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Synthesis and anticorrosion study of bio-based polyurethane coatings

Abstract

In the present work, bio-based polyol resin was prepared from the non-edible castor oil with reaction of diethanol amine. The prepared polyol was utilized in polyurethane synthesis by using different types of diisocynates. The spectral study of synthesized polyol was performed by FTIR. The prepared polyurethanes were coated on mild steel panel and glass plate. The coating properties such as gloss, corrosion, electrochemical, mechanical properties were performed on mild steel plates. While coating films were obtained by peeling out from glass plates. TGA of coated films was performed for their thermal stability.

Keywords: Biobased polyol resin, polyurethane coating, corrosion, electrochemical property, TGA

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1. Introduction

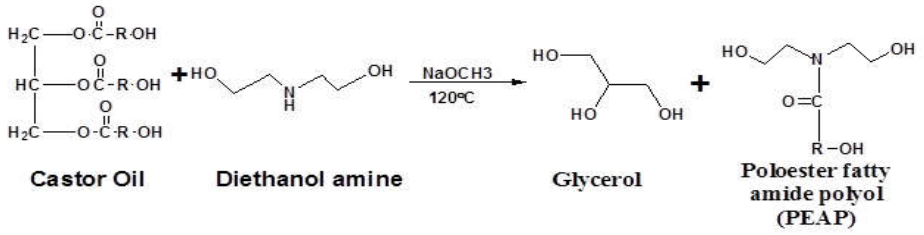
Today there is shortage of fossil fuels resources also they have serious environmental pollution problems. Therefore researchers are attracting their attention towards the renewable natural resources for production of biobased plastics. 1–3 There are various types of natural compounds such as carbohydrates (mainly cellulose and starch) oil, available forbio based polymer synthesis. The varieties of oil-based polymers were synthesized and studied which include spolyolefin, polyester, and polyurethane. Generally Preparation of oil-based polyurethanes is fulfilled by converting the plant oils into polyols, followed by curing with diisocynate reagents.4–6

The compositions of oil such as saturated, unsaturation and stereochemistry of the double bonds are most important parameters which affects on properties of oil based coatings. Different types of resins prepared from vegetable oils which include alkyds, polyester amides and polyurethanes. Among these polyurethanes has industrial importance. They have various applications in coatings, foams, micro encapsulations. Many researchers utilizes the vegetable oil such as castor oil and copolymers like styrene, methyl methacrylates and others have gained much attention over the last decades due to their interesting properties [5].Various plant oils such as canola, sunflower, soybean, linseed, sunflower and cornwere also used to prepare epoxidized oil followed by polyols [6]. Another routes explored for utilization of plant oils in coatings are in the form of polyetheramides [7] and polyesteramides [8–11]. Polyesteramide of oils have also been reported for preparation of anticorrosive PU coatings [12].

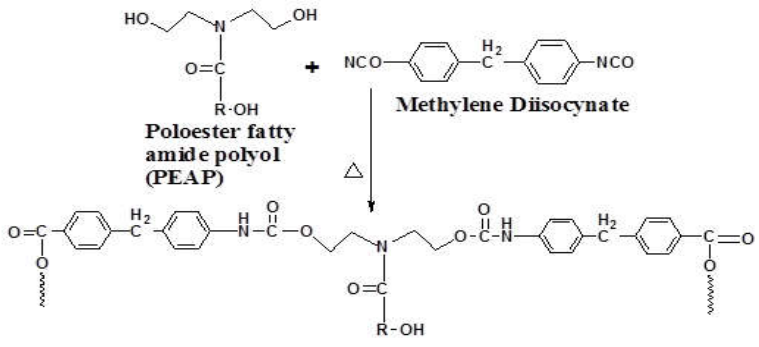
In the present work, polyester amide polyol was synthesized from castor oil. Castor oil contains about 90% ricinoleic acid contains hydroxyl group. Polyol was utilized for PU synthesis using various diisocynate.

