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SYNTHESIS AND CHARACTERIZATION OF ANTIMONY INCORPORATED POLYESTERAMIDE DERIVED FROM *MELIA AZEDARACH* SEED OIL A SUSTAINABLE RESOURCE

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ABSTRACT

The renewable resources are the remarkable alternative of petrochemicals for the syntheses of polymeric materials. Among different renewable resources, vegetable oils especially those are non-edible play vital role in polymer synthesis. Melia azedarach seed oil are non-edible and abundantly available in the country is utilized in the making antimony containing polyesteramide with view to provide more fruitful utilization of significantly going to waste in every season. Coating properties of the developed resin were also investigated as per standard laboratory methods. The physic-mechanical and chemical resistance performances proved that the antimony incorporated Polyesteramide derived from Melia azedarach seed oil can be used as corrosion protective coating materials.

Key Words: Melia Azedarach Seed Oil, Antimony Containing Polyesteramide, Renewable Resources, Coating Materials

I. INTRODUCTION

Utilization of renewable resource especially obtained from plant origin like cellulose, lignin, cashew nut cell liquids, and vegetable oil in the development of useful materials have got the prominent position in the field of Chemistry and Technology now-a-days[1-3]. This is due to fast depletion of petrochemical reserves and fluctuation in prices both[4]. Among the different renewable resources, vegetable oil obtained from different seeds play vital role in the synthesis of polymeric resins like alkyds[5], epoxies[6], polyurethanes[7], polyamides[7], poly(ester-amide)s[2,8] and many others. These polymeric resins are extensively used in coatings, adhesives and paints industries. The traditional vegetable oils, like castor, soybean, coconut, sunflower, linseed and others are successfully utilized in the synthesis of theses polymeric resins[7,8]. However, among these oils some are edible and other possess the medicinal values. Therefore, it is desire to utilized non-edible and non-traditional seed oils in the development of polymeric materials of more practicable utility and explores the natures blessing for mankind.

Melia azedarach is a oil seed bearing plant largely cultivated in the many part of the country especially in the rural areas due to its valuable timber as well as ornamental look[9]. *Maleia azedarach* seed oil (MASO), a

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triglyceride contains fatty acids of with high unsaturation, provoke to utilize in the synthesis of polymer of film forming ability.

Polyesteramides are amide modified alkyds known for improved performances over normal alkyds in terms of physic-mechanical and chemical resistance[8,10,11]. Incorporation of metals, metalloids and organic moieties improve the performances of the polymeric resins as well as also reduce the baking temperature required for curing[12-14]. Furthermore, incorporation of antimony in the polymeric materials reported to improve the film performances remarkably and also confer the flame retardant ability[15]. Keeping these facts in mind in present work efforts have been made to synthesize antimony containing poly(ester-amide) from *Melia azedarach* seed oil a precursor of natural renewable resource with the objective to provide more valuable utilization of non-edible, non-traditional vegetable oil.

II. EXPERIMENTAL

2.1 Materials

Oil was extracted from air dried and crushed seeds of *Melia azedarach* (collected from different places of Shahjahanpur, India) through a soxhlet apparatus, using petroleum ether (boiling point range 60-80 ^{o}C) as a solvent. Physic-chemical characterizations of the *Melia azedarach* seed oil (MASO) were performed as per earlier reported method. Phthalic acid, methanol, pyridine, chloroform, were used of analytical grade (S.D.Fine Chemicals India). Antimony acetate (Rolex Laboratory Reagents, India), sulphuric acid, sodium hydroxide, acetic acid glacial, xylene (Fisher Scientific, India) were used as received. Diethanolamine of analytical grade (S.D.Fine Chemicals, India) was distilled under pressure before use.

2.2 Synthesis

N, N-bis(2-hydroxyethyl) *Melia azedarach* oil fatty amide (HEMAFA) and Polyesteramide of HEMAFA with Phthalic acid (MAPEAP) HEMAFA and MAPEAP were synthesized and characterized as per previously reported method.[1,2,16-19]

2.3 Antimony Incorporated Polyesteramide (Sb-MAPEAP)

Antimony was incorporated in MAPEAP by reacting the resin with antimony acetate [$(CH_3COO)_3Sb$]. The aforementioned setup was used for the synthesis of Sb-MAPEAP. MAPEAP (0.05 mole) and $(CH_3COO)_3Sb$ (0.006 mole) along with xylene as solvent placed a four necked round bottom flask attached with Dean-Stark, thermometer, electrical stirrer, condenser and dropping funnel. The mixture was heated at the rate of 10 ^{o}C/min up to 60 ^{o}C. This temperature was maintained for one hour, followed by an increase in temperature upto 160 ± 5 ^{o}C and maintained till the completion of reaction.

