resistant coatings or linings are needed to protect concrete structures from chemical and corrosive deterioration. In order to protect from a wide range of chemicals, epoxy coatings are the primary choice for the protection of concrete floors and walls in chemical processing plants due to a broad chemical resistance and excellent adhesion to substrates. The coatings based on aromatic amine curing agents have been used in aggressive chemical environments when the coatings require the broad range of chemical resistance particularly to organic acids and strong solvents. However the health effects of Methylene Dianiline (MDA), and most aromatic amines, have limited the use of MDA based epoxy coatings.

Advancement of hybrid siloxane epoxy coatings has led to better chemical resistance than MDA based epoxy coatings. Epoxy coatings have excellent alkali resistance and good solvent resistance but generally they have weak resistance to mineral and organic acids. On the other hand, siloxane coatings have excellent acids and solvent resistance, but poor alkali resistance.

The hybrid of epoxy and siloxane offers the advantages of both polymers giving resistance to acids, bases and solvents. A significant problem of this hybrid epoxy siloxane coating is the development of severe stress of film when the coating continues to cure after application. The coating develops cracks and also the disbondment from concrete substrate due to the severe deformation of the film.

In this work, the elastomer modified epoxy resin was incorporated into the hybrid of siloxane epoxy coating to minimize the stress of the film. The effects of elastomer modified epoxy resin and amine curing agents in the hybrid coating were studied by testing chemical resistance, compressive strength and outdoor exposure.

Epoxy polysiloxane hybrid coating

Epoxy polysiloxane hybrid coating is the interpenetrating network of epoxy and polysiloxane network. When this interpenetrating network forms, the hybrid coating is resistant to a wide variety of solvents, organic acid and even some concentrated mineral acids.

Epoxy network forms by reacting epoxy novolac resin with amine or aminosilane. The phenolic epoxy coatings are known as a good corrosion resistant, a good adhesion to substrate and a good chemical resistance. Epoxy polymer offers excellent base and solvent resistance however poor UV resistance and also embrittlement on aging.

Polysiloxane consists of silicone-oxygen networks. This silicone –oxygen molecular structure is much stronger than carbon-carbon chain of typical organic coatings. This stable bond strength gives resistant properties to chemicals, high temperature, and weathering. However this type of the coating has tendency to develop severe shrinkage and stress of the film due to the condensation reaction.

Both epoxy and polysiloxane network structures are tendency to develop stress of the film with the aging process. The epoxy polysiloxane hybrid coating is no exception to the stress and shrinkage of films with aging process. The current hybrid coating is prone to develop severe cracking of the film or disbondment from the concrete.

Experimental

Composition

In these experiments, 10 different samples, including control, were prepared in the lab. The control is the current polysiloxane modified epoxy coating. The composition of siloxane modified epoxy coating consists of three components: resin, cure and powder. The resin component consists of epoxy resin, alkoxy functional silicone intermediate, color pigments, additives, and solvents. The cure component is an amino functional silicone compound. The powder component is the blend of different grades of silica.

System 1 is the epoxy surfacer without aminosilane. System 2, 3 and 4 is elastomer modified epoxy resin components. Three different resin component compositions were prepared to get the maximum amount of elastomer content. System 2 contains carboxyl terminated butadiene-acrylonitrile (CTBN) modified epoxy resin by 5% of total weight. System 3 contains 10% and System 4 contains 15% of total weight. If higher than the 15 % of elastomer modified epoxy resin was added in the resin component, the self-leveling property of the coating was compromised.

After achieving the maximum amount of elastomer modified epoxy resin composition, cure components were evaluated to improve the flexibility without compromising chemical resistance properties. Four different cure compositions were evaluated to improve flexibility without compromising the chemical resistance properties. System 5 is modified with difunctional aminosilane. System 6, 7 and 8 are the blend of aminosilane with two different aliphatic amines. Table 1 summarizes lists of experimental coating composition.

Chemical resistance test

1-inch diameter and 1-inch width of cylinders of material were cured at room temperature for 14 days, then for 7days it was immersed completely into the concentrated sulfuric acid, concentrated hydrochloric acid, methanol and 50% ammonium hydroxide. After drying at room temperature for 7 days, each cylinder was evaluated for the integrity of the coating. Each cylinder was rated as pass or fail depending on the integrity of the coating. If the cylinder retains about 95 % of original shape, the coating is rated as pass and if the cylinder loses more than 5 % of original shape, the coating is rated as failure.

