



Synthesis and Characterization of Polyesteramide Urethane Derived from Melia Azedarach Seed Oil

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ABSTRACT

Polyesteramide urethane resin has been synthesized from a nontraditional Melia Azedarach seed oil. The oil converted to N,N-bis (2-hydroxy ethyl) maleia azedarach oil fatty acid (HEMFA) by reacting with diethanol amine. HEMFA reacted with phthalic acid to obtain Melia Azedarach polyesteramide (MAPEA). The MAPEA treated with toluene-2,4-diisocyanate (TDI) in different ratios to synthesize polyesteramide urethane (MAPEAU). The optimum wt-% ratio of the TDI to the MAPEA is selected on the basis of fluidity and film properties of the MAPEAU. The synthesized intermediates and final resin have been characterized by FT-IR, ¹HNMR spectroscopic analyses and by the measurement of physico-chemical properties like specific gravity, refractive index, acid value, iodine value, saponification value.

Key words: Melia Azedarach, Vegetable oil, Polyesteramide, Urethane

INTRODUCTION

Vegetable oils have attracted renewed attention as a raw material for the preparation of commercial polymers¹⁻³. These polymers can offer versatile applications in the field of coatings and adhesive⁴⁻⁷. The utilization of vegetable oils in the manufacture of useful polymer based end product solves not only the problem of waste disposal but it also helps in bringing down the cost of the products^{8,9}. Vegetable oils are triglycerides of different saturated and unsaturated fatty acids and have been widely used in making alkyd, polyester, epoxy, polyesteramide resins¹⁰. The oil of different seeds like linseed, castor, soybean, sunflower, pongamia glabra etc. have been largely used as starting materials in

making many valuable polymers^{10,11}. Polyurethane resins as a class are well recognized for their excellent adhesion, flexibility, weather resistance and resistance to chemical and solvent attack¹². In addition to the presence of urethane linkages in polyesteramides also makes it feasible to cure it at ambient temperature^{13,14}.

Melia azedarach (Bakain) is a moderate sized tree. It is found growing wild in the sub-Himalayan tract up to 1800 meters. Under natural conditions the plants regenerate freely from seeds during the rainy season. The plant has great utility with reference to its wood and is largely cultivated by the farmers in rural areas. Melia Azedarach tree also yields non-edible seeds which contain about

40 % oil content with sufficient unsaturated fatty acid¹⁵. Literature survey reveals that oil of this seed still wait for satisfactory utilization especially in making polymers^{6-8,14}. Keeping these facts in mind in present communication we make an effort to utilized the vegetable seed oil in making polyesteramide urethane.

EXPERIMENTAL

Materials

The seeds of *Melia Azedarach* were collected from the different places of the shahjahanpur district. The oil was extracted from the dried and crushed seeds through the soxhlet apparatus using petroleum ether as a solvent (60-80°). The fatty acid composition and the results of the physico-chemical characterizations are summarized in the Table 1. Phthallic acid, diethyl ether, methanol were used of analytical grade (Merck-India). Diethanol amine of analytical grade procured from the S.D. Fine chemicals India and was distilled under reduced pressure before use.

Syntheses

Synthesis of N,N-bis (2-hydroxy ethyl) Melia Azedarach oil fatty acid (HEMFA)

Diethanol amine 0.007 mol was taken in four necked round bottom flask fitted with an electrical stirrer, thermometer, dropping funnel and condenser. The reaction mixture was heated at 180±5 °C. The Melia azedarach oil (0.1 mol) was added drop wise into the reaction mixture over a period of one hour. The progress of the reaction was monitored by TLC. After the completion of the reaction the product was dissolve in diethyl ether and washed with dilute aqueous sodium chloride solution. The ethereal solution filtered and evaporated in rotatory vacuum evaporator to obtained HEMFA.

Synthesis of Melia Azedarach Polyesteramide (MAPEA)

HEMFA and phthalic acid in equal molar ratio and xylene as a solvent were placed in four necked round bottom flask fitted with a Dean-stark trap thermometer and mechanical stirrer. Reaction mixture was heated up to 200±5 °C. The progress of reaction was monitored by taking the acid value¹² at regular intervals. After the completion of reaction the product was taken out from the reaction flask

and excess of xylene was remove under reduce pressure to obtain MAPEA.

Synthesis of urethane modified Polyesteramide (MAPEAU)

Polyesteramide of Melia Azedarach seed oil dissolved in xylene were placed in four necked round bottom flask fitted with Dean-stark trap, thermometer and mechanical stirrer. The toluene-2,4-diisocyanate (TDI) added to reaction mixture in different wt-% ratio of the polyesteramide given in Table 2. The progress of reaction was monitored by the thin layer chromatography and also by the determining the acid values and hydroxyl values at different intervals.

