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Enhancement of anticorrosive performance of epoxy coating by pistachio shell ash

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ABSTRACT

Epoxy-amine is one of the popular systems for anticorrosive application. Here, anticorrosive performance was further enhanced by incorporation of pistachio shell ash. Calcination process was used for ash synthesis. Calcination was carried out in limited oxygen supply in the muffle furnace and the temperature was maintained at 800ºC for the duration of 2 hours. Surface of synthesized ash was coated with amino-silane to introduce amine group on its surface. The performance of ash in coating system was studied by varying its concentration at 1%, 3% and 5% (w/w) of total binder system. The confirmation of amino group on the surface of ash was done by FTIR and XRD analysis. Ash acts as filler which increases the hardness of the coating. Due to presence of inorganic elements such as Fe_2O_3 (~35%), SiO_2 (~8%), MgO (~3-4%), Al_2O_3 (~1.5%) in the ash increases the anticorrosive performance of the coating. Due to surface treatment the ash becomes a part of coating backbone. Hence inorganic elements and surface treatment these are the two prime factors to enhance the anticorrosive performance.

Keywords: pistachio shell; anticorrosive coating; epoxy; surface treatment

INTRODUCTION

Recycling is an integral part of waste utilization and waste management is becoming an interesting field for study. The biomass waste is one of the type of waste seen in the environment [1, 2]. Shells of different fruits nuts come under the category of biomass waste shells. Shells of different nuts is readily available and renewable source for wide range of application in the coating field [3, 4]. Till now, groundnut shell ash, rice husk shell ash used in the coating is reported for enhancement in the coating properties. In this study we used pistachio shell ash to enhance the performance of the coating. The pistachio annual production is 916,921 metric tons. Pistachio shell contains metal oxide such as P_2O_5, Fe_2O_3, SiO_2, Al_2O_3 etc. These metal oxides are used in the coating to improve the performance properties.

Among the various technologies, the organic polymeric coating is a general and economic approach to enhance corrosion resistance of metals [5]. A large part of the anticorrosive coatings industry belongs to epoxy coatings. Being a class of thermosetting polymers, epoxy has been mostly used as a protective coating material to protect the metal from corrosion because of its excellent chemical resistance, good adhesion to the metal surface, good electrical insulating properties and ease of processing [6]. Moreover, the epoxy coating is used as an anticorrosion coating cause of its superior strength, low shrinkage, better bonding with different substrate, good dimensional stability and long term corrosion and chemical resistance [7, 8].

Here in this study, the ash of pistachio was made by calcination process in absence of oxygen. The ash was treated with aminosilane to introduce amine functionality. The treated ash was added at 1%, 3% and 5% concentration in epoxy-amine coating system.

EXPERIMENTAL PROCEDURE

MATERIALS

The pistachio shells are obtained from local market. Solvents like xylene, n-butanol and acetone are obtained from S.D. Fine India Pvt. Ltd. The silane precursor N-(2-amino ethyl)-3-aminopropyltrimethoxysilane is obtained from Wacker. Epoxy is used as a base resin and amine as its hardener.

SYNTHESIS OF PISTACHIO SHELL ASH

Prior to calcination, the pistachio shells were immersed in water for an hour and then were properly washed with water which helped to remove any dirt, dust as well as salt attached to it since the pistachio shell is generally added with the salt to enhance its life span. The washed shells were dried in an oven at 80ºC for four hours. The dried shells were crushed in the mixer and fine powder was made of the same. The powder was first weighed in a nickel crucible and was kept covered with another nickel crucible during calcination to carry out calcination in limited supply of oxygen. The calcination was carried at 800ºC for two hours in the muffle furnace. After two hours the samples were allowed to cool at room temperature.

SILANE TREATMENT OF THE ASH

The ash obtained was silane treated with aminosilane namely N-(2-amino ethyl)-3 aminopropyltrimethoxysilane. This treatment introduces amine functionality to the ash. Weighed amount of ash was added into the round bottom flask with toluene added as solvent media for the reaction. Ash and toluene were added in the ratio of 1:5 by weight. This mixture was stirred for an hour for proper dispersion of ash in the media. Then aminosilane was added to the reaction mixture at 10% (w/w) of the ash sample. The reaction mixture was stirred using 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 which was then filtered and dried and the final product was obtained [9].

SYNTHESIS OF COATING

Firstly, the plain coating was made with epoxy as base resin and amine as its hardener in the ratio of 10: 3 on weight basis. For the remaining batches, the ash was added into epoxy resin at 1%, 3% and 5% (of total epoxy-amine system) respectively and stirred on overhead stirrer till proper dispersion was achieved. The solvent was added into the mixture depending upon requirements for proper dispersion. Xylene and n-butanol were added in the ratio of 70: 30 (v/v) as the solvent mixture. After completion of dispersion, the amine hardener was added into the same and coating was applied on the mild steel panels. The formulations of batches represented in Table 1.