Compressive strength

Compressive strengths of the cylinders immersed into above chemicals were determined in accordance with ASTM C589-96.

Thermo cycle test

The coatings were applied on 3 inch x 6 inch x 0.5 inch concrete block by pouring the same mount of each sample and self-leveled on the surface. The amount of each sample was calculated from the theoretical coverage to get 60 mils. The film was cured at an ambient temperature for 3 days and 4 days at 160 F convection oven. 3 days at ambient temperature and 4 days at 160 F oven were cycled until the film showed any sign of cracking.

Mechanical properties

Mechanical properties of samples were prepared by casting the samples in molds. The castings were cured for 14 days before testing. Compressive strength was measured according to ASTM C579. Tensile strength was measured according to ASTM C307. Flexural strength and Elasticity were measured d according to ASTM C580.

Field testing

Both control and system 8 were applied on 6 feet x 6 feet concrete block by pouring on the concrete and spreading over a with gauge rake around 60 mils and 120 mils. The bottom half of the concrete block applied around 60 mils and top half is 120 mils. The metal pin roller was used to eliminate bubbles from inside of the film.

The coated concrete block was placed on a horizontal surface to expose to the southern California weather. After a year, this concrete block was inspected for cracking and lifting.

Results and Discussion

Chemical resistance

Table 2 summarizes the results of chemical immersion in concentrated sulfuric acid, concentrated hydrochloric acid, methanol and 50% ammonium solution. All coating systems, excluding system 1, passed in all four chemical immersion tests. The test results suggest that acid resistance of the coating will affect when the siloxane linkage is reduced from system 1.

Compressive strength

Table 3 summarizes the results of compressive strength of the coatings after exposed to above chemicals. The amount of elastomer modified epoxy resin in the coating will affect the compressive strength as shown for coating 2, 3, and 4.

There is a drastic reduction of compressive strength when 50% of trifunctional silane was replaced with difunctional silane as shown for system 5.

System 6, 7 and 8 show the effects of low molecular weight aliphatic amine modification. Regarding 50% or 75% trifunctional amino silane replacement with aliphatic amines by stochiometric amount, system 6, 7 and 8 show very similar compressive strength.

Table 5 summarizes the results of compressive strength of control and system 8 after exposed to 36 different chemicals.

Thermo cycle test

Table 4 summarizes effects of epoxy and siloxane networks in the thermo cycle tests. The control had no flexibility when cured with amino silane. The System 1 surfacer showed excellent flexibility when cured with low molecular weight aliphatic amine. This indicates that the reduction of siloxane network improves the flexibility of the coating, however this will compromise the acid resistance.

The coating will improve flexibility when modified with elastomer modified epoxy resin as shown in 2, 3, and 4 systems. This will also compromise the compressive strength of coatings when the amount of elastomer modified epoxy resin increases from 5% to 15%.

System 5 shows the interesting result in terms of crack resistance properties. When modified with 50 % of amino silane with difunctional alkoxy amino silane, the coating was expected to perform better flexibility than the system 4 due to the lower cross-link density of siloxane network. On the contrary, the coating not only compromises the flexibility, but also loses the compressive strength of the coating.

When modified with a low molecular weight aliphatic amine, system 6 exhibits the improvement of compressive strength as well as some improvement of flexibility. System 7 shows drastic improvement of flexibility when the amino trialkoxy silane was reduced to 25 % of original amount and replaced with low molecular weight aliphatic amine. The other option is that even better results can be obtained when 50 % of amino trialkoxy silane was replaced with lower functional aliphatic amine as shown in system 8.

Mechanical properties

Table 6 compares mechanical properties of three different type coatings including a solventless epoxy surfacer(System 1). Compressive strength of System 8 is lower than control due to the elastomer epoxy resin modification, but system.8 shows better compressive strength than a conventional epoxy surfacer. System 8 did not compromise the tensile strength property compared to control. This data indicates the flexibility improvement of a elastomer modified epoxy siloxane coating compared to control and a solventless epoxy coating.

Field testing

Picture A clearly shows the improvement of system 8 over control after a year exposed to southern California weather. The control system shows extensive cracking at 120 mils thickness and disbondment from concrete due to the shrinkage. The control also shows some cracking even at 60 mils thickness.

