



Studies on Iron Embedded Polyesteramide Resin Derived from *Melia-azedarach* Seed Oil-A Renewable Resource

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<http://dx.doi.org/10.13005/ojc/320531>

(Received: June 04, 2016; Accepted: August 13, 2016)

ABSTRACT

Due to the depletion of petroleum oil reserves and the environmental issues both, efforts have made to utilize the renewable resources in the polymer synthesis now-a-days. Among the different renewable resources seed oils of different plants pay considerable attraction due to its unique properties. *Melia azedarach* is a medium sized tree largely cultivated throughout the country as a shadow tree. The seeds of the plant have approximately 40-wt% non edible oil with sufficiently high unsaturation. In the present work, oil of the *Melia azedarach* seeds utilized in making iron embedded polyesteramide with the objective to provide satisfactory utilization of abundantly available raw material significantly going waste in every season. The physico-chemical characterization of the polymeric material and intermediates were carried out as per standard laboratory methods. The structural elucidation of the polymeric resin was carried out by spectral analyses. The film properties of the iron embedded polyesteramide were also investigated in different environments. The results show that the iron embedded polyesteramide derived from *Melia azedarach* show good physic-mechanical and corrosion resistance performances in different service conditions.

Keywords: *Melia .azedarach* seed oil, Iron-filled polyesteramide, coating material.

INTRODUCTION

Polyesteramide resins are amide modified alkyds contain both amide and ester linkages in the polymeric chain¹⁻³. They have reported for improved characteristics over normal alkyds in terms of hardness, ease of drying and better resistance ability

towards water vapor⁴⁻⁶. Therefore, these resins are largely used as a coating materials or binder for paints to protect the metals from environmental corrosion and wood from biological organisms⁷⁻⁸. Furthermore, incorporation of metals, metalloids and organic moieties like styrene, acrylates, methacrylates in the polymeric materials improve the performances

like scratch hardness⁹, chemical resistivity¹⁰ as well as reduces the baking temperature required for curing notably. The primary raw material used for the synthesis of commercially important polymers has been petroleum for the last five decades¹¹⁻¹². However, the petroleum resources are going to deplete day by day, consequently it become costly due to scarcity. In recent years search for alternative renewable resources have been stimulated, which can be grown again and again^{1,2,13}. Furthermore, their productivity can be raised as per demand by more plantations.

Among the different renewable resources, vegetable oils are widely used as an alternative sustainable resource for petroleum based monomers, in the synthesis of different kinds of polymers^{1,3,14,15}. Numerous vegetable oils like sunflower, coconut soybean, linseed and castor have been extensively used for the syntheses low molecular weight polymers¹⁴⁻¹⁷. However, among these vegetable oils some are edible and other are also poses some medicinal values¹⁷. Therefore, it is required to explore the nature's blessings and utilized the non-edible and non-traditional seed oils in making value added polymeric materials which ultimately provide suitable utilization to them as well as reduce the pressure on traditional vegetable oils.

Melia azedarach tree yielded non edible seeds which contain about 40- wt% oil with appropriate percentage of unsaturated fatty acids¹⁸. Physico-chemical properties, especially high iodine value encourage us to utilized this vegetable oil in developing iron embedded polyesteramide with the view to provide more satisfactory utilization. In present work efforts made to utilize the seed oil of the *Melia azedarach* in making iron embedded polyesteramide resins with double objective utilization of non-conventional seed oil in making coating material and reduce the pressure on utilization of petrochemicals.

EXPERIMENTAL

Materials

Oil was extracted from air dried and crushed seeds of *Melia azedarach* tree (collected from the R.T.O. office compound, Shahjahanpur, India) through a soxhlet apparatus, using petroleum ether

(boiling point range 60-80 °C) as a solvent. Phthalic acid, methanol, pyridine and chloroform were used of analytical grade (S.D.Fine Chemicals India). Ferric acetate (Rohm laboratory reagents, India) was used as received. Diethanolamine of analytical grade (S.D. Fine Chemicals, India) was distilled under pressure before use. Petroleum benzene, xylene (Fisher scientific, India) and were used without further purification.

