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New modified poly(ester amide) resins and their uses as a binder for surface coating with different applications.

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:of new modified poly(ester amide) resins and use it as a binder for anticorrosive and antimicrobial coatings.modified PEA compositions were prepared based on 4-amino-N,N-bis(2-hydroxyethyl) benzamide as the ingredient source of the polyol used and evaluated as vehicles for surface coating. The structure of the modifier and PEA resin was confirmed by FT-IR , HÂ¹-NMR, MW, Thermogravimetric analysis and SEM studies. Coatings of 50Â±5 Î¼m thickness were applied to the surface of glass panels and mild steel strips by means of a brush. The coating performance of the resins was evaluated using international standard test methods and involved the measurement of phyisco-mechanical properties and chemical resistancetests carried out revealed that the modified PEA based on 4-amino-N,N-bis(2-hydroxyethyl) benzamide enhanced both phyisco-mechanical and chemical properties. Also, the resins were incorporated within primer formulations and evaluated as anti-corrosive and antimicrobial single coatings. The results illustrate that the introduction of 4-amino-N,N-bis(2-hydroxyethyl) benzamide, within the resin structure, improved the film performance and enhances the corrosion resistance and antimicrobial activity performance of PEA resins._RESEARCH_LIMITATIONS/IMPLICATIONS__(LIMIT_100_WORDS) :No data available.modified PEA compounds can be used as binder in paint formulations to improve chemical, physical, corrosion resistance and antimicrobial activity properties.fied PEA resins are cheaper and can be used to replace other more expensive binders. These modified PEA resins can compensate successfully for the presence of many the anticorrosive and antimicrobial paint formulations and thus lower the costs. The main advantage of these binders is that they combine the properties of both polyester and polyamide resins based on nitrogenous compound, are of lower cost, and they also overcome the disadvantages of both its counterparts. Also, they can be applied in other industrial applications

New modified poly(ester amide) resins and their uses as a binder for surface coating with different applications.

Abstract

Purpose-preparation of new modified poly(ester amide) resins and use it as a binder for anticorrosive and antimicrobial coatings.

Design/methodology/approach –new modified PEA compositions were prepared based on 4-amino-N,N-bis(2-hydroxyethyl) benzamide as the ingredient source of the polyol used and evaluated as vehicles for surface coating. The structure of the modifier and PEA resin was confirmed by FT-IR , H^1-NMR, MW, Thermogravimetric analysis and SEM studies. Coatings of 50±5 μm thickness were applied to the surface of glass panels and mild steel strips by means of a brush. The coating performance of the resins was evaluated using international standard test methods and involved the measurement of phyisco-mechanical properties and chemical resistance

Findings – The tests carried out revealed that the modified PEA based on 4-amino-N,N-bis(2-hydroxyethyl) benzamide enhanced both phyisco-mechanical and chemical properties. Also, the resins were incorporated within primer formulations and evaluated as anti-corrosive and antimicrobial single coatings. The results illustrate that the introduction of 4-amino-N,N-bis(2-hydroxyethyl) benzamide, within the resin structure, improved the film performance and enhances the corrosion resistance and antimicrobial activity performance of PEA resins.

Practical implications – The modified PEA compounds can be used as binder in paint formulations to improve chemical, physical, corrosion resistance and antimicrobial activity properties.

Originality/value – Modified PEA resins are cheaper and can be used to replace other more expensive binders. These modified PEA resins can compensate successfully for the presence of many the anticorrosive and antimicrobial paint formulations and thus lower the costs. The main advantage of these binders is that they combine the properties of both polyester and polyamide resins based on nitrogenous compound, are of lower cost, and they also overcome the disadvantages of both its counterparts. Also, they can be applied in other industrial applications

Keywords: 4-Amino-N,N-bis(2-hydroxyethyl) benzamide; Biological activity; Coatings technology; Corrosion resistance; Poly (ester amide); Resins; Surface coating.

1. Introduction

The development of polymeric resins from renewable resources has attracted much attention from academic and industrial scientists throughout the world (Alam, *et a,l* 2014; Ahmad *et al* 2005; Samarth and Mahanwar, 2015). This is primarily due to the gradual depletion of the globes petro-chemical resource, coupled with environmental concerns (Chattopadhyay *et al* ,2008)**.** Utilisation of vegetable oils for the synthesis of polymeric materials is currently in the spotlight within the chemical industry. This is because vegetable oils are the largest renewable resource due to their abundant availability, built-in biodegradability, low eco-toxicity, and In addition they have low toxicity for humans and annual renewability (Yadav *et al,* 2009; Lebarbe *et al*, 2012). The common seed oils, which include linseed, (Ahmad *et al*, 2001☺ , soyabean (Guner *et al* , 2006) and sunflower (Mahapatra and Karak, 2004) have mainly been used for the synthesis of low molecular weight polymers. Such polymers include alkyd epoxies, poly(ester amide)s, poly(urethane)s and a number of others (Ahmad *et al,* 2001)**.** Polymeric systems based on poly(ester amide)s (PEA) are essentially high performance materials that utilise the combined properties of polyester and poly(amide) resins. Thus, new modified compositions have been prepared and evaluated as surface coatings vehicles, in an attempt to improve film performance and enhance the corrosion resistance properties of poly(ester amide) resins (Abd El-Wahab *et al,* 2012)**.** Also, the poly(ester-amide) resin has been additionally prepared and evaluated as an additive to incorporate into asphalt cement as a corrosion inhibitor. Concentration levels of 3 to 12% (w/w) were utilised (Abd El-Wahab *et al*, 2013). Poly(ester-amide) has proven antimicrobial activity against a number of bacteria, which includes both gram negative bacteria

(E.coli) and gram positive bacteria (S.aureus). In addition, it has also shown intermediate inhibition against further gram negative bacteria (P.aeruginosa)(Khane *et al,* 2016). Poly (ester-amide urethane) coatings based on Jatropha oil embedded with fumed silica nano-particles, have been prepared and the physico-mechanical and corrosion resistance results indicated that the modified nano-composite coatings showed the desirable properties of a mild steel substrate (Alam *et al,* 2019). Vegetable oil based poly (ester-amide)s are essentially amide modified alkyds which show improved coating film properties when compared alongside normal alkyds. These improved properties relate to drying time, water vapour resistance, hardness and both chemical and thermal resistance (Ahmad *et al,* 2001; and 2015). In addition, poly(ester-amide) resins are also recognised for high durability in many service environments (Zafar *et al,* 2007; Ahmad *et al,* 2003). However, there use as a versatile coating material is undoubtedly restricted due to the high baking temperature required for their curing (Ahamad *et al*, 2015). Boron modified poly(ester-amide) derived from Jatropha curcas seed oil has also been prepared and evaluated (Imran, *et al,* 2015). Alkyd and poly(ester-amide) resins are widely recognised as an important group of synthetic polymers for use within the paint industry and the coatings industry in general. Also, they are an essential raw material that is utilised in the production of metals, wood and wood-based materials such as floors and furniture, together with cement, cement-lime and gypsum plasters. Synthetic pentaerythritol, glycerine and phthalic anhydride are raw materials commonly utilised for the production of alkyd resins, alongside plant oils such as linseed oil and soya bean oil (Gandini , 2011). New modified poly(ester-amide) resins with anti-microbial properties, have been prepared and evaluated by means of partial replacement with the ingredient source of the polybasic acid, based on tetrabromophthalic anhydride (Abd El-Wahab and Alian, 2015). Poly(ester-amide) and alkyd resins have a wide range of application in a number of fields, including paint, coatings, adhesives and binders as composites (Pramanik *et al* 2012). In the present research work the aim has been to synthesize a new poly(ester-amide) resin from the polyol source using 4-amino-N, N-bis (2-hydroxyethyl) benzamide as a modifier. The key idea being to take advantage of the new polyol resource and the improved physico-chemical properties due to the aromatic ring and the free NH2 in the 4-amino-N, N-bis (2-hydroxyethyl) benzamide modifier. The synthesized resins were then characterised by means of physico-chemical analysis and further spectral studies. The physic-mechanical performance of the polymeric films was also investigated.