Thin layer chromatography (TLC) used to monitor the progress of reaction. After the completion of reaction, the end product was allowed to cool down at room temperature while stirring. The product was 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 Sb-MAPEAP polymeric resin.

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2.4 Characterization

Physic-chemical analyses such as specific gravity, refractive index, iodine value of the polymer were carried out as per standard laboratory methods. The structural elucidation of the polymeric resin was done by spectral analyses. FT-IR spectrum of the Sb-MAPEAP was taken on a Perkin Elmer 1750 FTIR spectrophotometer, using NaCI cell. ^{1}HNMR and ^{13}CNMR spectra were recorded on JEOL GSX 300MHZ FX 1000 spectrometer using deuterated chloroform as a solvent and tetramethylsilane as an internal standard.

2.5 Preparation and testing of polymeric coatings

Coatings of Sb-MAPEAP polymeric resin were prepared on commercially available mild steel strips 30X10X1 mm for chemical resistance and 70X25X1 mm for gloss, scratch hardness and impact resistance, by the brush technique using a solution of 40-wt% of the resin in acetone. Coated samples were baked for 5-30 minutes in an oven at different temperature (170-200 ^{o}C) to find out the optimum baking time and temperature. The best coatings were obtained by baking at 180 ^{o}C for 10 minutes. Coating thicknesses was measured by Elcometer and were found between 120-150 µm. Flexibility on conical mandrel, scratch resistance (BS 3900) and impact resistance (IS: 101(Part5/Sec. 3) 1988) of the coatings were also tested. Corrosion tests were performed 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 examination was conducted until the coating showed evidence of softening or deterioration.

III. RESULTS AND DISCUSSION

Figure 1(a,b,c), illustrate the reaction scheme for the synthesis of HEMAFA, MAPEAP and Sb-MAPEAP. The MASO on amination with diethanolamine gives HEMAFA (a diol), undergo poly(condensation) reaction with phthalic acid (a dibasic acid) to produce MAPEAP polymeric resin. The progressive decrease in acid value indicates the formation of ester linkages with the condensation of carboxylic groups with alcohol of fatty amide diol. The resulting MAPEAP then react with $(CH_3COOH)_3Sb$ to yield Sb-MAPEAP polymeric resin.

The FT-IR spectrum of the Sb-MAPEAP shows the band of alcoholic group at 3510 cm^{-1} (broad band of a primary alcoholic group), CH_2 asymmetric and symmetric stretching band at 2924 cm^{-1} and 2856 cm^{-1} respectively. The bands for carbonyls of amide and ester are observed at 1649 and 1755 cm^{-1} respectively. The CN stretching band (C-N group) appears at 1666 cm^{-1}, the C-O-C symmetric and asymmetric bands are observed at 1280 and 1285 cm^{-1}, whereas characteristic band of disubstituted benzene of phthalic acid appears at 769.0. The ^{1}HNMR spectrum of Sb-MAPEAP shows the peak at δ = 0.82-0.90 ppm for terminal methyl group, whereas broad peak of chain CH_2 group appear at δ =1.26-1.30 ppm. The protons of double bonded carbons are appear at δ=5.40-5.42 ppm, protons of aromatic ring are appear at δ=7.52-7.60 ppm, supporting the structure of Sb-MAPEAP as shown in reaction scheme 1. ^{13}C-NMR spectrum shows the characteristic signal of carbonyl of ester at δ =180.2 ppm, whereas carbonyl of amide appears at 176.2 ppm. Various ring carbon of benzene ring appears at δ =135.2, 134.0, 129.4 ppm. The peaks for different CH_2 group of the fatty amide chain appear at 36.4-26.2 ppm, the peaks for double bonded carbons of fatty amide chain appear at δ =129.8-130.0 ppm respectively whereas terminal methyl group of fatty amide chain appears at 16 ppm.

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3.1 Coating properties

Coatings of Sb-MAPEAP polymeric resin were made on required sized coupons using brush technique. The developed coatings were baked at different temperatures (170-200 ^{o}C) and time (05-30 minutes) to obtain the optimum baking temperature and time at which coatings show best film properties.