Syntheses

N, N-bis(2-hydroxyethyl) *Melia azedarach* oil fatty amide (HEMAFA)

HMAFA was synthesized and characterized as per previously reported method¹⁹.

Polyesteramide of HEMAFA and Phthalic acid (MAPEAP)

MAPEAP was synthesized as per step-growth polymerization technique for fatty amide diol and dibasic acid¹⁵. HEMAFA and Phthalic acid in equiv-molar ratio along with 50 ml xylene as a solvent were taken in a four-necked round bottom

Table 1: Physico-chemical, mechanical and chemical/corrosion resistance properties of Fe-MAPEAP polymeric resin

Test	Fe-MAPEAP
Physico-chemical analyses	
Color value	8.0
Specific gravity	0.972
Refractive index	1.509
Iodine value	30.8
Physico-mechanical properties	
Bending test (1/8 in)	Passes
Gloss at 45°	95
Impact resistance (lb/in)	200
Scratch hardness (Kg)	3.1
Chemical/corrosion resistance*	
H ₂ O (10 days)	E
HCl (3-wt%) 10 days	E
NaOH (2-wt%) 2 hrs	C
NaCl (3.5-wt%) 10 days	E
Xylene 10 days	D

*A= Film detached; B= Film partially detached; C=Loss in gloss; D= Slight loss in gloss; E= Unaffected

flask attached with a Dean-stark trap, nitrogen inlet tube, thermometer and a mechanical stirrer. The Reaction mixture was heated at $180 \pm 5^\circ\text{C}$ and maintained until the calculated amount of water was collected in the Dean-Stark trap. The progress of reaction was also monitored by taking acid value at regular intervals. After the completion of reaction, the reaction contents were allowed to cool at room temperature under stirring. The product was taken out from the reaction flask and excess of xylene was removed from the reaction mixture in a rotary vacuum evaporator.

Synthesis of Iron embedded Polyesteramide from MAPEAP (Fe-MAPEAP)

Iron was incorporated in MAPEAP by reacting the resin with ferric acetate $(\text{CH}_3\text{COO})_3\text{Fe}$. The aforementioned setup was used for the synthesis of Fe-MAPEAP. MAPEAP (0.050 mole) and $(\text{CH}_3\text{COO})_3\text{Fe}$ (0.006 mole) along with 50 ml xylene were placed in afore mentioned setup. The reaction contents were heated at the rate of $10^\circ\text{C}/\text{min}$ upto 60°C . This temperature was maintained for one hour, followed by an increase in temperature upto $160 \pm 5^\circ\text{C}$ and was further maintained for 2 hours. TLC was used to monitor the progress of reaction. After the completion of reaction, the end product was allowed to cool down at room temperature and diluted in ether, then washed with 5 wt-% aqueous NaCl solution. After washing, the product was dried over anhydrous sodium sulphate and the excess of solvent was removed in a rotary vacuum evaporator under reduced pressure to obtain the Fe-MAPEAP.

Characterization

Physic-chemical characterizations like refractive index, specific gravity, acid value, iodine value of polymeric material was determine as per standard reported laboratory methods⁹⁻¹⁰. Spectral analyses of polymer sample were used for the structural elucidation. FT-IR spectrum of the polymer sample was recorded on FT-IR spectrophotometer

(Perkin-Elmer) using a NaCl cell. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on JEOL GSX 300 MHz FX-1000 spectrometer, using tetramethyl silane (TMS) as an internal reference, where as deuterated chloroform as a solvent.