2. Experimental

2.1. Materials

The chemicals utilised during the course of the research were either obtained locally, or from global companies. All chemicals were of high purity and used for the study without any additional purification. The materials included linseed oil fatty acid (LOFA) from Belgium, phthalic acid, glycerol, p-amino benzoic acid, p-phenylene diamine, chloro acetic acid and xylene from Elnaser company, Egypt, and diethanolamine from Merk , Germany.

2.2. Methods and techniques

2.2.1. Synthesis of [4-amino-N, N-bis(2-hydroxyethyl) benzamide

A mixture of freshly distilled diethanolamine (0.5 mole equals 52.5 g), p-amino benzoic acid (0.5 mole equals 68.5 g) and xylene (15 ml) were mixed in a 250 ml round bottomed flask which was fitted with a Dean and Stark apparatus. The mixture was allowed to reflux until the approximate total amount of water (9 ml, 0.5 mole) was collected. This indicated the full formation of 4-amino-N, N-bis(2-hydroxyethyl) benzamide, through the chemical equation represented in **Scheme 1.**

2.2.2. Synthesis of the modified poly(ester-amide) resin

The synthesis of long oil, poly(ester-amide) resin was undertaken via a solvent process in two steps. Step 1: Formation of hydroxyl ethyl linseed oil fatty acid amide (HELA). Here a mixture of freshly distilled diethanolamine (0.1 mole equals 10.5 g), linseed oil fatty acid(0.1 mole equals 28 g) and xylene (15 ml) were mixed in a 250 ml round bottomed flask with a Dean and Stark apparatus. The mixture was allowed to reflux until the approximate total theoretical amount of water (1.8 ml, 0.1 mole) was collected. This indicated the complete formation of hydroxyl ethyl linseed oil fatty acid amide (HELA) according to the chemical equation represented in **Scheme 2** (Abd El-Wahab *et al,* 2012)**.** Step 2: Formation of modified poly(ester-amide) resin based on 4-amino-N, N-bis(2-hydroxyethyl) benzamide (Abd El-Wahab *et al,* 2012), as shown in **Scheme 3,** with the formulation containing N, N-bis(2-hydroxyethyl) linseed oil fatty acid amide as a source of the polyol, phthalic anhydride as the source of the di-basic component, and 4-amino-N, N-bis(2-hydroxyethyl) benzamide (plus 10% xylene as an azeotropic solvent) as the modifier. The materials were mixed in a Dean and Stark apparatus, with the progress of the esterification being followed by means of observation of the water liberated over time. On completion, the resin samples were filtered and the combination of driers added. The driers were Cobalt, Zirconium and Calcium Octoates added at 0.04, 1.0 and 0.05% based on the metal/solid resin respectively. The mixing ratio of 4-amino-N, N-bis(2-hydroxyethyl) benzamide (AHEB) and N, N-bis(2-hydroxyethyl) linseed oil fatty acid amide (HELA) can be utilised to determine the resins ultimate properties, the level of water liberated from the reaction, and the potential for gelation risk. In addition, the calculation of the water liberated can also be a useful aid for following the progress of the esterification to determine the theoretical yield (represented in **Tables I**).

Take in table I

2.2.3. Preparation of paint formulation based on the modified PEA varnishes

The primer coating composition was prepared by means of incorporating Iron oxide red-brown pigment into the poly(ester-amide) varnish. The modified coating composition is tabulated in **Table II**. The coating material itself was then applied onto both glass panels (ASTMD3891-02) and steel strips (ASTM D609-00). The application of the coating was undertaken using a brush and carried out at room temperature.

Take in table II

2.3. Characterisation

Bruker FT-IR analyzer;

ALPHA-Platinum FT-IR Spectrometer with ATR Platinum–Diamond sampling module from 400 to 4000 cm^{-1}

^{1}HNMR spectra (DMSO-d6) were recorded on a Varian Mercury-300 NMR spectrometer at Microanalytical Centre, Cairo University, Egypt.

2.3.1. Thermal analysis

TGA analysis was undertaken using a Shimadzu TGA-50 thermogravimetric analyser (Columbia, EUA). The samples were run at a heating rate of 10°C over the temperature range from room temperature to 600°C, using a nitrogen atmosphere.

2.3.3. SEM analysis

SEMs of the interior and interior surfaces of the char residue after LOI test were observed with the help of a scanning electron microscope (Joel Jsm 6360LA, Japan) at an accelerated voltage of 10 kV. The fracture surfaces were vacuum coated with gold for scanning electron microscope (SEM).

2.3.4. Antimicrobial screening

The antimicrobial activity of the synthesized modified poly(ester-amide) [AHEB] was exposed to five different Gram negative bacteria and one Gram positive bacteria. The organisms were as follows:

(a) Gram negative bacteria – Escherichia coli, Klebsiella pneumonia, Bacillus cereus, Pseudomonas and Aeruginosa.

(b) Gram positive bacteria – Staphylococcus.

Testing was undertaken at the regional Centre for Mycology and Biotechnology at Al-Azhar University, using the diffusion agar method. This involved placing a sample of the modified poly(ester-amide) into a petri-dish containing the agar plus bacteria. Following incubation at 37°C for 24 hours, inhibition zones were measured around the AHEB sample to ascertain resistance, or susceptibility, to the bacteria in question.

2.4. Film casting and testing

2.4.1. Film coating preparation and evaluation

The preparation of the steel substrate was undertaken according to the ASTM Method D609-17, with the dry film coating thickness (DFT) being measured according to ASTM Method D1005-13, using an Electro Physik Model 2100 mini test microprocessor coating thickness gauge. The anti-corrosive behaviour of the modified poly(ester-amide) coatings was done via visual evaluation, following immersion in a 3% solution of sodium chloride, in accordance with ASTM Method B117-19. The visual assessment was carried out by assessing a combination of the degree of blistering, scribe failure and the level of rusting present on the coated steel surface. This was done according to ASTM Methods D714-17, D1654-16 and D610-19 respectively. The specular gloss of the coated films was undertaken according to ASTM Method D523-18, using a Sheen gloss meter, and the hardness of the coated films according to ASTM Method D3363-11 using a Sheen hardness tester. Finally, adhesion was measured according to ASTM Method D3359-17 using a Sheen cross-cut adhesion tester, and a flexibility test according to ASTM Method D522-17 using a Sheen Mandrel bend tester.

3. Results and discussion

3.1. Spectral analysis of 4-amino-N, N-bis(2-hydroxylether) benzamide [AHEB]

Structural features associated with AHEB were confirmed by FT-IR analysis as shown in **Table III**, and by the ^{1}H-NMR analysis as shown in **Figures 1, 2** respectively. The ^{1}H-NMR spectrum shown in **Figure 2** illustrates the presence of CH_2 peaks attached to free hydroxyl, with amide nitrogen and amide carbonyl peaks present at 3.491 ppm, 3.56-3.745 ppm and 2.26-2.3 ppm respectively. Further peaks present in the aromatic region between 6.9-7.8 ppm represent ring protons.