The optimum baking temperature and time for the Sb-MAPEAP was found to 180 ^{o}C and 10 minutes.

On perusal of Table 1 it has been found that coatings of Sb-MAPEAP passes the bending test on 1/8'' conical mandrels, no visual cracks were noticed, reasonably due to presence of long pendant alkyl chain of fatty amide. Coatings of Sb-MAPEAP show good resistivity towards scratch hardness.

This is due to presence of antimony in the polymer backbone, which improve the adhesion of polymeric materials towards the metal surface remarkably, at the same time increase in molar masses of the polymeric materials, increases the cohesive forces among polymeric chains.

The same is also responsible for high values of impact resistance and gloss (Table1). The Table 1 indicates that the coatings of Sb-MAPEAP also show the good protection ability in water, acid solutions and salty environments.

These are reasonably due to the presence of antimony in the polymer chain not only imparting the adhesion between the polymeric resins and metal surface but also confer the various cross-ling sites through physical and chemical interactions.

The coatings of Sb-MAPEAP resins also show good performances in organic solvents, only slight loss in gloss was observed after 10 days.

IV. CONCLUSION

Melia azedarach seed oil is a renewable and sustainable raw material which is abundant, utilized successfully in the synthesis of Sb-MAPEAP which provides a more profitable utilization of non-traditional, non-edible and renewable resource. The synthesized resin was characterized by spectral studies as well as by physico-chemical analyses.

The physico-mechanical performances and chemical/corrosion resistance abilities of Sb-MAPEAP were also investigated. The study concludes that the synthesis of Sb-MAPEAP resin provides a fruitful route for the utilisation of *Melia azedarach* seed oil, rot away in every season.

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Table 1: Physico-chemical characterization of Sb-MAPEAP

Characteristics	Sb-MAPEAP
Gardener color no	8.0
Specific gravity	0.96
Refractive index	1.510
Acid value	1.0
Saponification value	132
Hydroxyl value	5.02
Iodine value	28.6