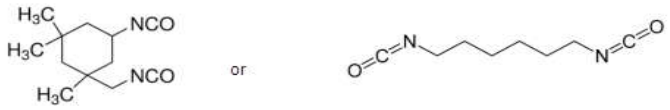
2. Experimental work

Scheme 1- Preparation of Fatty Amide



Scheme 2- Preparation of Polyurethane Coatings





(b) (c)

R= Ricinoleic Acid,

Different types of Diisocynates are used :-

a) Methylene Diisocynate, b) Isophorane Diisocynate c) Hexamethylene Diisocynate

Figure 1: Synthesis of polyester amide polyol (PEAP) and polyurethane of Polyesteramide polyol (PUPEAPM/PUPEAPH/PUPEAPI)

3. Materials

Castro oil, sodium methoxide and diethanolamine were purchased from s.d. fine chemical India. While diisobutyl tin dilaurate (DBTDL) hyexamethylenediisocynate (HDI), methylene diphenyl diisocynate (MDI) and isophoronediisocynate (IPDI) were purchased from Sigma-Aldrich. Solvents tetrahydro furane (THF), Xylene and methyl ethyl ketone (MEK) were purchased from s.d. fine chemical India. All the chemicals used without further purification.

Preparation of fatty amide

Castor oil fatty amide was prepared by reaction with diethanolamine (0.32 M) in the presence of Sodium methoxide (0.007 M) as a catalyst in a 250-mL three-necked round bottom flask. The flask was placed in an oil bath and fitted with an overhead stirrer, thermometer, dropping funnel, and condenser. The three-necked flask was stirred at 80°C for 20 min in the presence of N_2 atmosphere. Castor oil (0.1 M) was then added drop by drop into the reaction mixture over 60 min with constant stirring and a steady increase in temperature up to 120°C. The reaction mixture was then heated for the next 3 h with continuous stirring at 120°C. Product formation was verified by Thin Layer

Chromatography (TLC). Cooled product was dissolved in diethyl ether, washed with 15% aqueous NaCl solution, and dried over anhydrous sodium sulfate. The solvent was evaporated in a rotary vacuum evaporator to obtain fatty amide. [11,12,13]

Preparation of polyurethanes from polyester amide polyol

Polyurethanes (PU) were synthesized by using PEAP and different diisocynates like MDI, IPDI and HDI. The NCO: OH ratio 1.2:1 was maintained for all PU. DBTDL was used as catalyst during PU synthesis. The PUPEAPI was prepared by PEAP dissolving in THF/MEK (3:1v/v) with IPDI and mixed it well. The reaction mixtures applied on the mild steel panels using brush. The coatings were allowed to cure at room temperature for 24 hrs. Further the panels were kept at 70^0C in oven for post curing for 45 minutes. This process repeated for PUPEAPM and PUPEAPH. [15,16]

Characterization

Determination of Acid value and hydroxyl Value of polyester amide polyol

The end group such as hydroxyl ASTM D1957-86 and carboxylic acid were determined by ASTM D 1980-87 respectively. Acid value is defined as the milligram of KOH required to neutralize the amount of acid group present in gram of polymer. The unit of acid number is mg of KOH/g of the polymer. [14]

$$\textbf{Acid Value} = \frac{56.1 * \text{mlofKOHconsumed} * \text{ExactNormalityofKOH}}{\text{Weightofsampleingm}}$$

Hydroxyl number or hydroxyl value of a polymer is defined as the milligrams of KOH required to neutralize the amount of acid produced as result of acetylating (of hydroxyl group) of 1 g of polymer sample (when anhydride is used as an acetylating regent).
Unit of hydroxyl number is mg of KOH/g of polymer. [14]

$$\textbf{Hydroxyl Value} = \frac{56.1 * \text{mlofKOHconsumed} * \text{Exactnormalityof KOH}}{\text{Weightofsampleingm}} - \textbf{Acid Value}$$

FTIR and NMR studies of polyester amide polyol

The functional groups like hydroxyl group and ester of PEAP was characterized by using FTIR (Shimadzu FTIR-8400) on KBr disk. The NMR (Bruker-400 MHz spectrometer) spectroscopy is an important equipment and technique used for determination of structure of PEAP. The spectrum was recorded in dimethylsulfoxide-d6 (DMSO-d6) with tetramethylsilane (TMS) as an internal standard at room temperature.