Take in table III

3.2. Spectral analysis of AHEB modified poly(ester-amide) resin (PEA)

Structural features associated with the AHEB modified poly(ester-amide) resin were confirmed by the FT-IR analysis as illustrated in **Table IV**, and by ^{1}H-NMR analysis as illustrated in **Figures 3, 4** respectively. The ^{1}H-NMR spectrum shown in **Figure 4** indicates the presence of CH_2 peaks attached to free hydroxyl, with amide nitrogen and amide carbonyl peaks at 3.491 ppm, 3.56-3.745 ppm and 2.26-2.3 ppm respectively. Further peaks present in the aromatic region between 6.9-7.8 ppm represent ring protons.

Take in table IV

3.3. Thermogravimetric analysis (TGA) of modified poly(ester-amide)

Thermogravimetry was used to ascertain the thermal stability of the poly(ester-amide) and its relation to chemical structure and the stoichiometry of the derived volatile decomposition products. The resulting TGA thermograms are illustrated in **Figure 5**. It is clear that there are differences in the thermal behaviour and it is clear that the polymer undergoes decomposition in one very distinguished stage and in a further two stages between 250-500°C, due to the presence of chemical interaction to form copolymer during the thermal degradation.

3.4. SEM study of paint based on modified poly(ester-amide)

The resulting SEM electron micrograph (**Figure 6)** of the cured paint film based on the modified poly(ester-amide), indicates that there are no morphological irregularities. This indicates that the modified poly(ester-amide) is compatible with the other components of the paint formulation, and that the mixing process has been successful.

3.5. Measurement of mechanical properties

This involved (a) the coated films based on the modified poly(ester-amide) resins and (b) the coated paint films based on the primer formulation incorporating the modified poly(ester-amide).

The mechanical test results for the coated film blends are presented **Tables V, VI**.

Take in table **V**

Take in table VI

3.5.1. Gloss measurement

The gloss measurements of the coatings, undertaken using a Sheen gloss meter, were recorded at a 60° angle. It could be observed that the samples prepared using the modified poly(ester-amide) and the paint incorporating the modified poly(ester-amide), all showed improved gloss degree. This positive result can be attributed to the structure of the modifier which contains a number of aromatic rings, coupled with the oil content in the poly(ester-amide) based on linseed oil fatty acid (Abd El-Wahab *et al*, 2012).

3.5.2. Scratch hardness

The results for the various coatings, undertaken using a Sheen scratch hardness tester, indicated that the coating resistance to scratching is improved with an increase in the modifier percentage present in the poly(ester-amide) content. This positive attribute is due to the presence of ester repeat units (COOR) in the polymeric chain of the oil-based poly(ester-amide). These units enhance the hardness of the coating blend and also result in easier application, coupled with faster drying properties.

3.5.3. Crosshatch adhesion

The conduction of the testing, courtesy of a Sheen crosscut adhesion tester, involved creating a six-cut lattice in each direction, spaced at a distance of 1mm. Pressure-sensitive tape was then applied over the lattice and then pulled apart.

The results indicated that all coatings had good adhesion characteristics, implying that the modified poly(ester-amide) resins, and the paint formulation incorporating the modified poly(ester-amide), do not negatively affect the adhesion performance of the materials. A key factor in this can be attributed to incorporation of drying oil within the coating blend.

3.5.4. Flexibility (bending)

The conduction of the testing, with the panel surface positioned to face outward, was undertaken courtesy of a Sheen ¼ inch Mandrel bend tester. All compositions prepared and subjected to the test passed, with both varnish and paint coatings deemed to have satisfactory flexibility. This was concluded following no evidence for dislodging, or presence of cracks, in the coatings. A contributing factor for the successful results is likely to be attributed to the resin having a poly(ester) backbone with highly branched polymer and dangling fatty acids.

3.5.5 Chemical resistance of modified poly(ester-amide) resin

The testing of the poly(ester-amide) resins was done on the samples coated on glass panels. The size of the panels was 25 x 75mm, with the edges sealed using paraffin wax. Half of each individual sample was then immersed in the range of test solutions. The test solutions were water, 5% by weight anhydrous sodium carbonate, 10% by weight sulphuric acid, and a 1:3 by volume benzene/turpentine solvent mixture. Following completion, the panels were removed, carefully wiped, and then allowed to dry at room temperature prior to testing. The data obtained from the testing is presented in **Table V**, based on the modified poly(ester-amide) resins (Pramanik *et al,* 2012). The actual data indicates that an increase in the levels of 4-amino-N, N-bis(2-hydroxyethyl) benzamide [AHEB] leads to a substantial improvement in the film coatings resistance to both acid and alkali conditions. This could well be attributed to the introduction of the 4-amino-N, N-bis(2hydroxyethyl) benzamide within the resin structure. However, the 4-amino-N, N-bis(2-hydroxyethyl) benzamide does not seem to affect solvent and water resistance properties. This was proven, as all examined films demonstrated excellent performance for the 28-day duration of the test. The results are represented in **Tables V, VI**

3.6. Corrosion resistance of modified poly(ester-amide) resin (in paint formulation)

Prior to testing, primer formulations based on both modified and unmodified poly(ester-amide) were prepared and the formulations are presented in **Table VII**. Evaluation of the primer formulations as anticorrosive paints were carried out on steel panels coated with the primer. Prior to paint application, pre-treatment of the panels was undertaken to remove any surface contamination. This involved brushing the surface with a wire brush, followed by cleaning with sandpaper. On completion of the testing, which involved full immersion of the coated steel panels in a 3% solution of sodium chloride, the samples were visually examined and blistering of the coatings for the test conditions used. Results from the corrosion testing are presented in **Table VII** and **Figure 7**. The results indicate that there are significant differences between the formulations, and this is dependent on the level of 4-amino-N, N-bis(2-hydroxyethyl) benzamide modifier present. It is observed that the performance of the coatings containing the modifier improves with increased levels. This improvement in corrosion resistance can be attributed to the modifier present containing both amide and imide linkages as a result of the presence of the 4-amino-N, N-bis(2-hydroxyethyl) benzamide within the resin structure. In addition, the modifiers high molecular weight decreases the permeability of the coating to water, oxygen and aggressive ions such as chloride. Also, corrosion resistance could be assisted by the absorption of resin onto the metal surface due to its hydroxyl function (Abd El-Wahab *et al,* 2012). The size of blisters present is graded from ten to zero, where ten represents the largest blister and zero represents no blistering. The frequency of the blistering is also categorised as few (F), medium (M), medium dense (MD) and dense (D). In addition, coated panels subjected to a corrosive environment are also evaluated by reporting both maximum and minimum mean creepage from the scribe mark. Together with this information, scribe failure is also reported on a ten to zero scale, with ten being zero from the scribe mark and zero representing 16mm from the mark. The final part of the resistance assessment involves visual comparison with photographic reference standards. This assessment centres round the percentage level of surface area that has rusted. This visual standard was developed in cooperation with the Steel Structure Painting Council (SSPC). It is perceived to be an important assessment as the level of rusting either underneath or through a paint film is a key factor in deciding as to whether a coating system could be repaired, or whether it should be totally replaced. The rust grading system is like previously mentioned systems with a scale from ten to zero, with ten relating to no rusting and zero to severe rusting (Aqeela *et al,* 2010).

Take in table VII

3.6.1. SEM analysis of modified and unmodified paint surfaces following corrosion

It can be observed from **Figure 8** that prior to corrosion testing the surface of the control steel surface shows evidence of abrading scratches. Following immersion in seawater at room temperature, close examination of the SEM electron micrographs indicate that the surface of the control sample has been damaged due to aggressive attack by the seawater medium. However, in the presence of the modified poly(ester-amide) the steel is observed to have a smooth surface with only a relatively minor number of small notches. This result implies that both varnishes and paint formulations based on the modified poly(ester-amide) inhibit the dissolution of iron. In so doing, this reduces the corrosion rate and therefore affords better protection against corrosion.

