The Bombay Technologist

ARTICLE

Novel Use of Waste Fruit-Seeds for Enhancing Anti-Corrosive Performance in Epoxy System

Aparna Agrawal[a,*], Shweta Amrutkar[a]

[a] Department of Polymer and Surface Engineering, Institute of Chemical Technology, Matunga, Mumbai, India

(**Corresponding author**: Aparna Agrawal (aparnaagrawal73@gmail.com)

Epoxy coating system with enhanced corrosion resistance was prepared. The epoxy resin was used as a base resin and polyamine was used as its hardener. The ashes of Karwand (*Carissa carandas*) seeds and Pumpkin (*Cucurbita pepo*) seeds were used to increase the anticorrosive performance of the coating. These ashes were prepared by the method of calcination in a muffle furnace by heating at 800°C for 2 hours. Surface treatment was done to introduce amine functionality to the ash which was confirmed by FTIR analysis. The surface treated ash was then added into the epoxy-amine system at 1%, 3%, 5% (w/w) of the total epoxy-amine coating system. The coating was then applied to mild steel panels by the method of brush coating and was tested for mechanical properties and chemical resistance. The coating was also subjected to the salt spray test for analysis of anticorrosive performance. It was observed that the anticorrosive performance of the coating increases as the concentration of ash in the epoxy-amine system increases. This is due to ash constituents such as ZnO, MgO, Fe_2O_3, CuO etc. which work either by barrier mechanism or passivation mechanism and prevent corrosion. The scratch resistance and the hardness also increased with an increase in the concentration of ash. This is because the ash in the epoxy-amine system acts as filler in the coating. Also, surface treatment introduces amine functionality which reacts with the epoxy group and tends to increase hardness. Thus, presence of inorganic elements in the ash and surface treatment are prime factors responsible for enhancing corrosion resistance of the system.

1. Introduction

Epoxy coatings contribute substantially to the anticorrosive coating industry. Epoxy is a thermosetting polymer. It has various properties that make it an excellent choice for a coating material. These properties include good bonding with different substrate, resistance to electric conduction, excellent resistance to chemical attack and ease of processing. It also possesses some other properties which make it an excellent choice for an anticorrosive material for coatings. These properties include superior strength, low shrinkage, good dimensional stability and long term corrosion resistance [1, 2]. But the problems faced while using this thermosetting resin are that it is brittle and shows great affinity towards water. To overcome these problems, researches have been carried out and polysiloxanes have been established as widely accepted materials to blend with epoxy owing to their numerous properties which provide toughness to the epoxy resin. In this study we have used ash modified by N-(2-amino ethyl)-3 aminopropyltrimethoxysilane to blend with epoxy [5].

In the past 20 years, a lot of researches have been reported that have tried to enhance the properties of the epoxy paint. A lot of these studies have used the approach of adding different inorganic particles like silica which becomes expensive. [6] Thus, it would be useful to find inexpensive sources of such materials like seeds of Pumpkin and Karwand used in this research. The ash of Pumpkin seeds and Karwand seeds when added can impart anti-corrosive properties to the coating owing to their mineral composition [3, 4]. The ash can be synthesized as filler material by calcination process and can be dispersed in the epoxy coating system to synthesize the coating as done in the study on rice husk ash by Azadi, Mahboobeh, Mohammad Ebrahim Bahrololoom, and Fatemeh Heidari [7].

2. Experimental

2.1 Materials

Seeds of Pumpkin and Karwand were obtained from the local market. Epoxy resin was used as a base resin and polyamine was used as its hardener in the ratio of 10:3 by weight. The N-(2-amino ethyl)-3 aminopropyltrimethoxysilane was used for surface treatment and is obtained from Wacker. The solvents xylene, n-butanol, toluene, and acetone were obtained from S.D. Fine Chemicals Pvt. Ltd.

