



Studies on enhancement of surface durability for steel surface by camphor oil modified epoxy polyamide coating

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Abstract

Epoxy polyamide coatings are generally used to protect mild steel structures from corrosive atmosphere due to their better adhesion over under prepared surface and effective barrier protection. But the coating has the ability to disintegrate due to UV radiation and high humidity condition. To improve the weatherability and chemical resistance performance of epoxy polyamide, there is a need to modify it with suitable cross linking agent. In this work, it has been found that camphor oil at 5 wt.% as the optimum level to protect the mild steel structures from corrosive electrolyte. Further the impedance study has shown that the resistance exerted by the Camphor oil incorporated coating in 0.5 M NaCl solution after 60 days is $3 \times 10^7 \Omega \text{cm}^2$ where as the resistance of the coating without this modifier is $3 \times 10^6 \Omega \text{cm}^2$. The FTIR spectral study indicates that the formation of ether linkages in the dried film and also the other functional groups present in the epoxy polyamide polymer is completely disappeared in the modified coating. Similarly the TG and DTA analysis showed that considerable shift in the degradation temperature has been noticed for the polymer coating with modifier. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

A good organic coating will protect steel structures from corrosive and industrial environments. The mechanism by which it protects the substrate from the environment is a complex process, which is not well understood. The protection offered by an organic coating can be described by any one of the following mechanism: (i) decrease of anodic or cathodic reaction, (ii) introduction of a high electrical resistance into the circuit of the corrosion cell and (iii) as a barrier to aggressive species like oxygen, moisture and electrolytes [1].

Polymeric resin forms a strong barrier over the substrate and protect from corrosive electrolyte. Epoxy polyamide based coatings are commonly used to protect new as well as old steel structures, due to their better barrier protection and adhesion over under prepared surfaces [2]. However due to the presence of aromatic moiety in this structures, it will degrade in UV light and also under high humidity. So the weatherability of epoxy thin film is generally rated as fair because of dissolution and chalking [3,4]. To improve the weatherability and chemical resistance behaviour of epoxy resin, there is a need to modify it with new type of cross linking agents. Camphor oil contains generally 50% Camphor, which has excellent plasticizing and flexibility character [5]. The Camphor oil is chosen as a modifier and the effect of different percentages in epoxy resin has been investigated by corrosion resistance studies, impedance measurements, FTIR characterization and thermogravimetric analysis. The results are presented in this article.

2. Experimental

Epoxy resin of Bisphenol A type with epoxy equivalent 450–500 supplied by Ciba specialty chemicals was used for this experiment. The epoxy resin was refluxed with 1.25, 2.5, 5.0, 10 and 20 vol.% of Camphor oil for 3 h separately and stored as a base part.

The hardener part of polyamide with amine value 210–230 supplied by Synpol synthetic polymer limited, was used for this study. Mild steel panels of 15 × 10 cm size were sand blasted to get Swedish specification SA 2.5 of near white surface profile [6] and used for corrosion studies. Tin foil of 10 × 2 cm size were degreased with trichloroethylene and used for the study of polymer characterization. The polymer coatings were named as given in the Table 1.

The base part and the hardener part of the resin were mixed in suitable ratio and applied on the sand blasted mild steel panel, degreased Tin foils and dried for fifteen days. The coated thin Tin foils were floated on Mercury pool and the thin polymer film were

Table 1
The sample code of Camphor modified epoxy polyamide resin

S.No.	Sample code	Expansion of sample code
1	EPA	Epoxy polyamide polymer
2	1.25 CEPA	1.25% Camphor oil modified epoxy polyamide polymers
3	2.50 CEPA	2.50% Camphor oil modified epoxy polyamide polymers
4	5.00 CEPA	5.00% Camphor oil modified epoxy polyamide polymers
5	10.0 CEPA	10.0% Camphor oil modified epoxy polyamide polymers
6	20.0 CEPA	20.0% Camphor oil modified epoxy polyamide polymers

taken out and used for FTIR characterization and Thermogravimetric analysis. The coated mild steel panels were used for physio-chemical characterization and electrochemical impedance measurement.

The coating thickness on mild steel panels was measured by using Mikrotester as per the ASTM standard D1004. The panels with the coating thickness $50 \pm 5 \mu\text{m}$ were selected for further characterization.

2.1. Mechanical properties

The coated mild steel panels have been subjected to the following mechanical tests:

- (i) Scratch hardness test (ASTM D5178).
- (ii) Taber abrasion resistant test (Federal test method 6192).
- (iii) Flexibility test (British specification No.3900).
- (iv) Impact resistance test (ASTM – G 477).

