

Synthesis and Characterization of methyl Methacrylate Modified Poly (Ester-Amide) Resins from *Melia Azedarach* Seed Oil as Coating Material

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ABSTRACT

Synthesis of polymeric materials from natural renewable resources has attracted a lot of attention of researcher throughout the world as they not only reduce the dependency on petrochemicals but also friendly to the environment. Utilization of non-traditional and non-edible vegetable oils in the synthesis of valuable polymeric materials solves the problem of waste disposal as well as bringing down the cost of end products. *Melia azedarach* seed oil (MASO), a non-traditional and non-edible seed oil is utilized for the synthesis of poly (ester-amide) (MAPEA) by the aminolysis with diethanolamine followed by step-growth polymerization with phthalic acid. To improve the performances and utility of the MAPEA, methyl methacrylate (MMA) classified as hard monomer in the literature of acrylate embedded to it in different phr to obtained methyl methacrylate modified poly (ester-amide) (MMMAPEA) resins. The MMMAPEA resins were characterized by physic-chemical analysis as per standard reported methods. The structural elucidation of the resin was carried out by spectral analyses. Physico-mechanical and chemical/corrosion resistance performances of the MMMAPEA resins were investigated for the optimization of MMA content.

Keywords: *Melia azedarach*, methylmethacrylate, Poly (ester-amide), vegetable oil, coatings.

INTRODUCTION

Polymeric materials are playing very important role in the modern society and are replacing metals in diverse field of life¹⁻³. However, the major drawbacks of polymeric materials are their non-biodegradability especially those derived from petrochemicals^{4,5}. Furthermore use of petrochemicals largely affected the environment with the increase in emission of green house gases and accumulation of non-biodegradable waste on earth⁶. Worldwide potential demands for replacing petroleum derived raw materials with renewable ones are quite significant due to both realizations that our petroleum resources are finite and not suitable for environment^{6,7}. Recent investigations are therefore, focused on producing polymeric materials from natural renewable resources which have ability

to grow again and again and also posse's inbuilt biodegradability⁸.

Among different renewable resources vegetable oils obtained from the different seeds play vital role in the synthesis of polymers⁹. Seed oils are cost effective, eco-friendly, eco-toxic towards humans and are also biodegradable in nature⁹⁻¹¹. Common seed oils such as linseed¹², castor⁹, soybean⁹ and sunflower¹³ have been largely used in the synthesis of low molecular weight polymers like alkyds, epoxies, poly(urethane)s, interpenetrating polymer networks (IPNs) poly(ester-amide)s and many others¹⁴. These polymers are extensively used in the coatings, paints, and adhesives and bioengineering industries. Among aforesaid traditional oils some of them posses the medicinal values and edible too¹⁵. Therefore it is desirable to explore the spectrum of

nature's blessing and utilized non-edible oils in the synthesis of valuable polymer to maintain equilibrium of demand and availability of feed stock.

Melia azedarach belongs to the family *meliaceae*, largely cultivated in rural areas for its valuable wood. Its seed contain about 40 % triglyceride oil with appropriate composition of unsaturated and saturated fatty acids¹⁶. The results of physico-chemical characterization indicate that the oil is a suitable starting material for the polymer synthesis polymer with film forming ability.

Poly (ester-amide) resin obtained from different seed oils are amide modified alkyds known for improve film characteristic over traditional alkyds in terms of hardness, water vapor resistance and durability in many service environment¹⁷⁻¹⁹. However their utilization as viable coating materials is limited as they required high baking temperature for curing^{20,21}. Curing of the polymeric material at elevated temperature is a difficult process as well as energy consuming too. On review of literature it has been found that incorporation of metals, metalloids and organic moieties like styrene, vinyl acetate, poly (styrene-co-maleic anhydride) to the oil based polymers reduces the curing temperature as well as also enhances the scratch hardness and protective efficiency^{10,22}. Methyl methacrylate is classified in the literature of acrylates as a monomer of conferring the hardness to the resulting polymers²³.