3.7. Antimicrobial activity for various modified poly(ester-amide) resins

The results presented in **Table VIII** and **Figures 9-11** indicate that the modified poly(ester-amide) resins proved to be positive when exposed to Escherichia Coli and Staphylococcus aureus bacteria's, yet positive when exposed to Bacillus Cereus, Klebsiella pneumonia and Pseudomonas aeruginosa bacteria's. The positive results may be attributed to the free NH_2 in the modified poly(ester-amide), together with the repeated aromatic ring (Pramanik *et al,* 2012).

Take in table VIII

4. Conclusion

A modified poly(ester-amide) resin has been successfully prepared by the partial replacement of hydroxyl ethyl linseed oil fatty acid amide (HELA) with 4-amino-H, H-bis(2-hydroxyethyl) benzamide (AHEB) as the ingredient source of the polyol and phthalic anhydride as the di-basic acid source. The resulting modified resin exhibits improved physic-mechanical properties, including scratch hardness, mechanical damage resistance, gloss and adhesion. It can also be observed that the modified resin shows improved film performance with respect to corrosion resistance whereby the 4-amino-N, N-bis(2-hydroxyethyl) benzamide resins, incorporated within paint primer formulations, also improves with increased levels of modifier. It seems that this improvement could be due to (a) the combination of both amide and imide groups, resulting in poly(amide) containing 4-amino-N, N-bis(2-hydroxyethyl) benzamide within the resin structure; (b) ester and amide repeating units within the polymeric chain of the modified poly(ester-amide); and (c) the modifier high molecular weight decreasing the permeability of the coating to water, oxygen and aggressive ions such as chloride.

References:

Abd El-Wahab, H.; Abd El-Hai, F.; Naser, M.A.; El-Bialy, Z. and Mostafa, M., (2012),Synthesis and characterization of new modified anti-corrosive polyesteramide resins by partial replacement of the ingredient source of the polybasic acid for organic surface coatings, Pigment & Resin Technology, 41(5) pp. 276–283.

Abd El-Wahab, H.; Saleh, A.M.; Wassel, M.A.; Elkady, G.; Khalaf, N.S. and Ahmed, S., (2013), Preparation and evaluation of a new anti-corrosive coating based on asphalt cement blended with polyesteramide resin for steel protection, Progress in Organic Coatings, 76, pp. 1363–1368 .

Abd El-Wahab, H. and Alian, N.A., (2015), Synthesis and characterisation of new modified anti-microbial polyesteramide resins by partial replacement the ingredient source of the polybasic acid based on tetrabromophthalic anhydride for organic surface coatings, *Egyptian* Journal of Chemistry, 59(24), pp. 1-15

Abd El-Wahab, H. , Abd El-Fattah, M., El-alfy ,H.M.Z., Owda M.E., Lin, L., Hamady, I. (2020), "Synthesis and characterisation of sulphonamide (Schiff base) ligand and its copper metal complex and their efficiency in polyurethane varnish as flame retardant and antimicrobial surface coating additives" Progress in Organic Coatings 142, pp. 105577

Ahmad, S.; Ashraf, S.M.; Naqvi, F.; Yadav, S. and Hasnat, A., (2003), A Polyesteramide from Pongamiaglabra Oil for biologically Safe anticorrosive Coating, Progress in Organic Coatings, Vol. 47, (2), pp. 95-102.

Ahmad, S.; Ashraf, S.M.; Kumar, S.; Alam, M. and Hasnat, A., (2005), High performance paint from a sustainable resource, Indian Journal of Chemical Technology, 12, pp. 193-197.

Ahmad, S.; Ashraf, S.M.; Hasnat, A. and Noor, A., (2001), Studies on epoxidised and its blended with polystyrene and poly methyl methacrylate, Indian Journal of Chemical Technology, Vol. 8, pp. 176-180

Ahmad, S.; Ashraf, S.M.; Naqvi, F.; Yadav, S. and Hasnat, A., (2001), Synthesis and Characterization of methyl Methacrylate Modified Polyesteramide Resins from Melia Azedarach Seed Oil as Coating Material, Journal of Polymer Materials, Vol. 18, pp. 53-60.

Ahmad, S.; Ashraf, S.M.; Hasnat, A.; Yadav, S. and Jamal, A., (2001), Studies on urethane modified alumina-filled polyesteramide anticorrosive coatings cured at ambient Ahamad, S.; Ahmad, S.A. and Hasnat, A., (2015), Synthesis and Characterization of Styrenated Polyesteramide Resin from Melia Azedarach Seed Oil An Eco-friendly Resource, Chemical Science Transactions, Vol. 4, (4), pp. 1047-1053.

Alam, M.; Akram, D.; Sharmin, E.; Zafar, F. and Ahmad, S., Vegetable oil based eco-friendly coating materials: A review article, Arabian Journal of Chemistry, 7 (4), 469-479 (2014).

Alam, M.; Alandis, N.M.; Ahmad, N.; Alam, M.A. and Sharmin, E., (2019), Jatropha seed oil derived polyesteramide-urethane fumed silica nanocomposite coatings for corrosion protection, Open Chemistry, Vol. 17, pp. 206–221.

Aqeela, S.; Abd El-Wahab, H.; Mahdya, A.; Abd El-Hai, F. and Abd El-Fattah, M., (2010), New modified polyesteramide resin for industrial applications, Progress in Organic Coatings, Vol. 68 , (3), pp. 219-224.

Chattopadhyay Aaron, D.K.; MuehlbergDean, J. and Webster, C., (2008), Organic-inorganic hybrid coatings prepared from glycidyl carbamate resins and amino-functional silanes, Progress in Organic Coatings, Vol. 63, (4), pp. 405-415

Gandini, A., (2011), The irruption of polymers from renewable resources on the scene of macromolecular science and technology, Green Chemistry,Vol. 13, (5), pp. 1061-108.

Guner, F.S.; Yagci, Y. and Erciyes, A.T., (2006), Tribological Properties and Machining Performance of Vegetable Oil Based Metal Working Fluids-A Review, Progress in Polymer Science, Vol. 31, (7), pp. 633-670.

Imran, G.; Ahamad, S.; Altaf, I. and Ahmad, S.A., (2015), Synthesis and Characterization of Boron Modified Polyesteramide Derived from Jatropha Curcas Seed Oil, Chemical Science Transactions, Vol. 4, (4), pp. 1007-1012.

Khane, Y.; Lahcene, B. and Benali, M., (2016), Synthesis,characterization of polyesteramide biodegradable and evaluation of their antimicrobial activity, Biointerface Research in Applied Chemistry, Vol. 6,(2) pp. 1104-1111.

Lebarbe, T.; Maisonneuve, L.; Nguyen, T.H.N.; Gadenne, B.; Alfos, C. and Cramail, H., (2012), Methyl 10-undecenoate as a raw material for the synthesis of renewable semi-crystalline polyesters and polyesteramides, Polymer Chemistry, Vol. 3, pp. 2842-2851.

Mahapatra, S.S. and Karak, N., (2004), Synthesis and characterization of sacha inchi Plukenetia volubilis L. oil-based alkyd resin, Progress in Organic Coatings, Vol. 51, (2), pp.103-108.

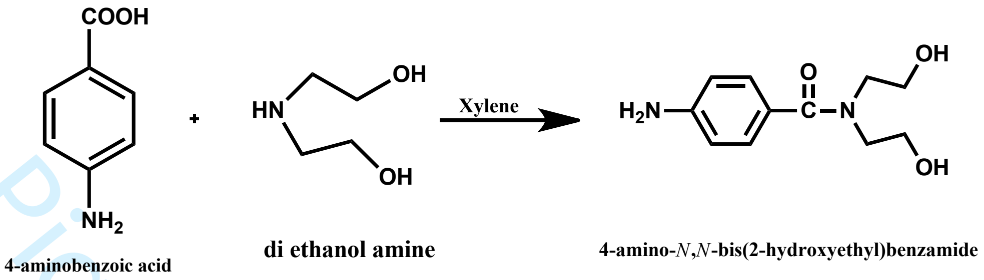
Mostafa, M.; Abd El-Hai, F.; Naser, A.M. and Abd El-Wahab, H., (2009), Various Modified Polyesteramide Varnishes as Antimicrobial Growth Control, Al-azhar Bulletin of Science Journal, Vol. 20, (1), pp. 113-123.