2.2. Chemical resistance and accelerated salt spray test

The coated mild steel panels in duplicate were immersed in the following solution for 30 days. Periodic observations have been carried out:

- (i) 2 vol.% of HCl solution.
- (ii) 3 wt.% of NaCl solution.
- (iii) 2 wt.% of NaOH solution.

Another set of panels in duplicate were exposed in the salt spray chamber for a period of 720 h. The experiment was conducted as per the ASTM standard B117. The panels were periodically observed for any blister or corrosion spots.

2.3. Impedance measurement

The corrosion resistance properties of the epoxy polyamide and modified epoxy polyamide polymers on steel surface in duplicate were evaluated by electrochemical impedance measurement studies. The impedance measurements were carried out with PAR electrochemical impedance analyzer (model 6310) system at frequencies 10 KHz to 10 mHz and the applied signal amplitude was 50 mV. The electrochemical cell used for this study consisted of polymer coated electrode as working electrode, a platinum foil as counter and a saturated calomel electrode (SCE) as reference electrode and 0.5 M NaCl solution as electrolyte. The impedance measurements were carried out periodically for different duration.

2.4. Fourier transformer-infra red spectroscopy (FT-IR)

FTIR for the polymer film was done by using FTIR spectrometer (Nexus-670, UK) to understand the extent in which the modifier Camphor oil react with the epoxy polyamide polymer by observing the appearance and disappearance of functional groups present in the polymer film.

2.5. Thermogravimetry (TG) and differential thermal analysis (DTA)

TG and DTA were carried out at nitrogen atmosphere to understand the thermal behaviour of the polymer, using simultaneous thermal analysis (STA-1400 polymer laboratory UK). The TG and DTA curves were recorded simultaneously.

3. Results and discussion

3.1. Physio-chemical properties

The mechanical and chemical resistance behaviour of the polymer on mild steel substrate was conducted in duplicate specimens and the variation of the result was found to be 2–3%. Thus the reproducibility of the coating behaviour is within the permissible limit. The mechanical properties of the polymer film on mild steel substrate are given in Table 2. It is found that the epoxy-polyamide and polymer modified with Camphor oil exhibit satisfactory performance when subjected to scratch hardness, Taber abrasion resistance, Flexibility test and impact resistance tests. From the table it is observed that the scratch hardness increases with the addition of Camphor oil, but the excess addition leads to a decreasing trend. This may be due to the formation of flexible ether linkage with the Camphor oil. Further the flexibility of the coating is also in excellent. Ether linkages are well characterized by higher adhesion and Flexibility [7]. Further the abrasion resistance result also indicates that the addition of Camphor oil has increased the abrasion resistance up to the optimum level at 5 wt.% Camphor oil in this polymer. In general all the composition of the polymer give good impact resistance and this is due to the better adhesion of the polymer on the steel substrates.

The chemical resistance behaviour of these polymers is given in the Table 3. From the table it is observed that in acidic solution 5 CEPA performed well than the other polymers. Similarly in other chemical solution also this percentage of Camphor modified epoxy-polyamide resin is worked well over the other system. The epoxy-polyamide polymer also has better performance in all these chemicals, except in acid solution. This poor performance of epoxy-polyamide film in acid solution is due to the acid hydrolysis of amide link present in the film. The better performance of 5 CEPA may be due to the formation of highly cross linked cured film on the surface of the steel by the formation of ether linkage with the Camphor oil. The lower percentage of Camphor may lead to insufficient cross linking with polymer and excess of Camphor forms soft surface respectively. Thus the 5 CEPA has given better performance than the other system.

Table 2
Mechanical properties of the modified epoxy resin on mild steel substrate

S.No.	Properties	EPA	1.25 CEPA	2.50 CEPA	5.00 CEPA	10.0 CEPA	20.0 CEPA
1	Scratch hardness (kg)	1.5	1.5	1.7	1.7	1.5	1.5
2	Abrasion resistance (mg wt.loss/1000 rev./1000 gm load)	2.09	2.10	2.01	1.58	1.89	2.38
3	Flexibility (3 mm mandrel dia)	Passes	Passes	Passes	Passes	Passes	Passes
4	Impact test (kg cm)	54	54	54	54	54	54

Table 3

Chemical and Salt spray resistance performance of epoxy polyamide and Camphor modified epoxy polyamide coatings on steel substrate