Keeping these facts in mind we have made an effort to develop the methyl methacrylate modified

poly (ester-amide) with the objective to provide the more practicable utility to the *Melia azedarach* seed oil a renewable resource of the nature generally destroyed in every season.

EXPERIMENTAL

Melia azedarach seed oil (MASO) was extracted from the crushed seeds of *Melia azedarach* collected from the different places of the shahjahanpur, U.P. India, through the soxhlet apparatus by using petroleum ether as a solvent (60-80 °C). The results of physico-chemical analyses and fatty acid profile¹¹ of MASO is presented in Table 1. Phthalic acid, diethyl ether, methanol, xylene and methyl methacrylate were procured from Merck, India. Diethanol amine of analytical grade procured from the s.d. Fine Chemicals, India and was distilled under reduced pressure before use.

Syntheses N,N-bis (2-hydroxy ethyl) Melia azedarach oil fatty amide (HEMAFA) and Melia azedarach Poly(ester-amide) (MAPEA)

HEMAFA and MAPEA were synthesized and characterize as per previously reported methods¹¹

Methyl methacrylate modified poly (ester-amide) (MMMAPEA)

MAPEA dissolved in xylene placed in a four necked round bottom flask equipped with water condenser, nitrogen inlet tube, thermometer and mechanical stirrer. The content was heated up to 140±5 °C and then methyl methacrylate (MMA) in different per hundred of resin (phr) along with benzoyl peroxide (0.1 wt% of MMA) added slowly in the aforementioned reaction mixture. The reaction mixtures were allowed continue for two hrs to obtained MMMAPEA resins as end products. On completion of reactions, the products were cooled at room temperature. The excess of solvent removed in a rotary vacuum evaporator under reduce pressure.

Characterization

Physico-chemical characterizations such as specific gravity, refractive index, viscosity, iodine value, hydroxyl value, saponification value of the developed polymers were performed as per standard reported laboratory methods^{6,12}. The structural

Table 1: Physico-chemical characterization of MASO

S. No.	Characteristic	MASO
1.	Oil content	40
2.	Gardener color	6
3.	Specific gravity	0.93
4.	Refractive index	1.4691
5.	Acid value (mg of KOH)	4.42
6.	Iodine value	134.7
7.	Saponification value	190.8
8.	Fatty acid composition	
	Saturated (Palmitic and Stearic)	11.4
	Unsaturated (Oleic and Linoleic)	88.6

elucidation of the polymer samples were done by spectral analyses. FT-IR spectrum of the MMAPEA was recorded on FT-IR spectrophotometer (Perkin-Elmer Cetus instruments, Norwalk CT, USA) using a NaCl cell. ^1H -NMR and ^{13}C -NMR spectra were recorded on JEOL GSX 300 MHz FX-1000 spectrometer using deuterated chloroform as a solvent and tetramethyl silane (TMS) as an internal standard.

Preparation of coatings

Coatings of MMAPEA resins were prepared on mild steel strips, 70x25x1 mm size for

physico-mechanical test and 30x10x1 mm size for chemical/corrosion resistance test. The mild steel strips were polished on various grade of silicon carbide papers, then washed with distilled water, degreased with alcohol and carbon tetrachloride. They were dried under vacuum for several hours. The coatings were developed on these specimens by brush technique using a solution of 60 wt % of resins. Coated strips were baked at 160 °C for 20 minutes. Elcometer (Model 345; Elcometer instrument, Manchester, UK) was used to measure the coating thickness. The thicknesses of these coatings were found between 75± 5µm. The coated

Table 2: Physico-chemical characterization of HEMAFA, MAPEA and MMAPEA

Properties	HEMAFA	MAPEA	MMMPEA -10	MMMPEA -15	MMMPEA -20	MMMPEA -25	MMMPEA -30
Gardener color	6	8	7	6	6	6	6
Specific gravity	0.938	0.956	0.968	0.972	0.974	0.978	0.980
Inherent viscosity	1.4697	0.612	0.626	0.636	0.648	0.652	0.656
Refractive index	1.4697	1.5062	1.5088	1.5098	1.5128	1.5132	1.5136
Acid value	-	7.42					
Iodine value	65.80	36.80	32.80	31.52	30.22	29.44	27.68