Pramanik, S.; Sagak, K.; Konwar, B. K., (2012), Synthesis, characterization and properties of a castor oil modified biodegradable poly(ester amide) resin, Progress in Organic Coatings, Vol. 75, pp. 569-578.

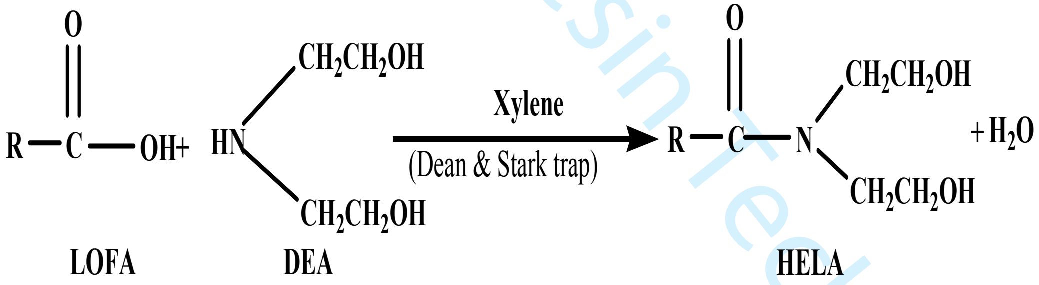
Samarth, N.B. and Mahanwar, P.A., Modified Vegetable Oil Based Additives as a Future Polymeric Material-Review, Open Journal of Organic Polymer Materials, 5, 1-22 (2015).

Yadav, S.; Zafar, F.; Hasnat, A. and Ahmad, S., (2009), Poly urethane fatty amide resin from linseed oil—A renewable resource, Progress in Organic Coatings, Vol.64, (1), pp. 27-32.

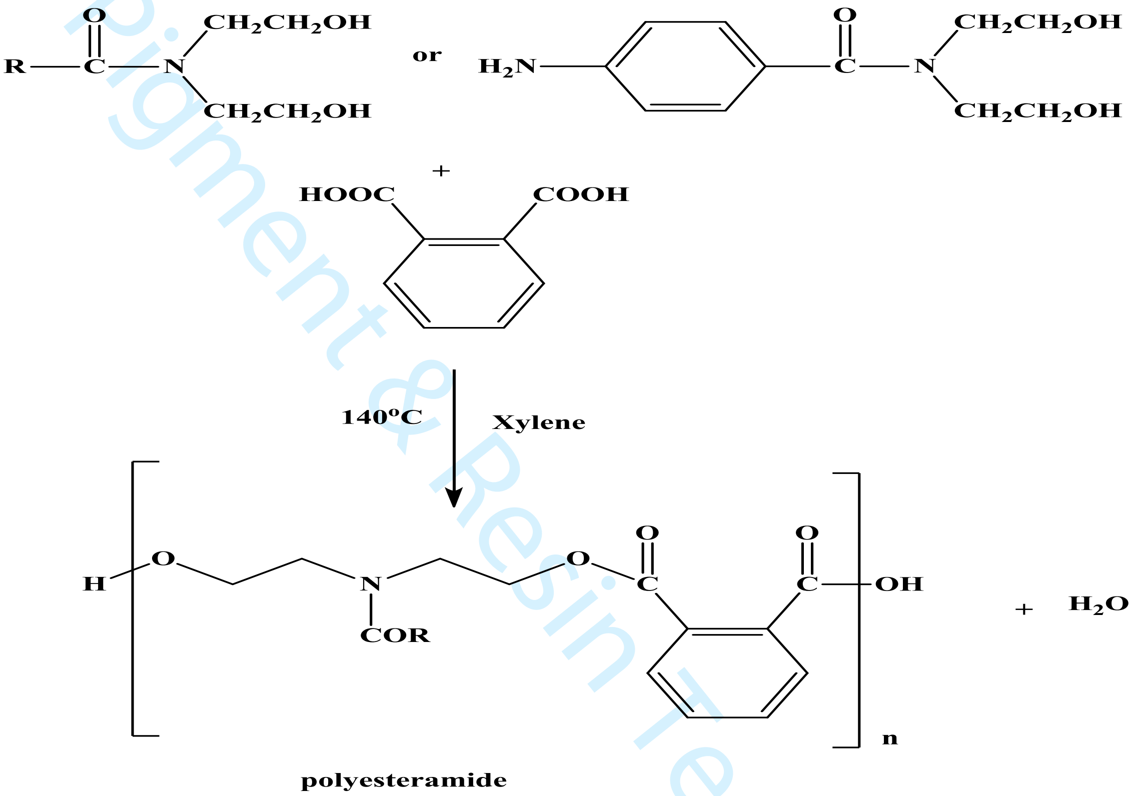
Zafar, F.; Ashraf, S.M. and Ahmad, S., (2007), Studies on zinc-containing linseed oil based polyesteramide, Reactive & Functional Polymers, Vol.67, (10), pp. 928-935.



Scheme 1: Synthesis of 4-amino -N,N-bis (2-hydroxyethyl) benzamide [AHEB].



Scheme 2: Synthesis of hydroxy ethyl linseed oil fatty acid amide (HELA).



Where:R= Fatty acid chain, n= Repeating unit
Scheme 3: Synthesis of the modified poly(ester amide) resin based on [4-amino-N,N-bis(2-hydroxyethyl) benzamide [AHEB].