S.No.	Chemical solution	EPA	1.25 CEPA	2.25 CEPA	5.00 CEPA	10.0 CEPA	20.0 CEPA
1	2% HCl (30 days)	c	d	c	b	c	e
2	3% NaCl (30days)	a	b	a	a	b	c
3	2% NaOH (30 days)	a	b	a	a	b	b
4	Salt spray test (720 h)	b	b	b	a	b	c

a = No rust spot appear on the surface.

b = 1–5 small black rust spots are seen on the surface.

c = 5–10 small rust spots are seen on the surface.

d = above 10 rust spots with blisters are seen on the surface.

e = rust spots are uniformly seen on the surface.

3.2. Accelerated salt spray chamber report

Table 3 gives the result obtained from salt spray test for the polymer film coated on steel substrate. From the table it is observed that all the systems perform well in the accelerated salt spray test except the 20 CEPA coating. This is due to the presence of excess Camphor, which leads to the softening of the film followed by failure. The 5 CEPA polymer coating performed better than the epoxy-polyamide and all other coatings. This is due to the presence of optimum level of Camphor oil required to form highly cross linked adhesive polymer layer over the steel substrate. All the duplicate specimens are giving identical result. This indicates that accelerated salt spray experiment also gives reproducible performance of these polymers.

3.3. Electrochemical AC impedance analysis

Figs. 1–6 shows the Bode impedance plots of EPA, 1.25 CEPA, 2.50 CEPA, 5 CEPA, 10 CEPA and 20 CEPA polymer coated steel in 0.5 M NaCl solution for different duration. It is seen from these plots that the resistance produced by these coating has decreased with duration. Analyses of impedance Bode plots indicate that the coating systems are capacitive in nature. The impedance spectra have the form of straight inclined at an angle of 45° in relative to the frequency axis. With the duration of immersion increases, a slight bend of the curve is started at the frequencies of approximately in between 10 Hz and 100 Hz. This indicates that a frequency resistance character depending upon the penetration of water into the metal surface through the pores present on the surface of the coating. The pore resistance is a measure of the porosity and the degradation of the coating. The pore resistance has been related to the number of pores or capillary channels present in the polymer coating, which is perpendicular to the substrate surface through which the electrolyte reaches the interface [1,8]. In this entire impedance spectrum, a decrease of resistance has been noticed after 24 h of immersion, without the change in shape of the plot. The resistance values derived from the Bode plots of the coated steel in 0.5 M NaCl solution for different duration is given in the Fig. 7. The resistance exerted by all the coatings after 24 h is in the order of 1×10^8 – $7 \times 10^6 \Omega \text{cm}^2$. This is due to penetration of water into the coating and a change of the associated dielectric constant of polymer layer. But the resistance produced by the coatings is in the protective range. The resistance value produced after 30 days immersion indicate that the 1.25 CEPA and 5.0 CEPA coatings give highest value in the order of $10^8 \Omega \text{cm}^2$, but the

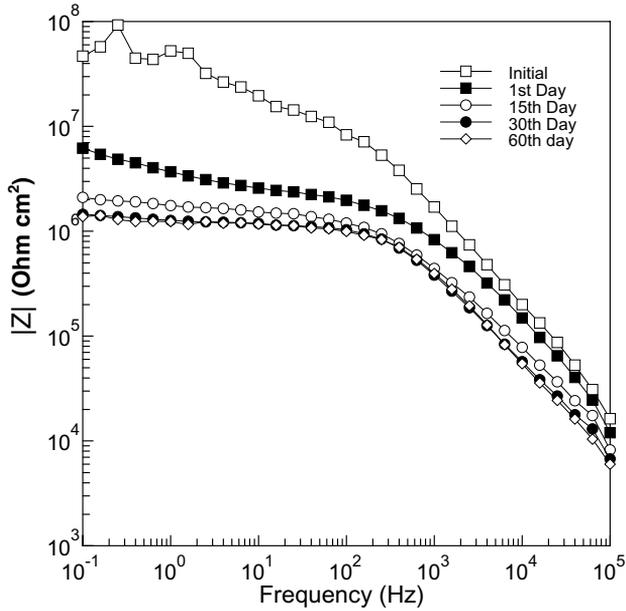


Fig. 1. Bode plots of EPA coated steel substrate in 0.5 M NaCl solution.