Table 3: Physico-mechanical and chemical/corrosion resistance properties of AAMAPEA coatings

Resin code ^a	Scratch hardness (Kg)	Impact resistance (lb/in)	Bending test (1/8')	Chemical/corrosion resistance ^b				
				Gloss at 45°	H ₂ O 10 days	HCl (5 %) 10 days	NaOH (3%) (3hrs)	NaCl (3.5 %) 10 days
MMMAPEA-5	1.5	100	Pass	42	C	B	A	C
MMMAPEA-10	2.5	150	Pass	48	D	D	B	C
MMMAPEA-15	3.0	200	Pass	58	E	D	C	D
MMMAPEA-20	3.5	200	Pass	68	E	E	D	D
MMMAPEA-25	3.5	200	Pass	68	D	D	C	D
MMMAPEA-30	3.5	150	Fail	66	D	C	C	C

aLast digit indicates the loading of MMA in phr,

bA= film completely removed; B= film cracked and partially removed; C=loss in gloss; D=slight loss in gloss; E= unaffected

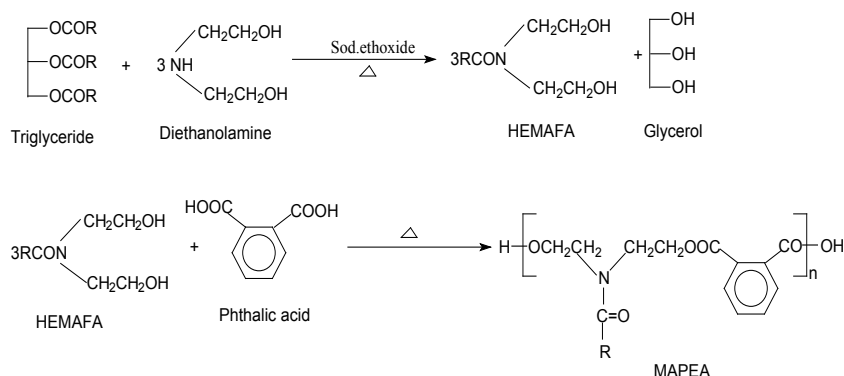


Fig. 1: Synthesis of polyesteramide (MAPEA) R= Long alkyl chain of fatty acid of oil