Preparation of coatings

Fe-MAPEAP polymeric resin were applied on mild steel coupons, $70 \times 25 \times 1$ mm size for physico-mechanical test and $30 \times 10 \times 1$ mm size for chemical/corrosion resistance test²⁰. The mild steel strips were polished on various grade of silicon carbide papers, then washed with distilled water and finally degreased with alcohol and carbon tetrachloride. The 60-wt% solution of Fe-MAPEAP polymeric resin was applied on these specimens' using brush technique²⁰. Coated samples were baked for 5-35 minutes in an oven at different temperature (170 - 200°C) to find out the optimum baking time and temperature. The best coatings were obtained by baking at 190°C for 15 minutes. Coating thickness was measured by Elcometer (345 digital coating thickness gauge). The coating thickness were found between 120 - $150 \mu\text{m}$. Flexibility (ASTMD 3281-84), scratch resistance (BS 3900) and impact resistance (IS: 101(Part 5/Sec. 3) of the coatings were also tested. Corrosion tests were done in water, acid (5-wt% HCl), alkali (5-wt% NaOH) and salt (3.5-wt% NaCl) by taking them in 3 inch diameter porcelain dishes and placing the coated samples in these dishes. Periodic investigation was carried out until the coating showed evidence of softening, loss in gloss or deterioration.

RESULTS AND DISCUSSION

Figure 1 (a,b,c) illustrate the reaction schemes for the synthesis of HEMAFA, MAPEAP and Fe-MAPEAP. The MAPEAP was synthesized by the amidation of MASO with diethanol amine and then by the step-growth polymerization of HEMAFA with phthalic acid. The resulting MAPEAP

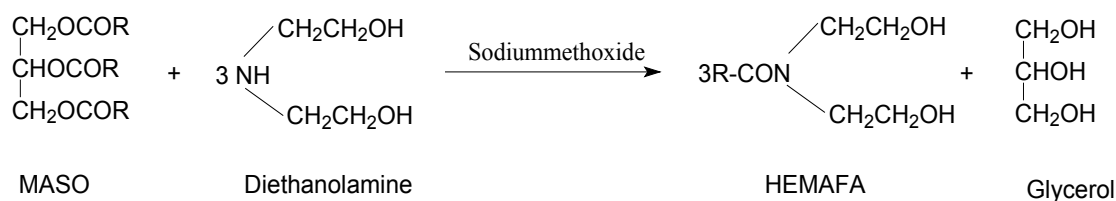
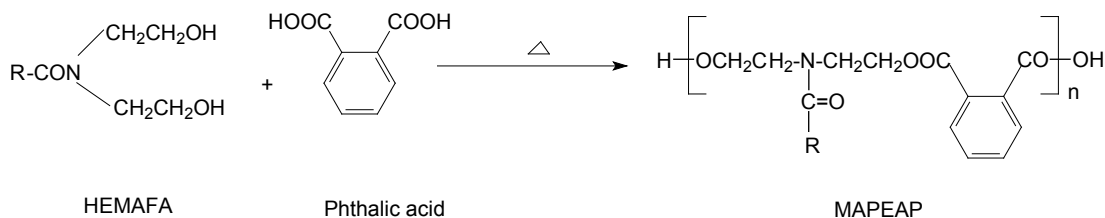
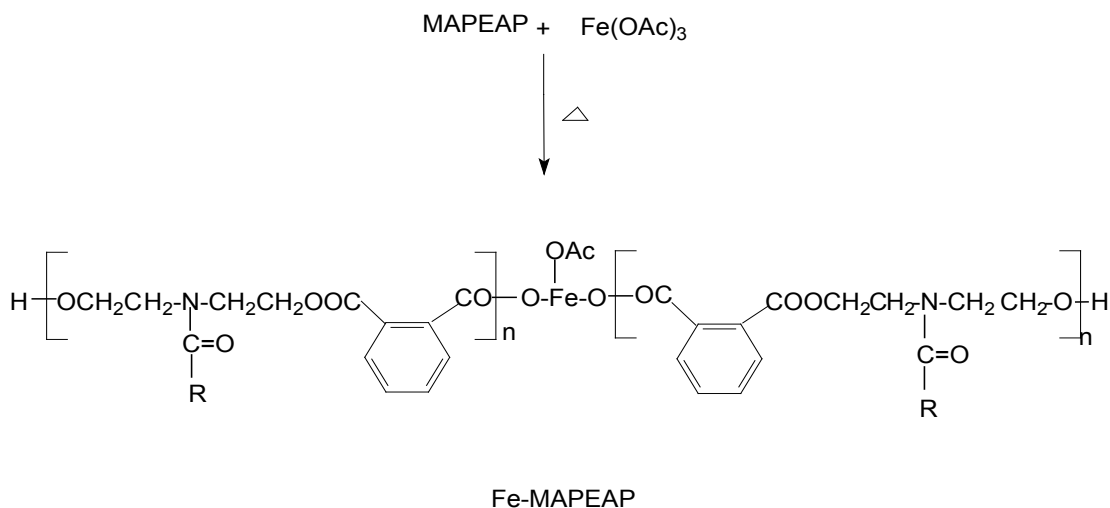