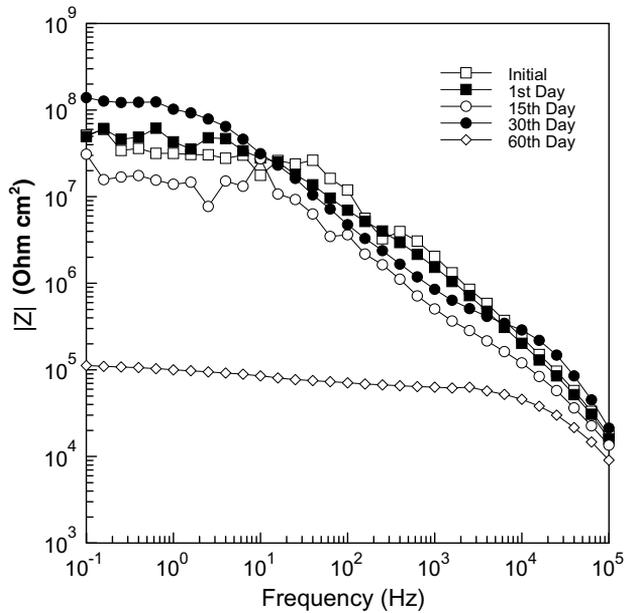


Fig. 2. Bode plots of 1.25 CEPA coated steel substrate in 0.5 M NaCl solution.

other systems also exerted the values in the range of $10^6 \Omega \text{ cm}^2$. This shows that the polymer coatings offer good protection to the steel surface in this saline condition. The decreasing resistance has been observed in all the systems except the EPA, 2.5 CEPA and 5 CEPA

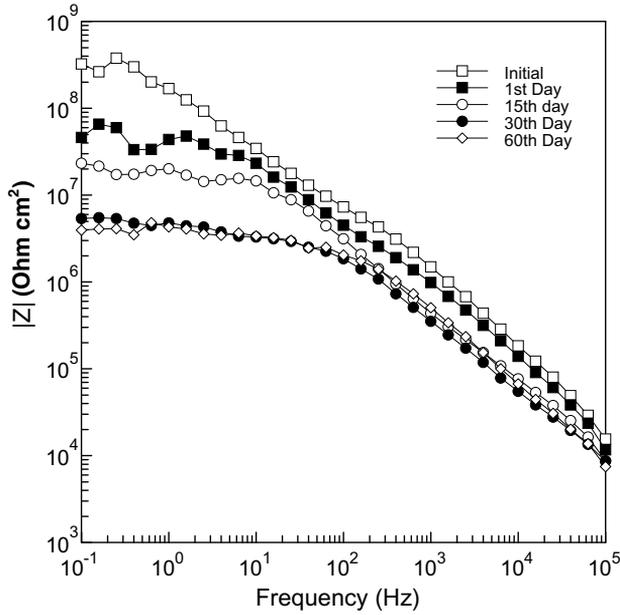


Fig. 3. Bode plots of 2.5 CEPA coated steel substrate in 0.5 M NaCl solution.

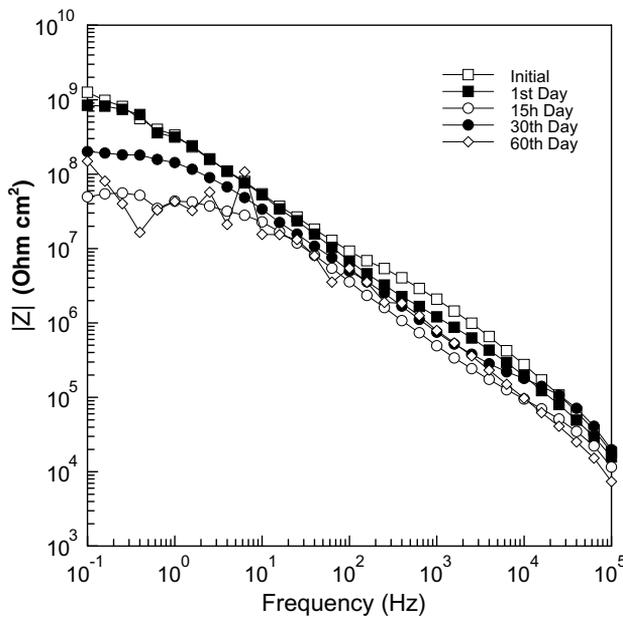


Fig. 4. Bode plots of 5 CEPA coated steel substrate in 0.5 M NaCl solution.

