



ORIGINAL ARTICLE

**Studies on poly (ester-amide) derived from succinic acid and fatty amide diol of
Melia azedarach seed oil- An Eco-friendly development**

A. Hasnat

Natural product and polymer research laboratory, Department of Chemistry,
Gandhi Faiz-E-Aam College (Affiliated to M.J.P. Rohilkhand University), Shahjahanpur-
242001 U.P. India
Email: hasnatgfc@rediffmail.com

ABSTRACT

Over the past few years efforts have been made to develop eco-friendly biopolymers from the natural renewable resources throughout the world with the objective to arrest the dependency on petrochemicals and also reduce risk of environmental pollutions. Synthesis of polymers of practicable utilities from the non-edible and non-conventional vegetable oils a precursor of natural renewable resource solves the problems of waste disposal as well as bringing down the cost of end products remarkably. In present work, *Melia azedarach* seed oil (MASO) is utilized for the preparation of poly (ester-amide) (MAPEAS) through the amidation with diethanolamine followed by poly (condensation) polymerization with succinic acid. The MAPEAS resin was characterized by physic-chemical analysis as per standard laboratories methods. The formations of ester as repeating linkage was also confirm by FT-IR spectroscopy. Physic-mechanical and chemical/corrosion resistance performances of the MAPEAS polymeric films were investigated.

Key words: Renewable resource, *Melia azedarach* seed oil, Poly (ester-amide), coatings

Received: 02nd August, 2016, Revised: 19th August. 2016, Accepted: 26th August. 2016

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How to cite this article:

Hasnat A. (2016): Studies on poly (ester-amide) derived from succinic acid and fatty amide diol of *Melia azedarach* seed oil-an eco-friendly development. *Annals of Natural Sciences*, Vol. 2[3]: September, 2016: 1-5.

INTRODUCTION

The consumers and industries interest in the development of environment friendly materials have catapulted agricultural resources as feed stocks for the chemical industries [1]. Now-a-days due to interdisciplinary approaches through research and development in biosciences, synthetic chemistry, biotechnology, it is possible to architect the eco-friendly materials from natural resources. Numerous renewable resources like starch, lactic acid, proteins, lignin, chitosen, vegetable oils and many others have used in development of polymeric materials of practical utility [2-6]. Among different renewable resources vegetable oils especially those obtained from the seeds of different plants spotted by the researchers largely due to their unique properties, functionalities, eco-toxicity towards human beings and worldwide abundant availability [7].

Seed oils such as linseed, sunflower, castor, soybean, coconut, and many others have already been utilized in making useful polymers [7-9]. Among these oils some of them have medicinal values and edible too. Therefore, it is desired to explore the spectrum of nature's blessings and utilized the non-edible, nontraditional vegetable oils in the syntheses of usable polymers. This will ultimately helpful in the establishment of equilibrium of demand and availability of feed-stock as well as provides useful application to the waste materials rotting away in every plantation seasons.

Melia azedarach is a medium sized tree, belongs to the family *meliaceae* and largely cultivated in rural areas due to its valuable timber [10 and 11]. The seeds of plants contain about 40-wt % triglyceride oil of unsaturated and saturated fatty acids. The physic-chemical analyses results show that oil has sufficiently high iodine value, suitable for the synthesis of viable polymers of film forming characteristics [7]. Meager utilization of *Melia azedarach* seed oil (MSO), especially in the polymer syntheses encourages us to utilize this triglyceride oil in the synthesis of poly (ester-amide) using succinic acid as a dibasic acid [12-14]. Polyesteramide resins are amide modified alkyds contain both repeating ester and pendent amide linkages, known for improve performances over alkyds in terms of hardness, water vapor resistance and chemical resistance [15 and 16]. In present communication efforts have been made to utilize the *Melia azedarach* seed oil in synthesis of poly (ester-amide) resin using succinic acid as the poly acid with the double objectives to provide practicable utilization of significantly gifted by the nature and solve the problem of waste disposal.