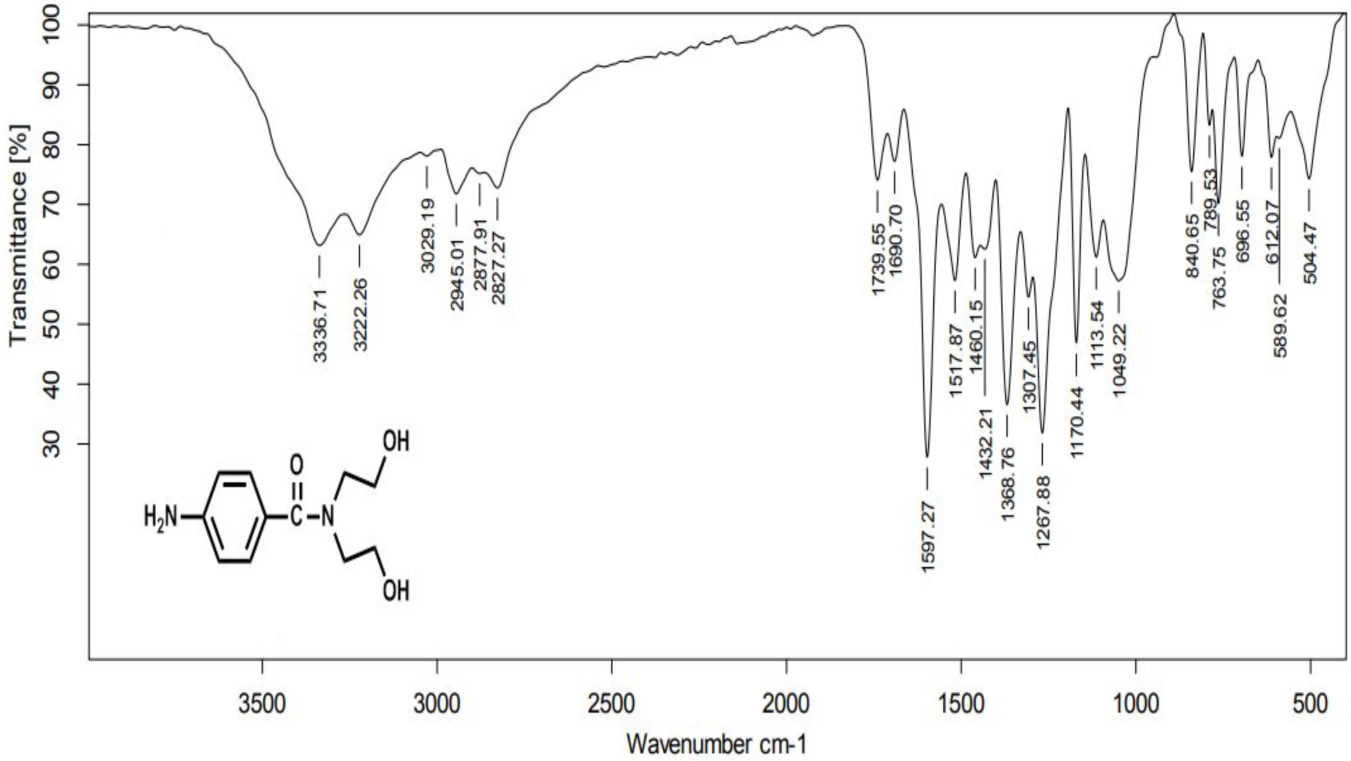


Figure 1: FT-IR spectra of the prepared 4-amino-N,N-bis(2-hydroxyethyl)benzamide [AHEB].

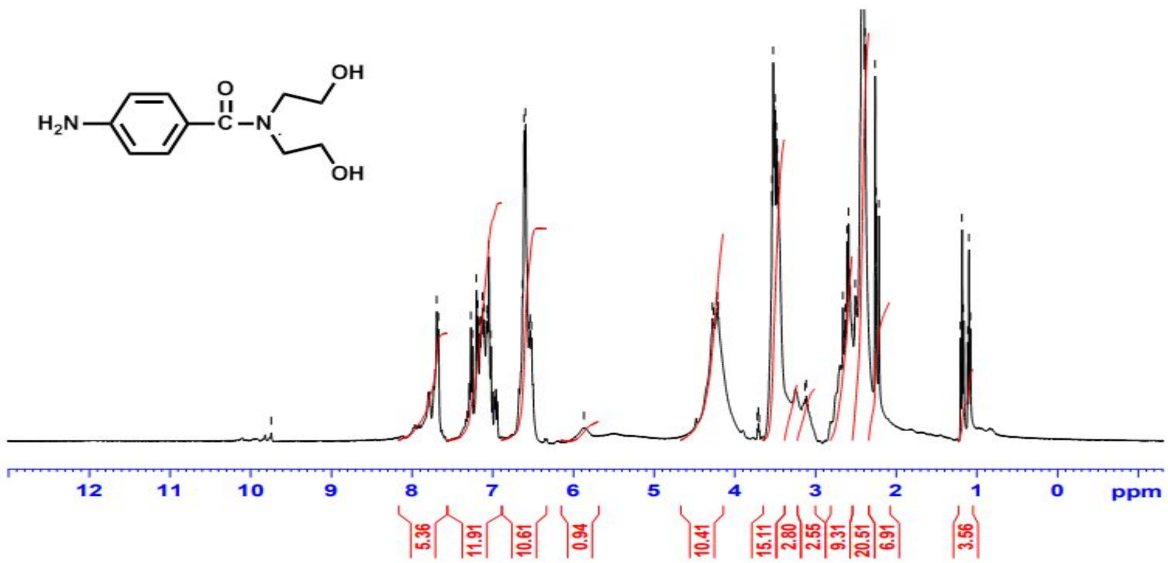


Figure 2: ^{1}H-NMR spectra of the prepared 4-amino-N,N-bis(2-hydroxyethyl) benzamide [AHEB].