coatings after 60 days of the study. In these three coatings, Bode plot indicates that a bend of the curve started at the frequency of 100–150 Hz. This suggests that the minor increase of coating capacitance due to the absorption of water. On the other hand, the other three coatings

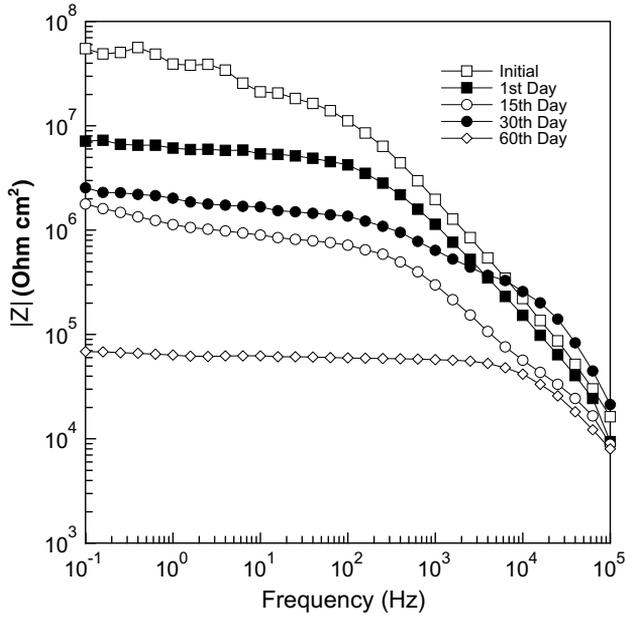


Fig. 5. Bode plots of 10 CEPA coated steel substrate in 0.5 M NaCl solution.

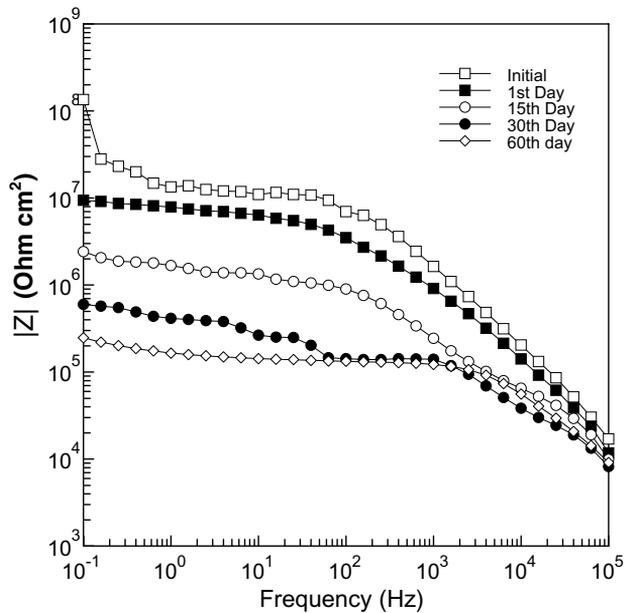


Fig. 6. Bode plots of 20 CEPA coated steel substrate in 0.5 M NaCl solution.

exhibit the resistance below the protective range, i.e. less than $10^5 \Omega \text{cm}^2$. This shows that the electrolyte passed through the pores and reaches the metal surface. Thus the iron/polymer interfacial wetting area increased with the corresponding decrease of charge transfer

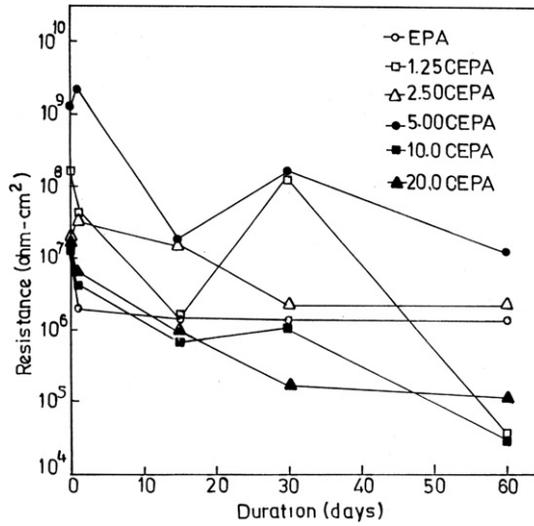


Fig. 7. Resistance produced by different concentration of camphor oil incorporated epoxy polyamide on mild steel substrate in 0.5 M NaCl solution.