2.2. Synthesis of ash from seeds

Seeds were properly washed and then dried in an oven maintained at 100°C for 2 hours to remove the moisture content. These seeds were then crushed in a mortar pestle. Crushed samples were put in a nickel crucible by weighing and kept in an oven at 800°C for 2 hours. Calcination was carried out in presence of oxygen. After calcination, the ash was allowed to cool to room temperature and then ash content was calculated by weighing the ash obtained. The composition of ash obtained is given in the tables below:

Ingredients	Composition (mg/100g)
K	630
Fe	10.73
Mg	90
Ca	79
P	950
Cu	1.49
Zn	8.01

Table 1: Mineral composition of Pumpkin seed ash (mg/100g dry basis) [8]

Ingredients	Composition (mg/100g)
Fe	150
Ca	115
P	66

Table 2: Mineral Composition of Karwand seed ash [9]

2.3. Surface treatment of ash

Surface treatment was carried out with aminosilane, namely N-(2-aminoethyl)-3-aminopropyltrimethoxysilane. A weighed amount of ash was added into a round bottom flask. Toluene was added as solvent media for the reaction. Ash and toluene were added in the ration of 1:5 (w/w). This was stirred for an hour for proper dispersion of ash in the media. Then aminosilane was added to the reaction mixture 10% (w/w) of the ash sample. The reaction mixture was stirred with a magnetic stirrer and the temperature of the reaction was maintained at 120°C for 24 hours. After completion of silane treatment, residue was obtained. It was then filtered and dried to obtain the final product. This treatment introduces amine functionality to the ash. This amine functionality then reacts with the epoxy group of the resin. This chemical bonding leads to increased strength for the coating.

2.4. Synthesis of Coating

Mild steel panels were used for coating. Panels were cleaned and wiped before application of the coating to remove oil, dust etc. Then panels were surface treated by sanding process to increase adhesion to the substrate. Again, panels were cleaned with acetone as a solvent. The coating was synthesized using epoxy resin as base resin and polyamine as its hardener. They were added in the coating system in the ratio of 10:3 (w/w). A mixture of xylene and n-butanol was used as solvent media for the coating system. Here, xylene acts as a diluent and n-butanol as a true solvent. The proportion of xylene and n-butanol added was 70:30 (v/v) respectively. The plain epoxy system was made by adding required quantity of prepared solvent mixture in the epoxy resin to attain proper viscosity for application and then the hardener was added in the system for curing. The plain epoxy system was applied on the panel to compare with the ash systems. The ash systems were prepared by adding ash into the epoxy resin by varying its concentration as 1%, 3% & 5% (w/w). Then it was stirred for an hour for proper dispersion of ash into epoxy resin. After stirring, polyamine as its hardener and solvent mixture were added. Then it was applied to the panels. These panels were kept for curing at room temperature

2.5.Characterization

The silane treated ash samples were characterized by ATR-FTIR. The coated panels were characterized for mechanical properties. Firstly, its dry film thickness (DFT) was measured using digital thickness gauge instrument and adhesion test was performed by cross hatch adhesion method. It showed 0% loss of adhesion i.e. 5B. The scratch hardness was tested by varying the load. In impact resistance test, the load of 1.36 kg was allowed to fall on coated panels from the maximum height of 60 cm. The pencil hardness was checked for pencil range of 6B to 6H. 6B represents lower hardness value and 6H represents higher hardness value. The chemical resistance test is performed by spot test method for 10% HCl and 10% NaOH solution to check its acid and alkali resistance. The solvent resistance was evaluated by rub method. Xylene and MEK were used and rubbed 200 times on coated systems. The anticorrosive properties are evaluated by salt spray test according to ASTM 117.5% NaCl solution was used for spraying.

3. Result and Discussion

3.1 FTIR analysis

FTIR analysis of Karwand seed ash and Pumpkin seed ash has been shown in the Fig. 1 and Fig.2 respectively. The KBr analysis technique was used for noise elimination. In both the figures, the top image shows the FTIR result of plane ash and the bottom image represents the FTIR of the silane treated seed ash. It is observed from the FTIR analysis that the peak appeared at 1013 cm^{-1} and 1128 cm^{-1} corresponds to the O-Si-O bond. The Mg-O peak is observed at 867 cm^{-1} and 883 cm^{-1}. The Ca-O bond is observed at 700 cm^{-1} and 703 cm^{-1}. Along with all the aforementioned peaks, the band appearing at 2918 cm^{-1} and 3237 cm^{-1} corresponds to the amine group from the silane. Hence, it confirms that the silane treatment was successful.