Test methods

Physico chemical characterizations of HEMFA, MAPEA and MAPEAU were performed as per standard laboratory methods. The structural elucidation was carried out by FT-IR, ¹HNMR spectroscopic techniques. The FT-IR spectra of these materials were taken on Perkin Elmer 1750 FT-IR spectrometer (Perkin Elmer Cetus instruments Norwalk CT) using NaCl cell. ¹HNMR spectra of the resins were recorded on Jeol GSX 300 MHz FX-1000 spectrometer using deuterated chloroform and DMSO as a solvent and tetra methyl silane as an internal standard. The polymeric films were developed on standard strips of 70x25x1mm size for the bending test.

RESULTS AND DISCUSSION

Figure 1(a&b) show the scheme for the preparation of HEMFA, MAPEA and MAPEAU. Significant increase in the hydroxyl value indicates the conversion of triglyceride into diol. The IR spectrum shows the strong band at 3410 cm⁻¹ (broad band for primary alcoholic group). The additional band for carbonyl of amide appears at 1640 cm⁻¹ indicated the formation of amide linkage. The characteristic band for the chain CH₂ symmetric and asymmetric stretching appears at 2850-2925 cm⁻¹.

The ¹HNMR spectrum of HEMFA show the peak at δ=3.5ppm for the CH₂ attached to the nitrogen of amide, CH₂ attached to hydroxyl group appears at 4.2 ppm. The multiplet peak for proton of double bonded carbon appears at 5.4-5.6 ppm. In

addition to these peaks terminal methyl group appears at 0.93 ppm and aliphatic chain CH_2 appears at 1.2-1.60 ppm.

The IR spectra of MAPEA shows band at 1740 cm^{-1} for the carbonyl of ester in addition to band at 1638 cm^{-1} of the amide confirm the formation of ester linkage. The other characteristic bands like band at 3380 cm^{-1} appears for alcoholic group, 2921 cm^{-1} and 2856 cm^{-1} for asymmetric and symmetric CH_2 groups where as the characteristic band for the disubstituted benzene ring appears at 770 cm^{-1} .

The ^1H NMR spectrum of MAPEA show the sharp peak of chain $-\text{CH}_2-$ adjacent to carbonyl of ester at 2.04 ppm, peak for the $-\text{CH}=\text{CH}-$ at $\delta=5.29-5.36$ ppm, aromatic proton appears at $\delta=7.30-7.48$ ppm, broad peak for chain $-\text{CH}_2-$ appears at $\delta=1.26-1.30$ ppm, terminal $-\text{CH}_3$ appears at $\delta=0.86$ ppm.

In the IR spectrum of the MAPEAU a more spread band appears at $3510-3180\text{ cm}^{-1}$ due to overlap of $-\text{OH}$ and $-\text{NH}$ groups. In MAPEAU the $-\text{NH}$ deformation mode appears at 1557 cm^{-1} . The band for carbonyls of ester appears at 1720 cm^{-1} where as carbonyl of amide appears at 1648 cm^{-1} . The characteristic band for the benzene ring appears at $1525, 1529, 1545\text{ cm}^{-1}$.

^1H NMR spectrum of the MAPEAU show the terminal methyl group aliphatic chain at $\delta=0.9$ ppm, where as the methyl group of the TDI appears at $\delta=2.1-2.14$ ppm. CH_2 adjacent to ester appears at $\delta=1.5$ ppm, CH_2 adjacent to amide appears at $\delta=1.62$ ppm and CH_2 adjacent to $-\text{C}=\text{C}-$ appears at $\delta=2.0-2.07$ ppm¹⁶.

Film property

The results of the experiment show that on increasing the wt% of TDI in the polymer the

Table 1: Characterization of MASO, HEMFA, MAPEA

S.No.	Characterization	MASO	HEMFA	MAPEA
1.	Oil Content	40		
2.	Gardener color no.	6	6	8
3.	Specific gravity	0.930	0.938	0.950
4.	Refractive index	1.4691	1.4697	1.5070
5.	Iodine value	134.7	65.8	36.2
6.	Acid value	4.45	-	7.00
7.	Saponification value	190.8	-	148.0
8.	Fatty Acid composition			
	Saturated (Palmitic and Stearic acid)	11.4 %		
	Unsaturated(Oleic and Linoleic)	88.6 %		