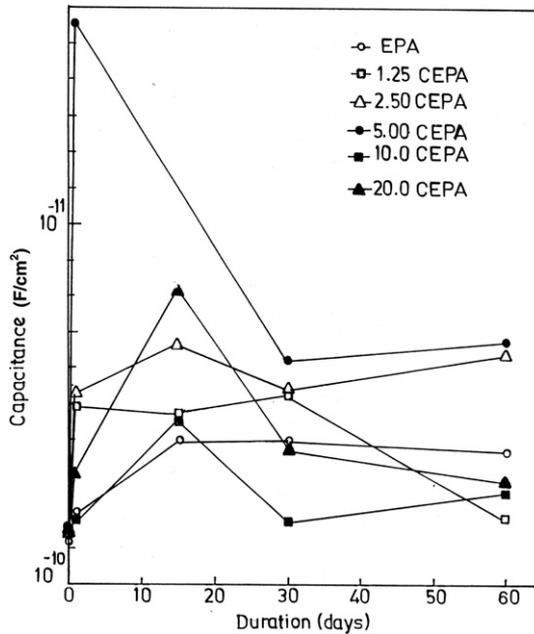


Fig. 8. Capacitance produced by different concentration of camphor oil incorporated epoxy polyamide on mild steel substrate in 0.5 M NaCl solution.

resistance [9]. This phenomena is further supported by the capacitance values exerted by the coatings are given in the Fig. 8. It is seen from the figure that the capacitance values for 2.5 CEPA and 5 CEPA coatings are 6.34×10^{-10} and 6.54×10^{-10} F/cm² after 60 days of immersion. The EPA coating has the capacitance value 3.68×10^{-10} F/cm² after 60 days of

duration and all the other three coatings exhibit below $2.5 \times 10^{-10} \text{ F/cm}^2$ for the period. These result indicates that the system 2.5 CEPA and 5 CEPA allows the penetration of water and electrolyte through it, Which is much lesser extent than the other systems This Bode plots indicates that the 5 CEPA coating gives $3 \times 10^7 \Omega \text{ cm}^2$ resistance after 60 days duration which is higher than that of epoxy polyamide ($3 \times 10^6 \Omega \text{ cm}^2$) for the same period. Similarly the capacitance produced by the coating is $6.54 \times 10^{-10} \text{ F/cm}^2$ after 60 days of duration, which is lesser than that of epoxy polyamide coatings capacitance value ($3.68 \times 10^{-10} \text{ F/cm}^2$) for the same period.

The resistance and capacitance values derived from the Bode plots of duplicate panels are identical with each other to the variation of 3–5% is observed. Thus the effect of camphor oil on epoxy-polyamide polymer leads to the formation of permanent chemical reaction with reproducible results.

3.3.1. IR spectrum analysis

The idealized structure for the Camphor oil modified epoxy polyamide coating is given in the Fig. 9. It is suggested that the Camphor reacts with the epoxy group of epoxy resin to form the ether linkage and additional reactive hydroxyl groups. The addition of polyamide hardener in this modified epoxy resin react with the hydroxyl groups present in the resin to form amide linkage to lead three dimensional network structures over the steel substrate.