EXPERIMENTAL TECHNIQUE

MATERIALS:

Oil was extracted from air dried and crushed seeds of *Melia azedarach* collected from the different places of Shahjahanpur district, UP, India, through a soxhlet apparatus, using petroleum ether (boiling point range 60-80 °C) as a solvent [13]. Succinic acid, xylene, methanol, diethyl ether (Merck, India), and diethanolamine were used of analytical grade (S.D. Fine Chemicals, India).

SYNTHESES:

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

HEMAFA was synthesized and characterize as per previously reported method [13].

***Melia azedarach* poly (ester-amide) from succinic acid (MAPEAS)**

MAPEAS was synthesized using poly (condensation) technique between polyol and polyacids [17]. HEMAFA and succinic acid in equal molar ratio along with xylene as a solvent were placed in a four necked round bottom flask attached with a Dean-Stark trap, a thermometer and a mechanical stirrer. Reaction contents were heated up to 170 °C and maintain till the completion of the reaction. The progress of reaction was monitored by determining the acid values periodically [18]. After the completion of reaction, the reaction content allowed to cool at room temperature under stirring. Finally the product was taken out from the reaction flask and excess of xylene was removed under reduced pressure using a rotary vacuum evaporator to obtain MAPEAS polymeric resin.

CHARACTERIZATION:

Polymeric resin was characterized by physic-chemical analyses such as specific gravity, refractive index, viscosity, acid value and iodine value as per standard laboratory methods. The formation new moiety while polymerization reaction was also confirmed by FT-IR spectrum. FT-IR spectrum of the MAPEAS was recorded on FT-IR spectrophotometer (Perkin-Elmer) using a NaCl cell.

PREPARATION OF COATING SPECIMENS:

Coatings of MAPEAS polymeric resin were developed on mild steel strips, 70x25x1 mm size for physic-mechanical tests and 30x10x1 mm size for chemical/corrosion resistance tests [16]. The mild steel strips were polished on various grades of silicon carbide papers, washed with distilled water and finally 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 polymeric resins. Coated samples were baked at 170 °C for 25 minutes. The coated specimens were subjected for

bending test on conical mandrel, the resistance to scratch hardness (BS 3900). Chemical and corrosion resistance tests were performed in water, acid (5-wt% HCl), alkali (3-wt% NaOH) and salt (3.5-wt% NaCl) by placing them in 3 in. diameter porcelain dishes, in aforementioned media and investigations were carried out at regular intervals until coating showed visual evidence of deterioration in gloss, softening, discoloration or weight loss and any other visual changes (Table 1).

Table 1: Physic-chemical, mechanical and chemical/corrosion resistance properties of MAPEAS polymeric resin

Test	MAPEAA
Physic-chemical and mechanical properties	
Color value	8.0
Specific gravity	0.952
Refractive index	1.504
Acid value (mg KOH/gm)	9.26
Iodine value	44.64
Bending test (1/8 in)	Passes
Scratch hardness (Kg)	1.2
Chemical/corrosion resistance*	
H ₂ O (10 days)	C
HCl (5-wt%) 10 days	C
NaOH (3-wt%) 2 hrs	B
NaCl (3.5-wt%) 10 days	B

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

RESULTS AND DISCUSSION

Reaction scheme for the synthesis of MAPEAS is depicted in Figure 1. MAPEAS polymeric resin was obtained by the amidation of MASO with diethanolamine followed by the poly (condensation) reaction with succinic acid. Collection of water in Dean-Stark trap during the reaction and results of physic-chemical analyses such as decrease in hydroxyl value as well as acid value indicates the formation of repeating ester linkages through the poly (condensation) of carboxyl and hydroxyl groups of polyacid and polyol respectively. The chain lengthening of the MAPEAS was also supported by its physical properties such as progressive increase in viscosity and specific gravity.