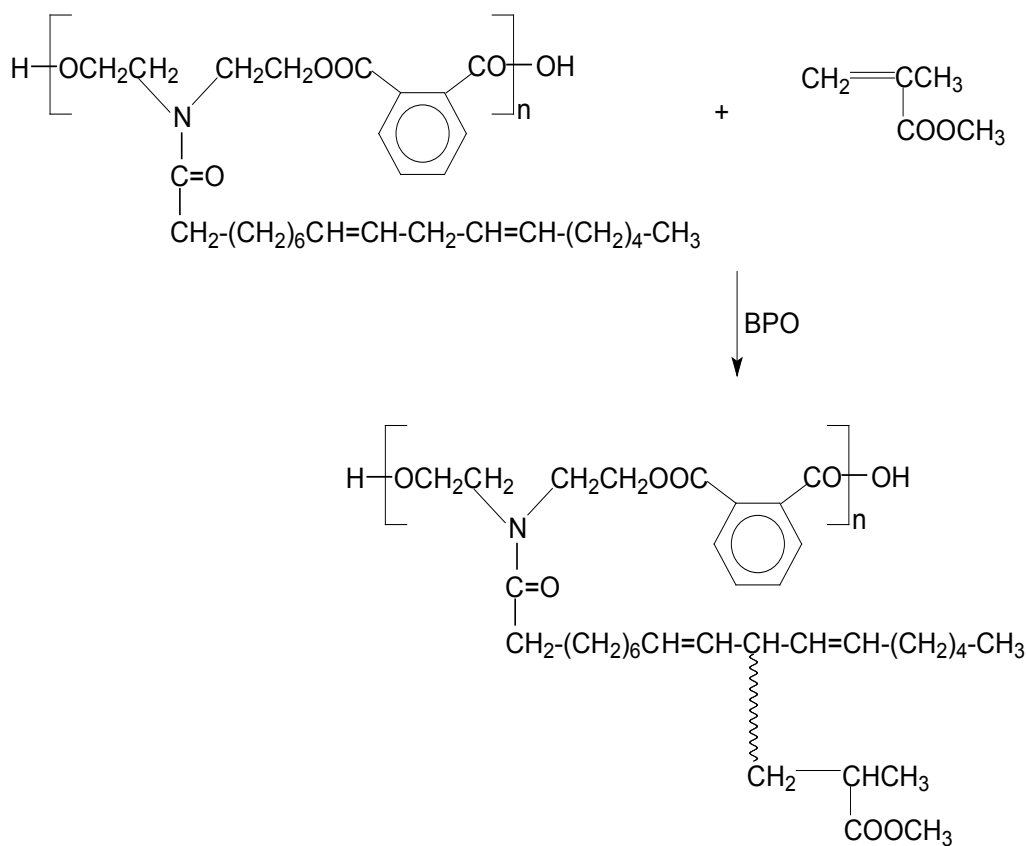


Fig.1: Reaction scheme for formation of MMAPEA

samples were evaluated for the scratch hardness (BS 3900), bending test on conical mandrels and impact resistance (IS: 101 part 5/Sec.31988) tests. The salt spray test (ASTM b117-94) was performed in a salt mist chamber containing 3.5 wt% NaCl

solutions. Chemical resistance tests of the coating samples were performed in water, acid (5 wt % HCl), alkali (5 wt% NaOH) by placing them in 3 in. diameter porcelain dishes, in aforementioned media. Periodic examinations were performed until coatings showed

visual evidence of softening, deterioration in gloss, discoloration or weight loss. The results of these investigations summarized in Table 3.

RESULTS AND DISCUSSION

Figure 1&2 illustrate the reaction schemes for the synthesis of HEMAFA, MAPEA and MMAPEA. The MAPEA was synthesized by the aminolysis of MASO with diethanol amine followed by the step-growth polymerization of HEMAFA with phthalic acid. MAPEA resin was then treated with methylmethacrylate in different phr (Table 2) to obtain a series of MMAPEA resins. Methylmethacrylate was grafted at allylic position of non-conjugated fatty acid chain, free radicals serve to modify the growth of methylmethacrylate chain by chain transfer mechanism. The analytical analyses revealed that acid values of the reaction mixture decreases progressively during the conversion of HEMAFA to MAPEA. This is due to formation of repeating ester linkages during the condensation polymerization. On perusal of Table 2 it reveals that, iodine value decreases gradually on increasing the MMA (phr) content but remain constant for the same amount of MAPEA in the reaction. These observations indicate that grafting occur at allylic position without affecting the unsaturation of fatty amide.

IR spectrum of MMAPEA shows the broad band at 3410 cm^{-1} for the O-H stretching vibration, band at 3080 cm^{-1} for Ar-H, bands at 2964 cm^{-1} and 2858 cm^{-1} for CH_2 asymmetric and symmetric stretching vibrations respectively. The bands for carbonyl of repeating ester linkages, ester of methacrylate and amide are appear at 1764 cm^{-1} , 1749 cm^{-1} and 1652 cm^{-1} respectively. The characteristic bands of aromatic ring appears at $1598, 772\text{ cm}^{-1}$. ^1H NMR spectrum of MMAPEA shows the peaks at $\delta = 7.38\text{-}7.62\text{ ppm}$ due to aromatic protons of phthalic acid while proton of double bonded carbons appear at $\delta = 5.42\text{-}5.46\text{ ppm}$. CH_2 attached to nitrogen of amide appear at $\delta = 3.78\text{-}4.12\text{ ppm}$ where as allylic methylene and methine protons appear at $\delta = 2.52$ and 2.94 ppm respectively. Sharp peak for CH_2 adjacent to ester appears at $\delta = 2.14\text{ ppm}$, fatty amide chain CH_2 appear as multiplet at $\delta = 1.32\text{-}1.56\text{ ppm}$ and proton of terminal methyl