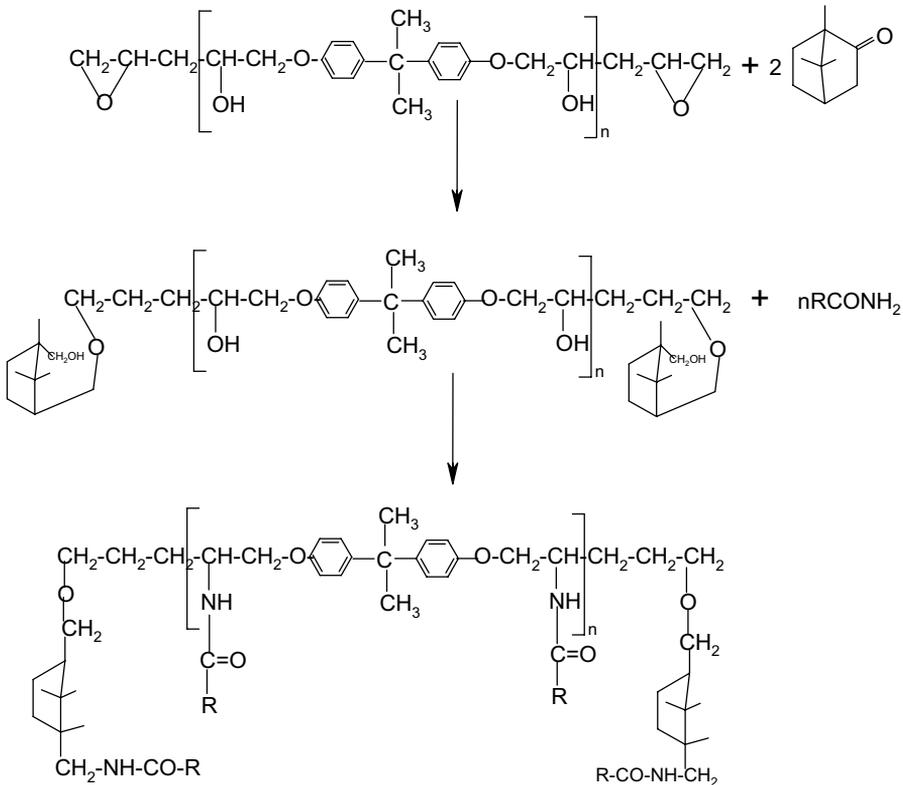


Fig. 9. Idealised structure of camphor oil modified epoxy polyamide film.

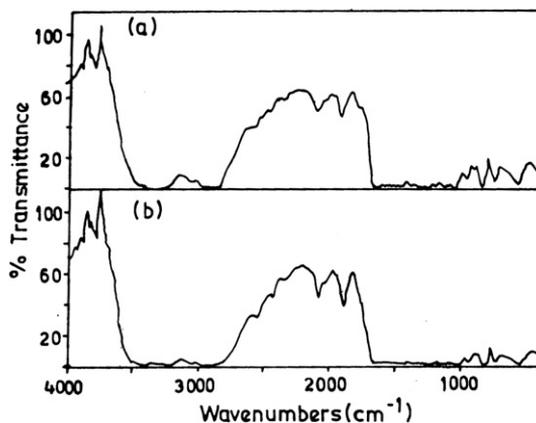


Fig. 10. (a) and (b) – FTIR spectra for EPA and 5 CEPA coating.

The Fig. 10(a) and (b) depict the FTIR spectra of epoxy polyamide cured film and Camphor modified epoxy polyamide film, respectively. Since these two spectrums are taken for the cured polymer films, most of the characteristic functional group bands and peaks are disappeared or weakened. The characteristic epoxy groups are observed in the region of 1250 cm^{-1} with a small peak and broader peak in the frequency range 947 cm^{-1} and 833 cm^{-1} . The amide linkage is also seen in 833 cm^{-1} region. In the epoxy polyamide cured films, the presence of traces of epoxy group has been observed. But the peaks in 1250 cm^{-1} region is completely absent in the case of modified coating. This clearly indicates that the epoxy group is completely reacted with the oxygen of Camphor group to form ether linkage in the region of 940 cm^{-1} and the appearance of small peak in between frequency of $1150\text{--}1070\text{ cm}^{-1}$. Further the broadening of the peaks in the region of $3500\text{--}3200\text{ cm}^{-1}$ indicates that the existence of amide linkage in the modified coating is much higher than the epoxy polyamide film. This is due to the cross linking reaction of hardener with the modified coating is much greater ratio than the unmodified film. Further the characteristic peak of $\text{C}=\text{O}$ group in the Camphor is generally observed in the region of $1650\text{--}1850\text{ cm}^{-1}$ with strong intensity, which is completely disappeared in the modified coating. This clearly indicates that the reactive point of Camphor is in this $\text{C}=\text{O}$ group position with the formation of ether linkage [10,11]. In general, the cured film does not have any functional group or the presence of very few intensity groups lead to long duration. The FTIR spectra also confirm that in the Camphor modified coating, the disappearance of many functional groups has been noticed.

3.4. Thermal analysis

The effect of the Camphor oil content on thermal stability of the epoxy polyamide polymer has been investigated by TGA and DTA and is shown in the Fig. 11(a) and (b). The thermograms indicate that the epoxy polyamide film degrades at 316°C , where as the modified epoxy polyamide film degrades at 356°C . Nearly 10 wt.% loss occur at 316°C for epoxy polyamide and that of modified resin this loss is noticed at 356°C , 50 wt.% loss was noticed at 450°C for epoxy polyamide film, where as the modified film the 50 wt.% loss is