Fig. 1(a): Synthesis of HEMAFA

**Fig. 1(b): Synthesis of MAPEAP****Fig. 1 (c): Synthesis of Fe-MAPEAP**

was then treated with $(\text{CH}_3\text{COO})_3\text{Fe}$ to obtain Fe-MAPEAP polymeric resin. The acid values of the reaction mixture decreases while the conversion of HEMAFA to MAPEAP and then MAPEAP to Fe-MAPEAP. This is due to the formation of repeating ester as well as iron carboxylate linkages during poly (condensation).

The various physico-chemical characterizations like specific gravity, refractive index, inherent viscosity, iodine value, acid value and saponification value of the developed resins were determined as per standard reported laboratory methods and summarized in Table 1.

The FT-IR spectrum of the Fe-MAPEAP shows the band of alcoholic group at 3490 cm^{-1} (broad band of a primary alcohol), CH_2 asymmetric and symmetric stretching band at 2923 and 2856 cm^{-1} respectively. The bands for carbonyls of repeating ester and amide groups are observed at 1756 cm^{-1} and 1648 cm^{-1} respectively. The CN

stretching band (C-N group) appears at 1464 cm^{-1} . The C-O-C symmetric and asymmetric bands are observed at 1279 and 1289 cm^{-1} . The band at 768.0 cm^{-1} is a characteristic of disubstituted benzene of a phthalic acid²¹.

The ^1H NMR spectrum of Fe-MAPEAP Shows the peak at $\delta = 0.88\text{-}0.92$ ppm for terminal methyl group. A broad peak of chain CH_2 group appears at $\delta = 1.28\text{-}1.3$ ppm, protons of double bonded carbons appear at $\delta = 5.3\text{-}5.40$ ppm, where as aromatic protons are observed at $\delta = 7.54\text{-}7.62$ ppm, supporting the structure of Fe-MAPEAP as shown in Figure 1. ^{13}C -NMR spectrum shows the characteristic signal of carbonyl of iron carboxylate and repeating ester at $\delta = 184.0$ ppm and $\delta = 180.2$ ppm, confirm the formation of these linkages²¹. The additional signal such as carbonyl of amide appears at $\delta = 176.0$ ppm. Various ring carbons of benzene ring appear at $\delta = 135.4$, $\delta = 134.2$, $\delta = 129.0$ ppm. The peak for double bonded carbons of fatty amide appears at $\delta = 129.8\text{-}130.0$ ppm, different CH_2 group of the

fatty amide chain appear at $\delta=26.0-36.2$ ppm, while terminal methyl group of fatty acid chain appears at 16.2 ppm.

Coating properties

Coatings of Fe-MAPEAP were developed by brush technique on the required size coupons. The developed coatings were baked at different temperatures (170-220 °C) and time (10-30 mints) to obtain the optimum baking temperature and time at which coatings show best film properties. The optimum baking temperature and time for the Fe-MAPEAP polymeric resin was found 190°C and 15 minutes.

Coatings of Fe-MAPEAP were passing the bending test on 1/8 inch conical mandrel; no visual cracks were seen, like the coating materials of other vegetable oils^{7,9}. Coatings of Fe-MAPEAP show remarkably high values for scratch hardness and impact resistance, reasonably due to incorporation of iron, which increase the chain length of polymer, ultimately cohesive forces among the polymer chains. The presences of iron in the backbone of the polymer chain also improve the adhesion between polymeric chains and metal surface and also increase the sites for secondary bonding. The Table 1 indicates that

the coatings of Fe-MAPEAP also show the good protection ability in water, acid solutions and salty environment. These are reasonably due to the high cross-linking density and adhesion of the polymeric resins towards metal surface⁹.