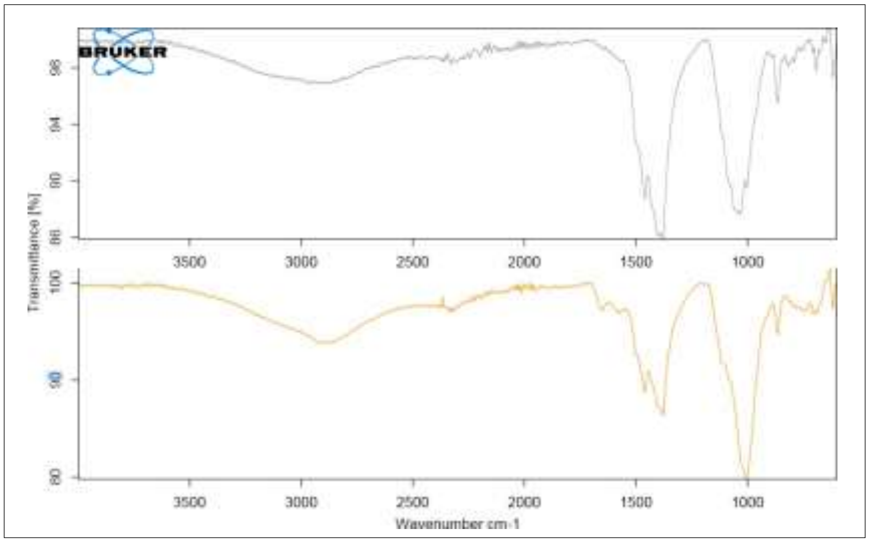


Fig.1 FTIR analysis of Karwand seed ash (Plain and silane treated)

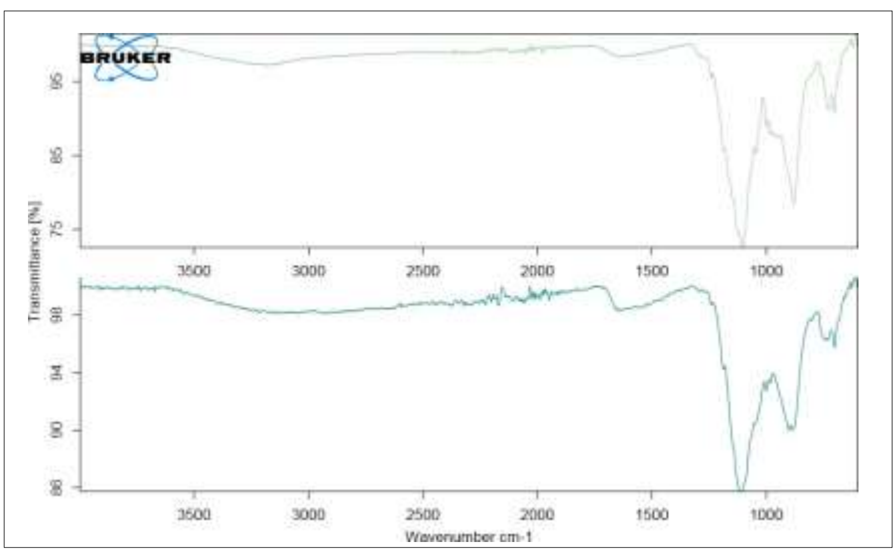


Fig.2 FTIR analysis of Pumpkin seed ash (plain and silane treated)

3.2 Mechanical properties

The mechanical properties of the coating system are given below in the table.