Table 1: Batches prepared by varying ash concentration

Batch Code	Pistachio shell ash concentration
Batch 1	0%
Batch 2	1%
Batch 3	3%
Batch 4	5%

APPLICATION OF COATING ON SUBSTRATE

Mild steel panel was used as the substrate for application of coating. Before application, the panels were properly cleaned using acetone to get rid of any dirt or oil impurity and sanding treatment was given to remove surface irregularities and proper adhesion. Again the panels were cleaned using acetone. Then the coating mixture was applied on the panels. Viscosity of application was maintained by addition of solvent mixture used for preparation.

RESULTS

The epoxy-amine coating system was modified by addition of pistachio shell ash at various concentrations. The coating systems were characterized using various testing methods which are reported along with their results below.

ASH CONTENT

Before calcination a fixed amount of powder sample was taken and the weight of same samples was noted after calcination process. Ash content was calculated by taking ratio of weight of samples after calcination to weight of samples before calcination. % Ash content of pistachio shell is reported in the Table 2 below.

Table 2: Ash content of pistachio shell

Category	% Ash content
Pistachio shell ash	6.62%

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The results for FTIR analysis is shown in Figure 1. The symmetrical stretching of P-O-P group appears at 718 cm^{-1}. Asymmetrical stretching of P-O-P appears at 925 cm^{-1}. The Mg-O bonds is appeared at 870 cm^{-1}. The Fe-O stretching, vibration appears at ~520 cm^{-1}. Peak at 1025 cm^{-1} and at 1100 cm^{-1} corresponds to plane Si-O-Si bond [10, 11]. In treated samples the broadening in the range of 2925-3331 cm^{-1} and peak at 1544-1576 cm^{-1} represents the N-H of amine groups. These peaks are absent in plain sample. Hence it confirms that the surface treatment has taken place successfully.

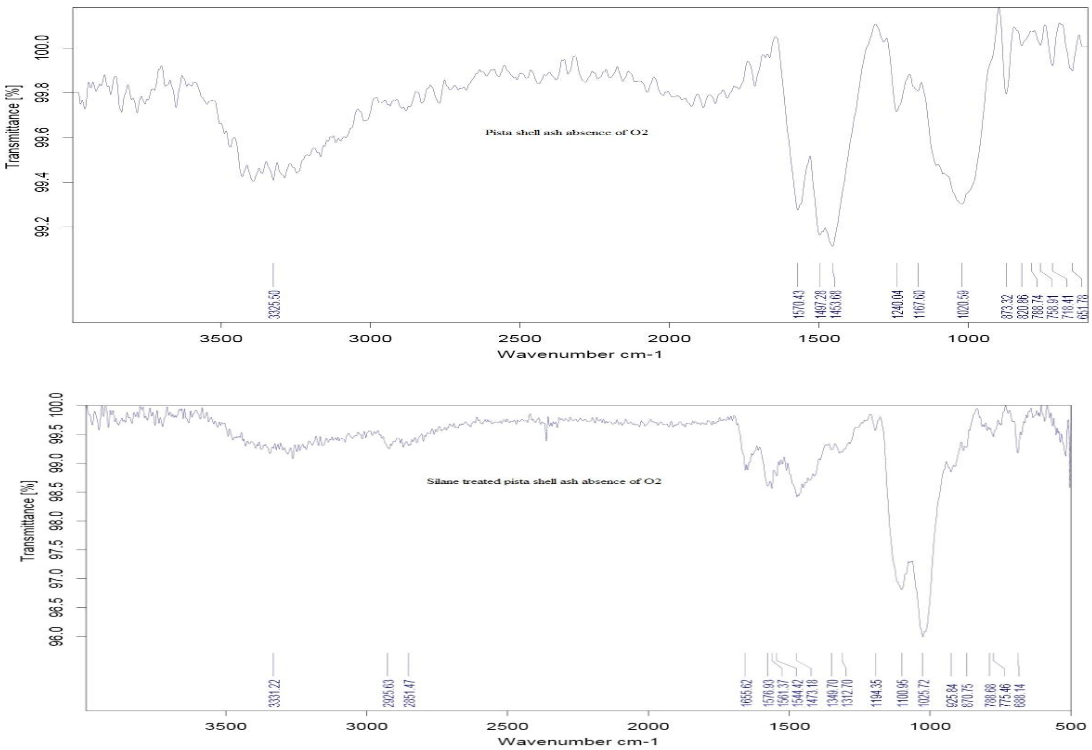

Figure 1: FTIR analysis of pistachio shell ash and modified pistachio shell ash

X-RAY DIFFRACTION

The characteristic peak of various metal oxides in XRD is represented in Figure 2. This confirms their formation and existence in the pistachio ash samples.