CONCLUSIONS

The synthesis of Fe-MAPEAP from *Melia azedarach* seed oils provides a more profitable utilization of non-traditional, non-edible and renewable resource. The synthesise resin was characterized by spectral studies as well as by physico-chemical analyses. The physico-mechanical performances and chemical/corrosion resistance abilities of Fe-MAPEAP were also investigated. The study concludes that the synthesis of Fe-MAPEAP resin provides a fruitful route for the utilisation of *Melia azedarach* seed oil, rot away in every season.

ACKNOWLEDGEMENTS

The authors are thankful to authorities of G.F. College for providing necessary facilities. Dr. M. Naseem is grateful to the Prof. S. W. Akhtar, Learned Vice-Chancellor, Integral University, Lucknow

REFERENCES

1. Ansari, S. H., Imran G., Naseem M., Ahmad, S. A. and Hasnat, A. *Orient. J. Chem.* **2012**, *28*, 607.
2. Ansari, S. H., Naseem M., Hasnat, A. and Ahmad, S. A. *Biosci. Biotech. Res. Asia*, **2011**, *8*, 829.
3. Ahmad, S., Ashraf, S. M., Hasnat, A., Yadav, S. and Jamal, A. *J. Appl. Polym. Sci.* **2001**, *82*, 1856.
4. Imran, G., Ahamad, S. and Ahmad S. A. *Orient. J. Chem.* **2015**, *31*, 53
5. Dutta, S. and Karak, N. *Prog. Org. Coat.* **2001**, *53*, 147.
6. Zafar, F., Ashraf, S. M., Ahmad, S. *Prog. Org. Coat.* **2004**, *51*, 250.
7. Mahapatra, S. S. and Karak, N. *Prog. Org. Coat.* **2004**, *51*, 103.
8. Ahamad, S., Imran, G., Ahmad, S.A. and Hasnat, A. *Orient. J. Chem.* **2015**, *31*, 1169.
9. Ahmad, S., Ashraf, S.M., Hasnat, A. and Noor, A. *Indian J. of Chem. Technol.* **2001**, *8*, 176.
10. Ahamad, S., Ahmad, S. and Hasnat, A. *Mater. Sci. Res. Ind.* (In press)
11. Ahmad, S., Ahmad, S. and Agnihotri S. A. *Bull. Mater. Sci.* **2007**, *30*, 31.
12. Weiss, K. D. *Prog. Polym. Sci.* **1997**, *22*, 203.
13. Meier, M. A. R., Metzger, J.O., and Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1788.
14. Samarth, N. B. and Mahanwar, P. A. *Open J. Org. Polym. Mater.* **2015**, *5*, 1.
15. Islam, M. R., Beg, M. D. H. and Jamari, S. S., *J. Appl. Polym. Sci.* **2014**, *131*, 40787.
16. Olufunke, A. C. *Nova J. Eng. Appl. Sci.* **2014**, *2*, 1.

17. Patel, V. C., Varughese, J., Krishnamoorthy, P. A., Jain, R. C., Singh, A. K. and Ramamoorthy, M. *J. Appl. Polym. Sci.* **2008**, *107*, 1724.
18. Ambasta S. P., *The Useful Plants of India*, CSIR, India 1994.
19. Imran, G., Ahamad, S., Altaf, I and Ahmad S. A. *Chemical Science Transactions.* **2015**, *4*, (4), 1007
20. Ahmad, S., Ashraf, S. M., Naqvi, F., Yadav, S. and Hasnat A. *Prog. Org. Coat.* **2003**, *47* 95.
21. Silverstein, R. M., Bassler, G. C. & Morrill, T. C., *Spectroscopic Identification of Organic Compounds*, 5th edn., John Wiley & Sons, New York, **1991**.