Table 3: Results for mechanical analysis

	Plain epoxy	1% Pumpkin	3% Pumpkin	5% Pumpkin	1% Karwand	3% Karwand	5% Karwand
DFT (µm)	120±5	120±5	120±5	120±5	120±5	120±5	120±5
Gloss	107.5	96.92	87.07	83.05	94.56	86.67	82.34
Cross hatch adhesion	5B	5B	5B	5B	5B	5B	5B
Pencil Hardness	2H	3H	3H	4H	3H	3H	4H
Scratch Hardness (kg)	4.1	4.4	4.6	4.7	4.5	4.7	4.8
Impact Resistance (kg-cm)	F.I B.I	F.I B.I	F.I B.I	F.I B.I	F.I B.I	F.I B.I	F.I B.I
	81.6 68	81.6 81.6	81.6 81.6	81.6 81.6	81.6 81.6	81.6 81.6	81.6 81.6
Flexibility (mm)	0mm	0mm	0mm	0mm	0mm	0mm	0mm

As seen from the table above, the mechanical properties of the coating were found to be very good. This is due to the excellent inherent mechanical properties of the epoxy-polyamine based system. The system has excellent adhesion to the metal surface, good dimensional stability, and development of a three-dimensional network after curing, which tends to develop good mechanical properties. The adhesion of the plain epoxy coating and all the other coatings was checked using the cross hatch adhesion method in which a X-shaped cut is made on the coating.

The adhesion of the plain epoxy coating was found to be 5B and it was observed that the addition of aforementioned ashes do not affect the adhesion of the coating negatively. The pencil hardness of the plain epoxy coating system was found to be 2H and a gradual increase in the hardness was observed with the increasing percentage of the ash in the coating. This trend is seen because the ash increases the strength of the film acting as a filler. The performance is further enhanced due to the chemical reaction that occurs between the amine functionality introduced by the surface treatment of the ash and the epoxy group of the resin. This also explains the increasing scratch resistance with increasing amount of ash incorporated in the coating. The plain epoxy coating has the scratch resistance value of 4.1 Kg which goes on increasing with the ash content in the coating. All the coatings have passed the flexibility test successfully. There is no crack formation (0 mm) after flexibility test. The forward impact resistance of the plain epoxy coating was found to be the same as that of all the other coatings wherein ash was incorporated. In the case of backward impact, the impact resistance of plain epoxy coating was found to be slightly lower than the filled systems. The reason for the same being that the added material acts as a filler increases the strength and hence the load bearing capacity of the film.

3.3 Optical Properties

In optical properties, the gloss of the coating was measured and the results for the same were represented in Table 4. It is observed that the highest gloss is obtained for the plain epoxy coating. The addition of ash to the system leads to decrease in the gloss of the coating. This is explained as the ash acting as a filler may introduce slight surface irregularities depending on shape and size.

Table 4: Gloss of the coating systems

Batch Code	Value of Gloss
Plain Epoxy	107.5
1% Pumpkin	96.92
3% Pumpkin	87.07
5% Pumpkin	83.05
1% Karwand	94.56
3% Karwand	86.67
5% Karwand	82.34

3.4 Chemical Resistance

The result for chemical testing is shown in the Table 5. 10% acid (HCl) and 10% alkali (NaOH) solution were used for testing. Solvents such as xylene, MEK were used for the solvent resistance test. From the table, it is observed that all the coating systems have excellent acid, alkali and solvent resistances. After curing with amine hardener it develops three-dimensional cross-linked structure. This resists the penetration of corrosive species or moisture into the coating system. Hence, it shows good resistance towards chemicals such as acid, alkali, and solvents.

Table 5: Chemical resistance of the coating systems

	Plain epoxy system	Jackfruit seed ash system			Karwand seed ash system			Pumpkin seed ash system		
		1%	3%	5%	1%	3%	5%	1%	3%	5%
Acid	A	A	A	A	A	A	A	A	A	A
Alkali	A	A	A	A	A	A	A	A	A	A
Solvent	A	A	A	A	A	A	A	A	A	A

A = Film remain unaffected, B = Loss of gloss, C= Softening of Film, D = Blister formation E = loss of adhesion

3.5 Anticorrosive properties

3.5.1 Salt Spray

The coatings were subjected to the salt spray test for the evaluation of anti-corrosive properties. In this test, the extent of corrosiveness is measured by the length of crack propagated when the coated panels are kept in a salt solution. The panels were tested after 5 weeks of exposure. The photographic references for the salt spray test are shown in figure 3 and figure 4 below. The result for the same is represented in Table 6.