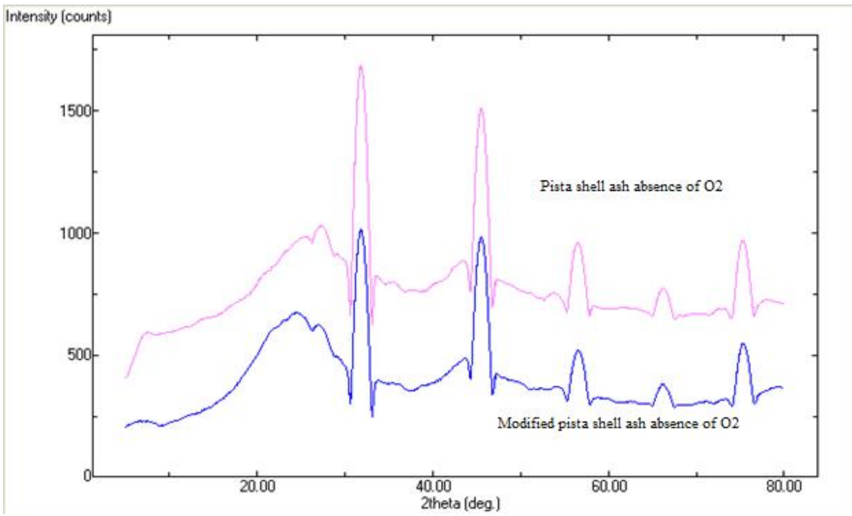

Figure 2: XRD analysis of ash samples

The results for crystallinity is shown in the Table 3 below. It is seen from the XRD results that the % crystallinity was decreased after surface treatment with silane. This was because in silane treatment, the amorphous layer was deposited on the surface and it decreases the value of % crystallinity. This confirms that the surface treatment was taken place successfully.

Table 3: % Crystallinity of pistachio shell ash and modified pistachio shell ash

Component	% Crystallinity
Pistachio shell ash	18.61%
Modified Pistachio shell ash	15.06%

MECHANICAL PROPERTIES

The mechanical properties analysis is represented in the Table 4 below. It is observed that the dried film on all the panel shows good adhesion to the metal surface. This is primarily because the epoxy-amine system has good adhesion to the metal substrate. Hence here also plain system has shown good adhesion to the metal. With addition of ash, the ash particles get properly dispersed into the binder system. Hence it does not affect the adhesion adversely. Not a single crack or loss of adhesion is observed in the falling dart impact resistance test and the conical mandrel test. Thus, all the coating systems can be said to have excellent impact resistance and flexibility. It is observed that the pencil hardness and scratch resistance value increases with increase in the percentage of addition of shell ash in the coating system. This is because; the pista shell ash is rich in metal oxides such as SiO_2, Fe_2O_3, MgO, Al_2O_3 which when used in a coating improves the hardness of the coating. Their proper dispersion in matrix which could be achieved by their surface treatment helps it to become a part of the coating backbone by chemically reacting with the same. With proper dispersion, the ash particles are uniformly distributed in the matrix, with the added concentration, there is sufficient binder to wet and surround the ash particles. Because of these two reasons, no agglomeration takes place. Hence the hardness improves and load distribution that takes place improves the flexibility of the virgin coating system.

Table 4: Mechanical properties analysis

<table>
<tr><td></td><td colspan="2">Batch 1</td><td colspan="2">Batch 2</td><td colspan="2">Batch 3</td><td colspan="2">Batch 4</td></tr>
<tr><td>DFT</td><td colspan="2">100±5 µm</td><td colspan="2">100±5 µm</td><td colspan="2">100±5 µm</td><td colspan="2">100±5 µm</td></tr>
<tr><td>Gloss</td><td colspan="2">106.82</td><td colspan="2">100.45</td><td colspan="2">97.02</td><td colspan="2">93.15</td></tr>
<tr><td>Cross hatch adhesion</td><td colspan="2">5B</td><td colspan="2">5B</td><td colspan="2">5B</td><td colspan="2">5B</td></tr>
<tr><td>Pencil Hardness</td><td colspan="2">2H</td><td colspan="2">3H</td><td colspan="2">3H</td><td colspan="2">4H</td></tr>
<tr><td>Scratch Hardness (kg)</td><td colspan="2">0.5</td><td colspan="2">0.6</td><td colspan="2">0.7</td><td colspan="2">0.7</td></tr>
<tr><td rowspan="2">Impact Resistance (kg-cm)</td><td>FI</td><td>BI</td><td>FI</td><td>BI</td><td>FI</td><td>BI</td><td>FI</td><td>BI</td></tr>
<tr><td>81.6</td><td>40.8</td><td>81.6</td><td>81.6</td><td>81.6</td><td>81.6</td><td>81.6</td><td>81.6</td></tr>
<tr><td>Flexibility (mm)</td><td colspan="2">0mm</td><td colspan="2">0mm</td><td colspan="2">0mm</td><td colspan="2">0mm</td></tr>
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CHEMICAL PROPERTIES