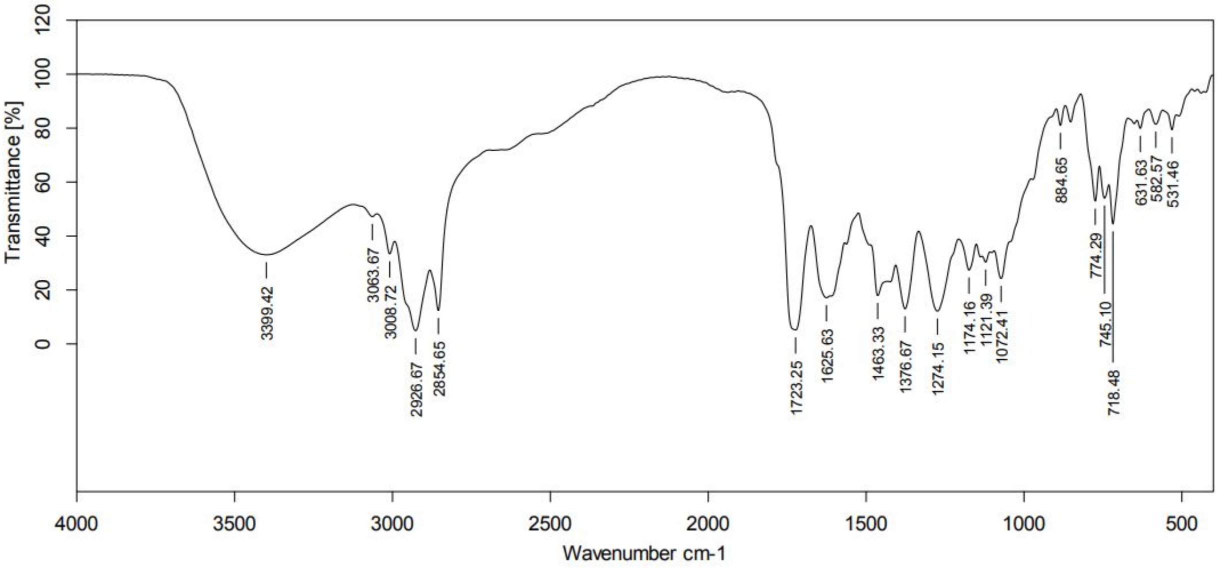


Figure 3: FT-IR spectra of the prepared [AHEB] (I) modified PEA

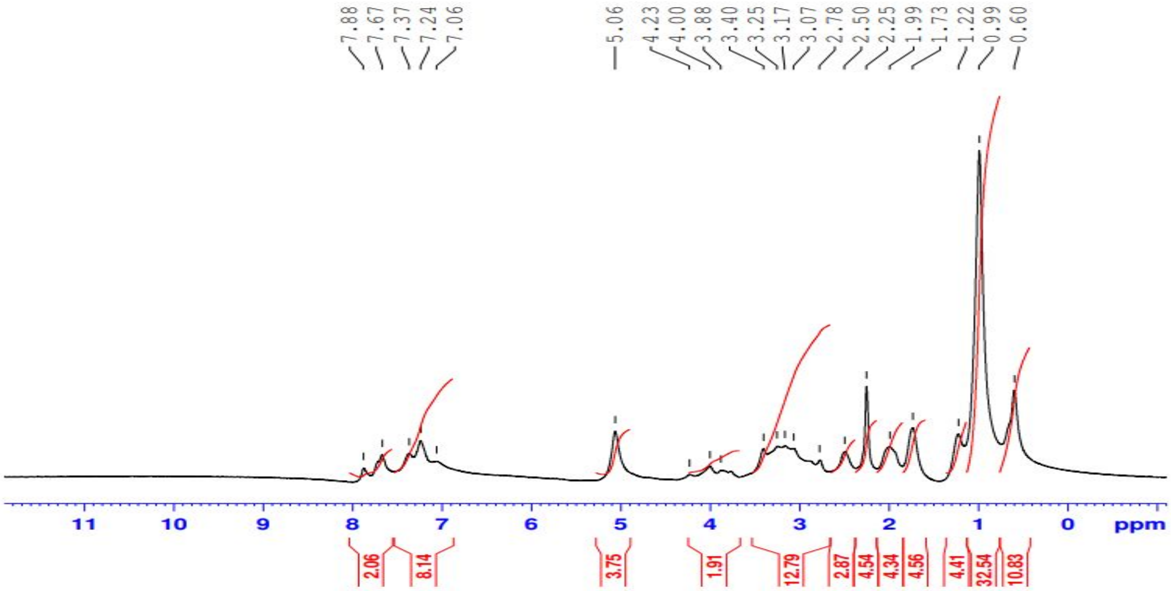


Figure 4: ^{1}H-NMR spectra of the prepared [AHEB] modified PEA

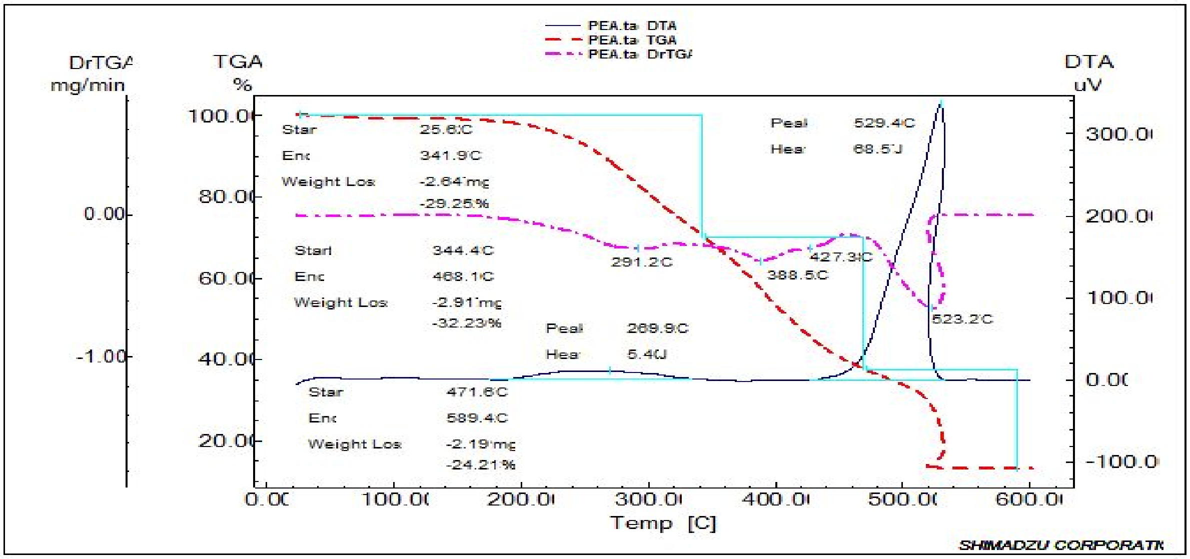


Figure 5: Thermogravimetric analysis (TGA) of [AHEB] modified PEA

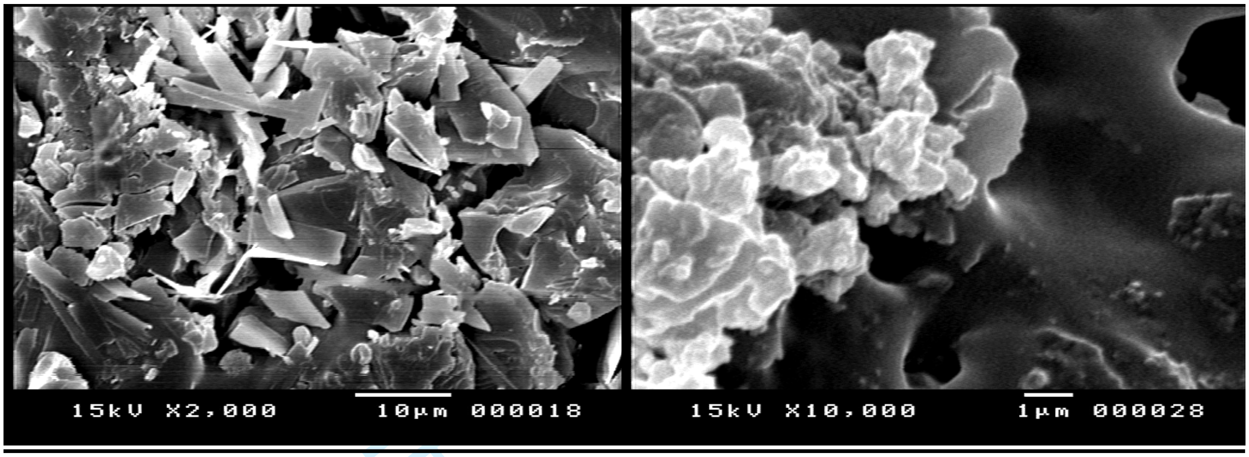
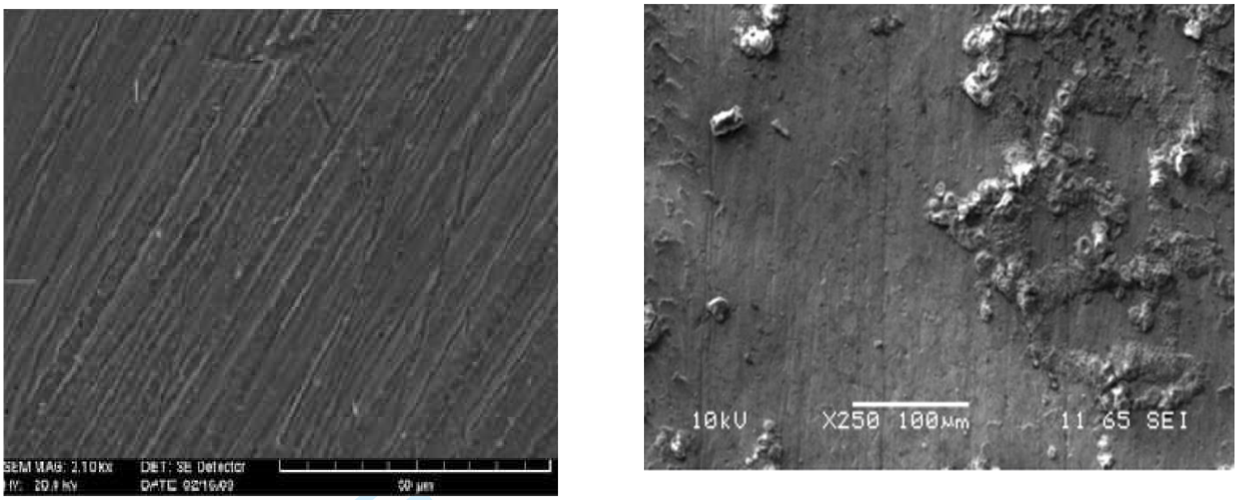