Table 2: Physico-Chemical characterization of Polyesteramide urethane resins

S. No.	Resin Code*	Acid Value (mg KOH)	Saponification value	Iodine value	Specific gravity	Refractive index
1.	MAPEAU-2	6.22	146	34.2	0.962	1.5080
2.	MAPEAU-3	6.14	142	32.8	0.966	1.510
3.	MAPEAU-4	6.02	138	30.4	0.968	1.514
4.	MAPEAU-5	5.88	136	28.2	0.972	1.518
5.	MAPEAU-6	5.74	132	26.8	0.974	1.520
6.	MAPEAU-7	5.68	130	24.4	0.976	1.520

*Last digit indicates the wt-% of TDI

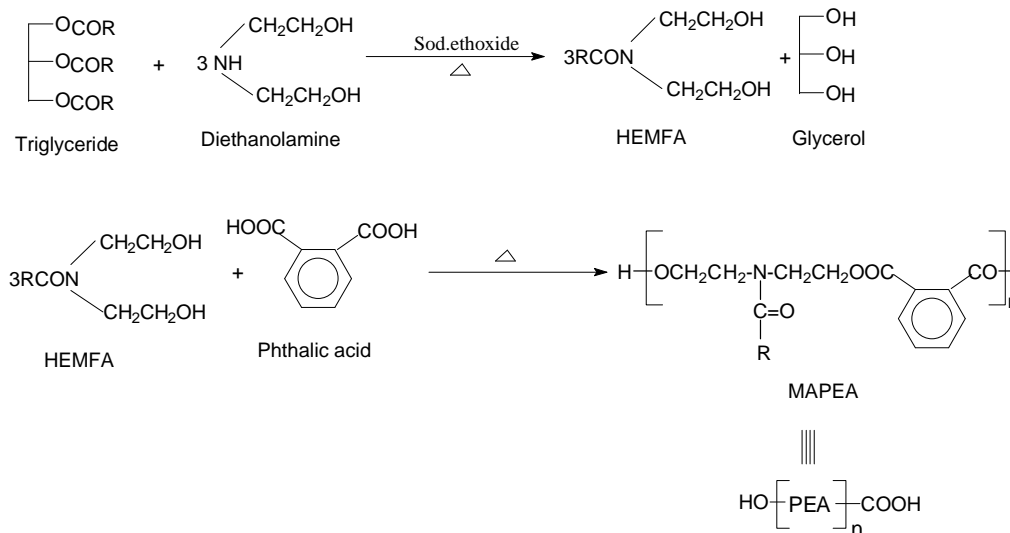


Fig. 1(a): Synthesis of Melia azedarach polyesteramide (MAPEA)

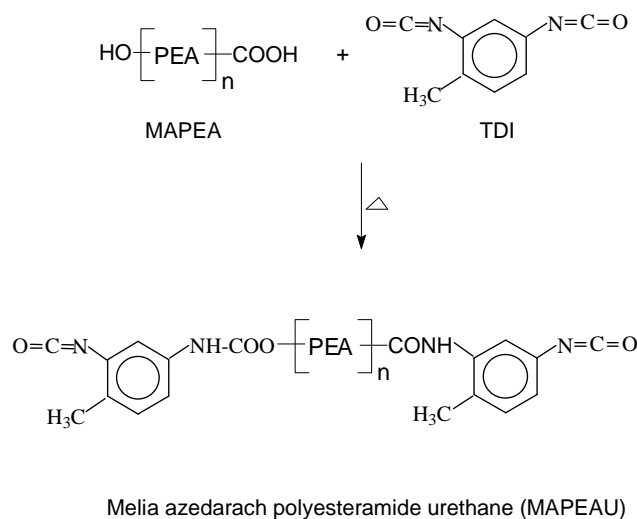


Fig. 1(b): Synthesis of Melia azedarach polyesteramide urethane

drying time decreases however at the same time viscosity of the polymer increases progressively. Therefore more and more solvent required while applying the coating materials. It has been found that after 7-wt % loading of the TDI resulting polymer forms lumpy aggregates and become unbrushable¹³. This is presumably due to excessive network formation. Furthermore polymeric film obtained by loading of TDI more than 6-wt% does not pass the bending test on 1/8 conical mandrel.

CONCLUSION

Polyesteramide obtained from nontraditional seed oil Melia azedarach, provides suitable utilization of significant born of the nature. Incorporation of the urethane linkage in the polymer not only improves the performances but also make it curable at room temperature. Preliminary results indicate that urethane obtained by 6-wt % loading of TDI is most suitable polymeric resin for the coating.

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