The result for chemical testing is shown in the Table 5. 5% Hydrochloric acid (HCl) and 5% Sodium hydroxide (NaOH) solution were used for testing acid resistance and alkali resistance respectively. The solvents Xylene and Methyl-Ethyl Ketone (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. Also ash becomes an inherent part of the coating system which further increases the chemical resistance. Hence, it shows good resistance towards chemicals such as acid, alkali, and solvents.

Table 5: Chemical resistance of the coating systems

Batch Code	Acid	Alkali	Solvent
Batch 1	A	A	A
Batch 2	A	A	A
Batch 3	A	A	A
Batch 4	A	A	A

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

ANTICORROSIVE PROPERTIES

The anticorrosive properties were checked with salt spray test with 5% NaCl test solution for 1500 hours duration. The result for corrosion resistance which was performed by salt spray method is represented in the Figure 3. As seen from the figure, the corrosion resistance was improved with addition of pistachio shell ash. The ash works by two different mechanism which are responsible to improve the corrosion resistance. Firstly it works by barrier mechanism in which the diffusion of the corrosive species becomes difficult since the blockage is created in their path through which the penetration occurs and thus they take more time to reach the surface than that of virgin coating [12]. Presence of Al_2O_3 and Fe_2O_3 also works by the barrier mechanism. Another reason to improve the corrosion resistance is passivation mechanism in which in the aqueous atmosphere the sacrificial anode, gets sacrifices itself and gets converted into insoluble compounds which can deposited on the surface. Due to their insoluble nature and passive layer formation the attack of corrosive species gets inhibited and hence corrosion resistance of the coating enhance [12]. The MgO present in the ash works by this passivation mechanism. On the top of it the surface treatment helps the ash to get chemically bonded with the coating backbone which helps to enhance the corrosion resistance even further.

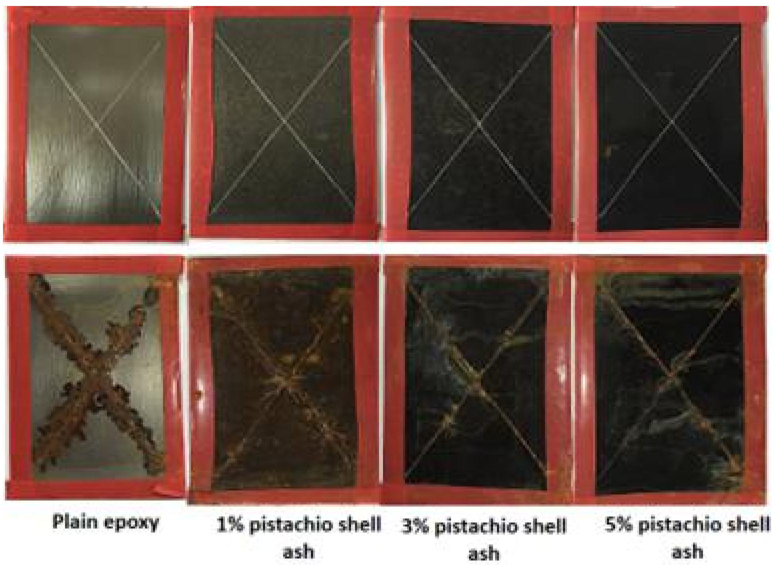

Figure 3: Salt spray testing results (After 1500 hours)

CONCLUSIONS

The pistachio shell ash was synthesized and surface treated for introducing amine functionality. This ash was incorporated into the epoxy-amine system and it gets chemically bonded to the system due the amine functionality. The binder present was enough to wet the entire ash present in the coating and this resulted in good adhesion of the coating to the substrate. This also resulted in good mechanical properties such as hardness, impact resistance, scratch resistance and flexibility. These properties were seen to improve with the increasing ash content in the coating. This is because the ash acts as filler in the coating system and increases the mechanical strength. The chemical and anti-corrosive properties also showed an increase with an increase in the ash content. Thus, an overall improvement in the properties was seen by incorporating pistachio shell ash in the coating system.

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