Characterizations of PU- PEAP Coatings

Gloss

The gloss of PU- PEAP coating panels were measured on calibrated digital gloss meter (BYK Additive &Instruments) at an angle of 60°.

Flexibility test by Conical Mandrel

The flexibility of coating mild steel panels of PU- PEAP were measured by using a conical mandrel instrument (Raj Scientific Co., Mumbai, India).

Pencil hardness

The pencil hardness tester (BYK Additive & Instruments) was used for measurement of pencil hardness of coating panels of PU- PEAP according to the ASTM D-3363 standard.

Crosscut adhesion

In this test, a cross hatch adhesion tester (Elcometer, model 107) was used to determine the adhesion of coatings with the substrate; a crosscut adhesion test of prepared coated panels was carried out using the ASTM D-3359-02 standard.

Chemical resistance properties of coatings

Anticorrosion properties of the coatings were evaluated byimmersion method. Anticorrosion properties of the prepared PUPEAPM, PUPEAPH, and PUPEAPI coatings with different loading were evaluated through an immersion method in an aqueous solution of 2 N HCl, 2NNaOH,3.5 % NaCl, water, and xylene.

4. Results and Discussion

The end group values such as hydroxyl 161 mg of KOH/g of polymer and carboxylic acid 8.5 mg of KOH/g of polymer were obtained.