group at $\delta = 0.96\text{ ppm}$. ^{13}C NMR spectrum show the peaks at $\delta = 172.8\text{ ppm}$, 170.4 ppm and $\delta = 164.8\text{ ppm}$ for the carbonyls of repeating ester, ester of methacrylate and amide. Closely spaced peaks at $\delta = 132.2\text{-}128.4\text{ ppm}$ due to carbon of aromatic ring^{18,24}. Double bonded carbons appear at $\delta = 132.4\text{-}126.2\text{ ppm}$ where as carbons of allylic methine and methylene appears at $\delta = 54.2$ and $\delta = 46.4\text{ ppm}$ respectively. Peaks for chain CH_2 of fatty amide appears at $\delta = 29.8\text{-}24.6\text{ ppm}$ while carbon of terminal methyl group appears at $\delta = 14.6\text{ ppm}$.

Coating properties

The films of MMAPEA containing different phr of MMA (Table 3) developed on the mild steel panels to investigate the physico-mechanical as well as chemical/corrosion resistance performances. Scratch hardness values were found to improve appreciably on increasing the MMA content in MAPEA up to 20phr. This is due to increase of pendent ester groups of MMA which provides sites for cross-linking as well as impart adhesion of polymeric resins towards the metal surface. However, beyond this loading of MMA improvement in these properties were negligible. All the coated samples show the good impact resistance and this property further improved remarkable up to the 20 phr loading of MMA, reasonably due to increase of polar groups in the MMAPEA which impart good adhesion between the coating material and metal surface. However above than 20 phr loading of MMA in the polymeric resin no significant improvement was observed. Furthermore, it has been observed that loading of MMA beyond 30 phr coating materials loss the fluidity and become unbrushable lumpy aggregates were formed. This is due to excessive electrostatic attractions among polar groups of different polymeric chains. Gloss values of polymeric films increases on increasing the amount of MMA, which expected for acrylate based coating materials and increased density of cross linking^{14,23}. The polymeric films pass the bending test on 1/8 conical mandrel up to the loading of 25 phr of MMA, a characteristic of vegetable oil based coating materials. Small cracks were observed in case of MMAPEA-30 presumably due to the excessive cross-linking which makes the film brittle. Table 3 indicates that chemical resistance ability of MMAPEA improved up to 20 phr of MMA.

MMMAPEA-20 among all MMMAPEA systems shows the best performance in water, acidic solution and salt solution. On perusal of Table 3 it has been observed that chemical resistivity of the polymer film not significantly improved after 20 phr loading of MMA where as start to deteriorate on increasing the component of MMA more than 25 phr. This is reasonably due to excessive cross-linking made the film not only brittle but also a cause of shrinkage of the film at edges. Coatings of MMMAPEA show inferior performance in alkaline medium like other oil based coating materials due presence of saponifiable ester linkages.

CONCLUSION

From this study it can be concluded that the non-edible, non-traditional and annually renewable significantly born of nature *Melia azedarach* seed oil can be utilized for the synthesis

of methylmethacrylate modified poly (ester-amide) resins. The synthesized resins were characterized by physico-chemical analyses and spectral studies. Physico-mechanical performances and corrosion/chemical resistance ability of the polymeric films were also investigated. Films of MMMAPEA resins show good performances in acidic, humid and saline environments. Furthermore, MMMAPEA-20 shows the best performance among all MMMAPEA resins. Studies show that methylmethacrylate modified Poly (ester-amide) derived from MASO is a practicable material for the coatings and paints.

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