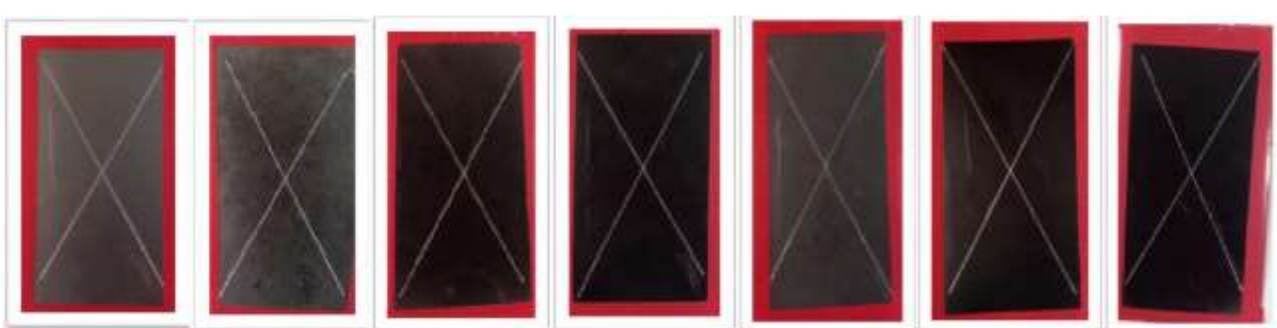
Table 6: Result of the coating systems after salt spray test

Batch Code	Corrosion propogation length
Plain epoxy coating	1.9 mm
1% Pumpkin	0.9 mm
3% Pumpkin	0.7 mm
5% Pumpkin	0.3 mm
1% Karwand	0.8 mm
3% Karwand	0.6 mm
5% Karwand	0.2 mm

It is seen from the salt spray analysis that the ash-incorporated coatings show better anticorrosive performance as compared to plain epoxy-polyamine based system. With increasing amount of ash in the coating the corrosion resistance increases progressively as compared to the plain epoxy system.

4. Conclusion

The Pumpkin seed ash and Karwand seed ash was synthesized. After surface treatment of the ash, it was introduced into the epoxy-amine system. Due to the introduction of amine functionality, it reacts with the epoxy group and gets chemically bound in the system. The binder is enough to wet the entire ash present in the coating. Hence, it shows good adhesion to the substrate. Also, good adhesion to the substrate is responsible for good hardness value and scratch resistance properties. The chemically bonded ash present in the coating acts as the filler which also results in increased hardness of the coating. These properties get enhanced as the concentration of ash goes on increasing. The ash contains MgO, Fe_2O_3, ZnO, and CaO which are responsible for increasing the anticorrosive performance of the coating. It acts as a barrier for various corrosive species.



Plain epoxy 1%Pumpkin 3%Pumpkin 5%Pumpkin 1%Karwand 3% Karwand 5%Karwand

Fig.3 Panels before salt spray test

The Bombay Technologist

ARTICLE

Fig. 4 Panels after exposure to salt spray test (after 1500 hrs)

5. References

1) S. Peng, W. Zhao, H. Li, Z. Zeng, Q. Xue, X. Wu, *Appl. Surf. Sci.* **2013**, *276*, 284.
2) E. Armelin, R. Pla, F. Liesa, X. Ramis, J. I. Iribarren, C. Alemán, *Corros. Sci.* **2008**, *50*, 721.
3) M. Arif, M. Kamal, T. Jawaid, M. Khalid, K. S. Saini, A. Kumar, M. Ahmad, *AJBPS*. **2016**, *6*, 14.
4) A. N. Olszańska, A. Kita, A. Biesiada, A. S. Łętowska, A. Z. Kucharska, *Food Chem*. **2013**, *139*, 155.
5) M. Y. Shona, H. S. Kwon, *Corros. Sci.* **2009**, *51*, 650.
6) E. W. Brooman, *Metal Finishing* **2002**, *100*, 42.
7) M. Azadi, M. E. Bahrololoom, F. Heidari, *J. Coat. Technol. Res*. **2011**, *8*, 117.