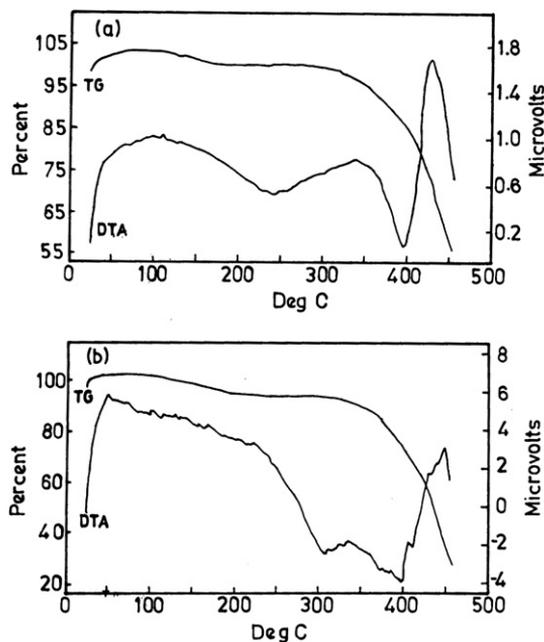


Fig. 11. (a) and (b) – TG and DTA spectra for EPA and 5 CEPA coating.

noticed at 425 °C. In both the film a sharp degradation pattern is observed after 375 °C and 400 °C, respectively. Beyond this temperature very slow rate of degradation is noticed [12]. These results indicate that the addition of Camphor oil in the epoxy polyamide film considerably shifts the degradation temperature from 316 °C to 356 °C and also minimize the weight loss.

The DTA of epoxy polyamide film shows a broad endothermic peak observed in the temperature span of 100–350 °C and is centered at 243 °C and another endothermic peak also noticed in this region of 350–420 °C and is centered at 397 °C. This indicates that some chemical reaction or the initiation of still higher polymerization reaction to take place. At the initial range the extents of polymerization is in higher order whereas the second region the polymerization is in lower range. Temperature range between 420 °C and 490 °C, there is an appearance of exothermic reaction with maximum at 429 °C. This is due to the disintegration of the coating to produce carbon dioxide and water molecules with the liberation of energy. This is also visible in TGA thermogram.

The DTA of modified epoxy polyamide film indicates that a broad endothermic peak from 119 °C to 340 °C with the minimum at 307 °C and another endothermic peak is also observed in the region of 340–420 °C with the counter at 397 °C. These two step polymerization reactions are somewhat similar to the unmodified polymer, but the initial reaction center has been shifted to 307 °C and also this reaction started in earlier stage at 50 °C. The temperature range between 420 °C and 460 °C an exothermic peak has been observed with maximum at 448 °C. In comparison with the unmodified polymer, the exothermic liberation of energy is in very low order i.e. the maximum point attained at 0.3 μV, whereas the epoxy polyamide films exothermic liberation peaks maximum point is reached at 1.7 μV range [13]. Thus the DTA analysis confirms that to the addition of camphor oil in this

epoxy polyamide formulation considerably shifted the thermal degradation temperature from 429 °C to 448 °C.

4. Conclusion

Epoxy polyamide resin has been modified with different ratio of Camphor oil and the physio-chemical and electrochemical character of this film on steel in 0.5 M NaCl solution have been studied. It is found that 5 wt.% of Camphor oil incorporated epoxy polyamide coating gives maximum protection for the mild steel surface. The impedance studies show that the epoxy polyamide coatings give $3 \times 10^6 \Omega \text{cm}^2$ of resistance in 0.5 M NaCl solution after 60 days of immersion. But the 5% Camphor oil modified coating exerts the resistance as high as $3 \times 10^7 \Omega \text{cm}^2$ in the same solution for 60 days. Thus this study has revealed that 5% Camphor oil incorporated epoxy polyamide resin film has got long term protection in different corrosive environment.

The FTIR spectral analysis also confirms the formation of ether linkages in the formulation, which gives better flexibility to the polymer. The spectral analysis also indicates that the functional group of epoxy present in epoxy polyamide coating has completely eliminated in the modified film. The thermogravimetric analysis indicates that the additions of camphor oil with epoxy polyamide polymer considerably shifts the degradation temperature from 316 °C to 356 °C and also minimize the weight loss during this temperature. The differential thermal analysis also indicates that to the addition of Camphor oil in epoxy polyamide polymer considerably shifts the degradation temperature from 429 °C to 448 °C. Thus the study reveals that the addition of 5 wt.% Camphor oil in the epoxy polyamide resin as a cross linking agent has considerably increased the protective property.

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