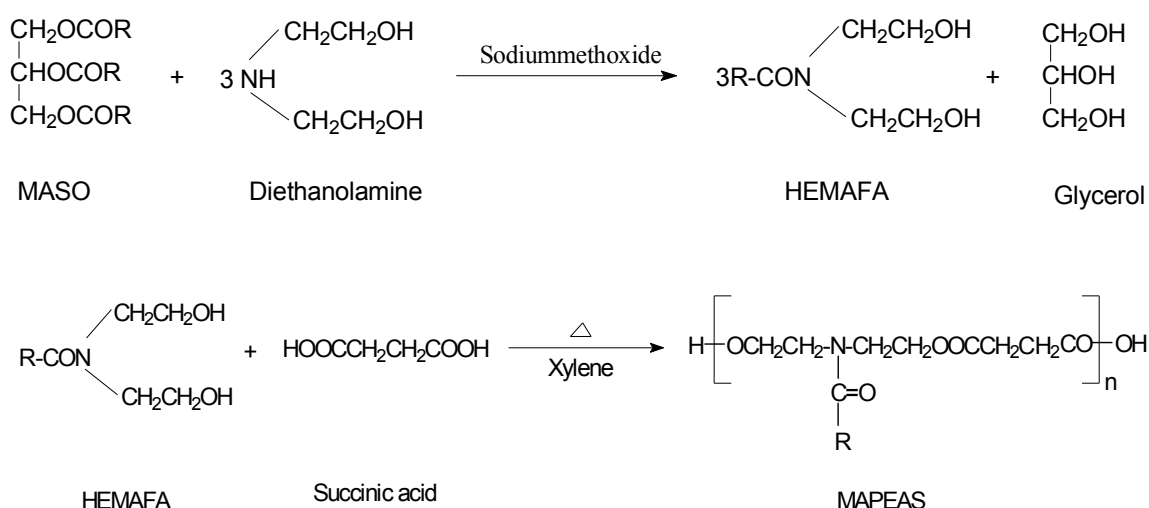


Fig. 1: Reaction scheme for the synthesis of MAPEAS

The FT-IR spectrum of MAPEAS shows characteristic band for carbonyl of ester at 1768 cm⁻¹ in addition to band of carbonyl for amide at 1646 cm⁻¹, confirms the formation of

ester linkage by the poly (condensation) of carboxylic groups of polyacid and hydroxyl groups of polyol [19]. The other characteristic bands like band at 3420 cm^{-1} for terminal alcoholic group, bands for CH_2 asymmetric and symmetric at 2936 cm^{-1} and 2864 cm^{-1} respectively.

FILM PROPERTIES:

The films of MAPEAS polymeric resin were prepared on the mild steel coupons to study the film characteristic like flexibility, resistance to scratch and chemical/corrosion resistance. Samples of MAPEAS pass the bending test on $1/8''$ conical mandrel, no visual cracks were found expected for oil based coating materials containing long alkyl groups [4 and 16]. The coated samples passes scratch harness test more than 1.0 kg. This is reasonably due to presence of amide linkages in addition to repeating ester which confer hardness to the polymeric film [5]. On perusal of Table 1 it observed that chemical resistance ability of MAPEAS polymeric resin is fairly good in water, acidic and salty solutions, reasonably due to hydrophobic character imparted by long fatty amide chain.

CONCLUSION

From this study it can be conclude that *Melia azedarach* seed oil, abundantly available can be utilized for synthesis of MAPEAS polymeric resin. The synthesized resin was characterized by physic-chemical analyses as well as formation of ester group as repeating linkages while polymerization was also studied. Physic-mechanical properties and corrosion/chemical resistance performances in different environments of the polymeric films of MAPEAS were investigated. The results reveal that MAPEAS has the prospective of coating materials. The synthesis of MAPEAS, therefore provide a profitable way of utilization of MASO.

ACKNOWLEDGEMENT

The author would like to thanks the authorities of G. F. College, Shahjahanpur, UP, India for providing necessary facilities to carry out this study.

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