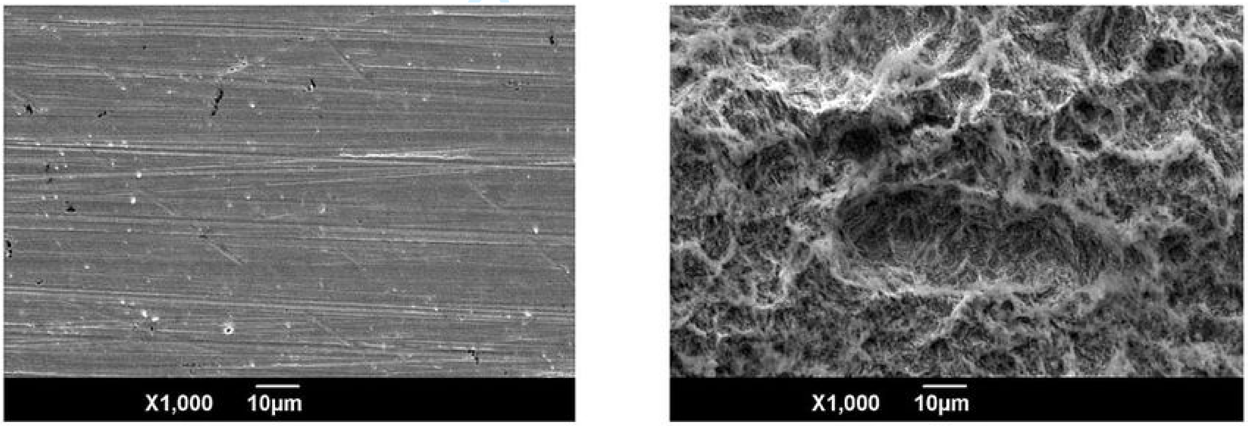
Figure 6: The SEM micrographs of [AHEB] modified poly(ester amide) resin

Figure 7: Image of coated steel after immersion in solution 3% (Wt/Wt) NaCl after 28 day paint) for coated sample by modified primer with PEA and by 30% modified PEA resin.



Steel panel coated by modified primer

Steel panel coated by primer without



modified PEA

Steel panel with 30% modified PEA

Steel panel by unmodified PEA

Figure 8: SEM photographs of the coated panels after corrosion process for primer based on modified PEA.

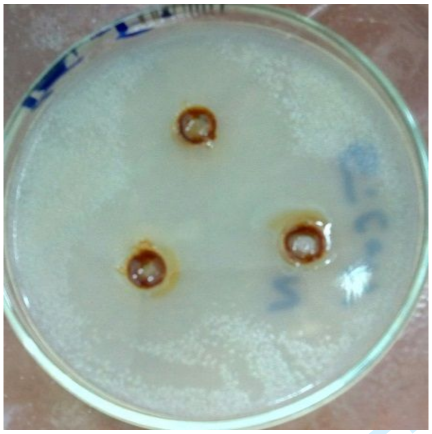


Figure 9: Antibacterial of *Escherichia Coli*
Sample ID: B, C and D (10,20and30 % PEA)

Figure10: Antibacterial of *Staphylococcus aureus.*
Sample ID: B, C and D (10, 20 and30 % PEA)

Figure 11: Antibacterial of Solvent, *E. Coli and Staphylococcus*.
Sample ID: S (solvent) and A (0 % PEA)

Table I: AHEB-modified poly(ester amide) resins.

No. ID	Ingredients	eo	E	eA	eB	F	mo= eo/F	R= eB/eA	K= mo/eA	W= E. eo	H2O off ml
A	HELA (1.00)	0.260	184	——	0.260	2	0.130	1	1	47.8	2.3
	AHEB (0.00)	——	——		——	—	——			——	
	PA	0.259	74.1	0.259	——	2	0.130			19.20	
					0.260		0.260				
B	HELA (0.90)	0.234	184	-------	0.234	2	0.117	1	1	43.10	2.3
	AHEB (0.10)	0.026	112	-------	0.026	2	0.013			2.912	
	PA	0.259	74.1	0.259	-------	2	0.130			19.20	
				0.259	0.260		0.260				
C	HELA (0.80)	0.208	184	-------	0.208	2	0.104	1	1	38.30	2.3
	AHEB (0.20)	0.052	112	-------	0.052	2	0.026			5.824	
	PA	0.259	74.1	0.259	-------	2	0.130			19.20	
				0.259	0.260		0.260				
D	HELA (0.70)	0.182	184	------	0.182	2	0.091	1	1	33.48	2.3
	AHEB (0.30)	0.078	112	------	0.078	2	0.039			8.736	
	PA	0.259	74.1	0.259	------	2	0.130			19.20	
				0.259	0.260		0.260				

NB:- **HELA** : Hydroxy Ethyl Linseed Amide, **PA** : Phthalic Anhydride, **AHEB** : 4-amino -N ,N-bis (2-hydroxyethyl) benzamide, **E** : Equivalent Weight, **e_A**: Number of acid equivalent, **e_B** : Number of hydroxyl equivalent, **e_0** : Total equivalent present at the start of the reaction, **F** : Functionality, **K** : Alkyl constant (m_0 / e_A), **R** : Ratio of total-OH groups to total-COOH groups (e_B/ e_A).

Table II: Semi- gloss primer formulations based on AHEB modified poly(ester amide) resin.

Ingredient (wt %)	Quantity No.
PEA	40
Ca CO_3	27
Iron oxide red brown	10
Zinc phosphate	5
Xylene	16
Benton	1
Methanol	0.2
Zr-octoate	0.4
Co-octotate	0.2
Anti skin	0.2

Table III: FT-IR spectra of the prepared 4-amino-N,N-bis(2-hydroxyethyl)benzamide [AHEB].

Functional group	IR peak (cm^{-1})
OH	3336 and NH_2
CON amide carbonyl	1690
COO ester carbonyl	1739
C-N	1460
CH_2 symmetric	2877
CH_2 a symmetric	2945
Ring stretching vibration of aromatic nuclei	736

Table IV: FT-IR spectra of polyesteramide resin.

Functional group	IR peak (cm^{-1})
OH and NH_2	3399
CON amide carbonyl	1625
COO ester carbonyl	1723
C-N	1463
CH_2 symmetric	2926
CH_2 a symmetric	2854
Ring stretching vibration of aromatic nuclei	745

Table V: Mechanical characteristic and chemical resistance of various AHED- Modified poly(ester amide) resins

Sample ID	Film thickness (µ)	Gloss	Scratch Hardness	Flexibility	Adhesion	Water resistance	Solvent resistance	Alkali resistance	Acid resistance
A(0%)	24	70	< 2kg	Ex	4B	>30	>30	Poor	>10
B(10)	25	74	>2kg	Ex	5B	>30	>30	Poor	>10
C(20)	25	75	>2kg	Ex	5B	>30	>30	5	>15
D(30)	25	75	>2kg	Ex	5B	>30	>30	8	>15

Table VI: Mechanical characteristic of painted film based on AHED- Modified poly(ester amide) resins

Sample ID	Film thickness (µ)	Gloss	Scratch Hardness	Flexibility	Adhesion
Primer paint based on modified PEA	45	50	>2kg	Ex	5B

Table VII: Evaluation of corrosion resistance of coating films composed of modified poly(ester amide) resin after 28 day.

Sample ID	Degree of rusting	Blistering		Scribe failure mm
		Size	Frequency	
Based on modified paint with PEA	9	9	M	10
Based on PEA varnish	8	7	F	6

Table VIII: Antimicrobial activity of various AHEB-modified poly(ester amide) resins

Sample ID	Resin No.	Escherichia Coli, NCTC 10416	Staphylococcus aureus, NCTC 7447	Bacillus Cereus, ATCC 14579	Klebsiella pneumonia, NCIMB 9111	Pseudomonas aeruginosa, KX 709967
A	0%	-ve	-ve	-ve	-ve	-ve
B	10%	+++V	++Ve	-ve	-ve	-ve
C	20%	++Ve	+Ve	-ve	-ve	-ve
D	30%	++Ve	+Ve	-ve	-ve	-ve
S	solvent	-ve	-ve	-ve	-ve	-ve