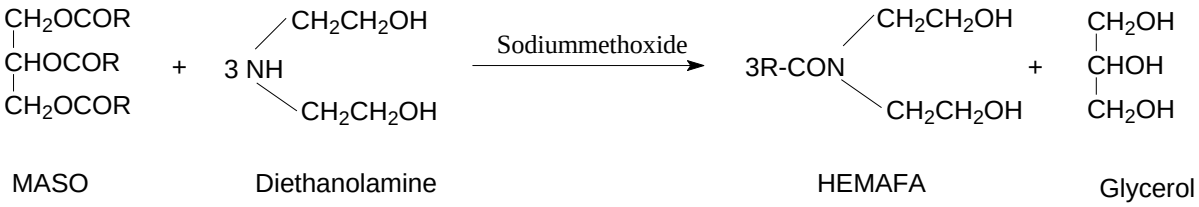

Fig. 1(a): Synthesis of HEMAFA

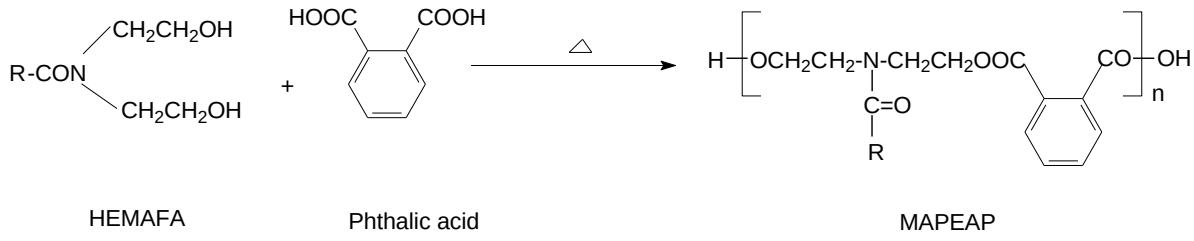

Fig. 1(b): Synthesis of MAPEAP

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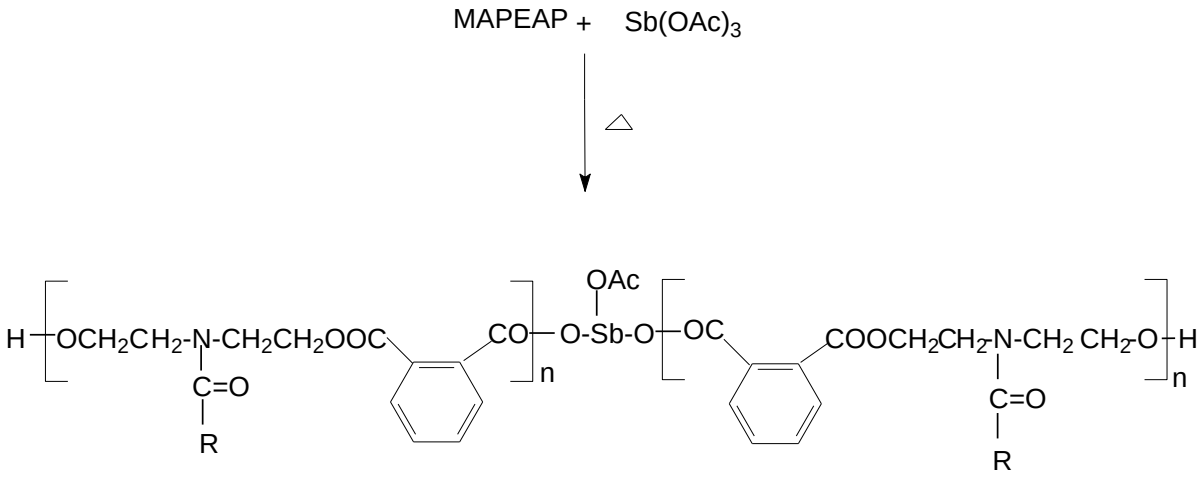

Sb-MAPEAP

Fig. 1 (c): Synthesis of Sb-MAPEAP

REFERENCES

[1] Imran, G., Ahamad, S. and Ahmad S. A. Orient. J. Chem. 2015, 31, 53

[2] Zafar, F., Ashraf, S. M., Ahmad, S. Prog. Org. Coat. 2004, 51, 250.

[3] Meier, M. A. R., Metzger, J.O., and Schubert, U. S. Chem. Soc. Rev. 2007, 36, 1788.

[4] Dutta, S. and Karak, N. Prog. Org. Coat. 2001, 53,147.

[5] Mahapatra, S. S. and Karak, N. Prog. Org. Coat. 2004, 51, 103.

[6] Ahmad, S., Ahmad, S. and Agnihotri S. A. Bull. Mater. Sci. 2007, 30, 31.

[7] Ahmad, S., Ashraf, S. M., Naqvi, F., Yadav, S. and Hasnat A. Prog. Org. Coat. 2003, 47 95.

[8] Ansari, S. H., Imran G., Naseem M., Ahmad, S. A. and Hasnat, A. Orient. J. Chem. 2012, 28, 607.

[9] Ansari, S. H., Naseem M., Hasnat, A. and Ahmad, S. A. Biosici. Biotech. Res. Asia, 2011, 8, 829.

[10] Ahmad, S., Ashraf, S. M., Hasnat, A., Yadav, S. and Jamal, A. J. Appl. Polym. Sci. 2001, 82, 1856.

[11] Ahamad, S., Imran, G., Ahmad, S.A. and Hasnat, A. Orient. J. Chem. 2015, 31, 1169.

[12] Ambasta S. P., The Useful Plants of India, CSIR, India 1994.

[13] Silverstein, R. M., Bassler, G. C. & Morril, T. C., Spectroscopic Identification of Organic Compounds, 5th edn., John Wile y & Sons, New York, 1991.

[14] Weiss, K. D. Prog. Polym. Sci. 1997, 22, 203.

[15] Ahmad, S., Ashraf, S.M., Hasnat, A. and Noor, A. Indian J. of Chem. Technol. 2001, 8, 176.

[16] Samarth, N. B. and Mahanwar, P. A. Open J. Org.Polym. Mater. 2015, 5, 1.

[17] Islam, M. R., Beg, M. D. H. and Jamari, S. S., J. Appl. Polym. Sci. 2014, 131, 40787.

[18] Olufunke, A. C. Nova J. Eng. Appl. Sci. 2014, 2, 1.

[19] Patel,V. C., Varughese, J., Krishnamoorthy, P. A., Jain, R. C., Singh, A. K. and Ramamoorty, M. J. Appl. Polym. Sci. 2008, 107, 1724.