System 8 shows no cracking at 120 mils as well as 60 mils. The coating shows very slight lifting at 120 mils.

Conclusion

A new elastomer modified epoxy siloxane coating was developed to improve the flexibility of coatings without compromising the chemical resistance properties. This elastomer modified silicone epoxy coating demonstrates the improvement of flexibility in accelerated temperature cycle tests, as well as actual weathering exposure test. The elastomer modified epoxy siloxane coating exhibits very similar chemical resistance properties as the unmodified epoxy siloxane coating. The composition is US patent pending.

Table 1 Composition of epoxy siloxane surfacer

Component	Std	1	2	3	4	5	6	7	8
Resin Std	100	100							
Resin A			100						
Resin B				100					
Resin C					100	100	100	100	100
Cure Std	25		25	25	25	12.5	12.5	6.25	12.5
Amine A		10.6					3.5	5.32	
Amine B									14.9
Silane A						12.5			
Powder	225	225	225	225	225	225	225	225	225

Table 2 Chemical immersion resistance

Chemical	Std	1	2	3	4	5	6	7	8
H_2SO_4	Pass	Fail	Pass	Pass	Pass	Pass	Pass	Pass	Pass
HCl	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Methanol	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
NH_3OH	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass

Table 3 Compressive strength after immersed in chemicals

C.S. (psi)	Std	1	2	3	4	5	6	8	9
Control	14,000	11,890	13,070	12,130	10,200	7,070	10,170	10,170	10,800
H_2SO_4	15,420	--	12,650	12,040	10,300	7,060	10,660	10,830	11,200
HCl	15,570	11,610	12,840	12,270	10,300	5,600	10,630	9,370	11,200
Methanol	15,070	11,650	12,880	12,400	10,100	6,970	10,740	10,700	11,140
NH_3OH	14,960	11,210	12,910	12,240	10,300	7,200	10,800	10,600	11,120

Table 4 Thermo cycle tests between 160F and ambient temperature

Cycle	Std	1	2	3	4	5	6	7	8
1	Fail	Pass	Fail	Pass	Pass	Pass	Pass	Pass	Pass
2		Pass		Pass	Pass	Fail	Pass	Pass	Pass
3		Pass		Fail	Pass		Fail	Pass	Pass
4		Pass			Fail			Pass	Pass
5		Pass						Pass	Pass

Table 5 Compressive strength after immersed in various chemicals

Chemical/CS (psi)	STD	System 8
Control	12,785	10,875
Acetic acid, 70%	12,340	10,020
Acetic acid, conc.	13,270	10,555
Acetone	13,055	10,855
Alum, 15%	12,170	10,710
$(NH_4)OH$, conc.	12,870	10,875
Acetylaldehyde	13,020	10,890
Ethanolamine	12,935	11,050
Brake Fluid	12,825	11,005
Citric acid, 25%	12,815	10,620
DMSO	12,835	10,745
Ethylether	12,595	10,715
Ferric chloride, sat.	12,650	10,680
Formaldehyde	12,475	10,675
Tall oil fatty acid	12,810	10,695
Gasoline	12,545	10,545
Gasohol	12,780	10,565
Hydrochloric acid, conc.	12,890	10,610
H_2O_2, 30%	12,540	10,850
Lime, sat.	12,360	10,365
Lye, NaOH, 25%	12,635	10,775
Methylpyrollidone	12,770	10,955
MTBE	12,810	10,875
Methanol	13,225	10,735
Nitric acid, 50%	12,180	10,630
Nitric acid, 25%	12,060	10,350
Potassium silicate	12,375	10,575
Petroleum ether	12,850	10,810
Skydrol	12,855	10,530
NaOH, 50%	12,515	10,735
Na hypochlorite, 5%	12,680	10,745
Styrene	12,360	10,905
Sulfuric acid, 98%	11,355	10,835
Tannic acid, sat.	12,545	10,605
Triethylamine	12,345	11,025
Vinyl acetate	12,140	11,165
Xylene	12,155	10,715

Table 6 Mechanical properties of std, system 1 and system 8

System	STD	System 1	System 8
Compressive strength (psi)	12, 800	8,250	10,875
Tensile strength (psi)	3,500	2,110	3,520
Flexural strength (psi)	5,200	3,930	6,980
Modulus of elasticity (x10^5)	11.0	8.0	6.7

Picture A One year field testing of std and system 8 in southern California weather