FT-IR Analysis

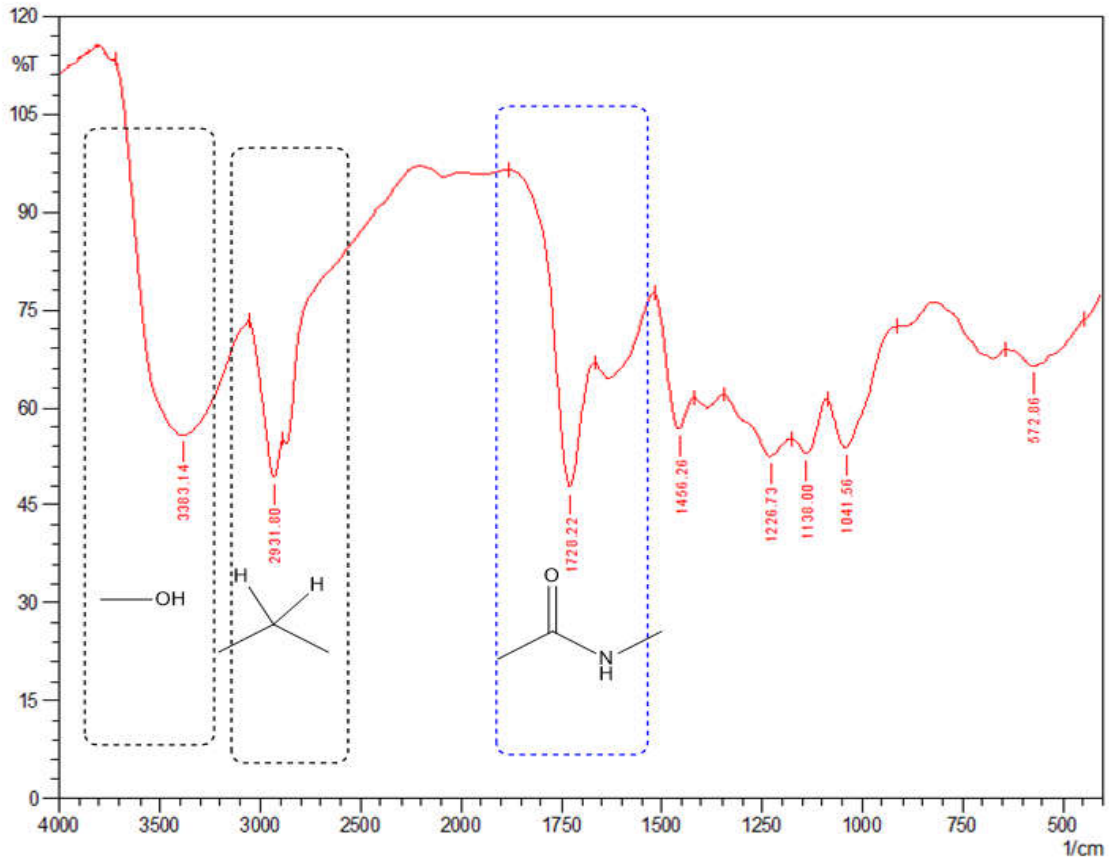


Figure 2: FTIR spectra of PEAP

FT-IR spectra of fatty amide with polyol are shown in figure. There are distinctive absorption bands at 3383.14cm-1 indicates that –OH stretching, the absorption bands at 1728.22 cm-1 and 1625 cm-1 indicates the presence of –C=O stretching in amide. The vibration in methylene groups due to presence of an antisymmetric and symmetric stretching of C-H bond in PEAP obtained between 2864 to 2931 cm^{-1}. [15,16]

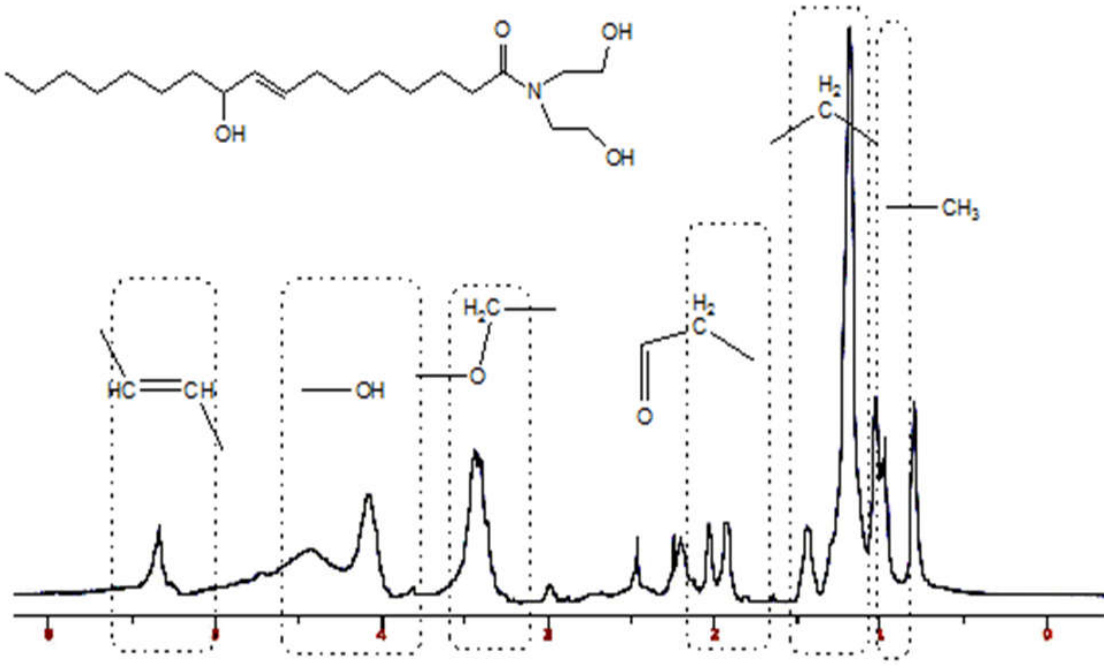


Figure 3: Proton NMR spectra of Fatty amide

Proton NMR spectra shows the different frequencies due to different protons. The vinyl protons (-CH_2=CH_2-) are at 5.4 ppm, hydroxyl proton (-OH) at 4.1 -4.5 ppm, methylene proton attached to oxygen (-O-CH_2-) as well as carbonyl (-CO-CH_2-) at 3.5 ppm and 1.9-2.3 ppm respectively. The methyl proton appears at 0.9 ppm.

Determination of gloss value of PU coating

Coated panels were tested for the gloss measurement at an angle 60° on a digital gloss meter. Before to analysis, the digital gloss meter was calibrated using the standard provided by the manufacturer. [15,16]

Cross cut adhesion, scratch resistance, pencil hardness, and flexibility test

The cross-cut adhesion test, scratch resistance, and pencil hardness test were carried out to determine the coating properties on mild steel panels. In cross-cut adhesion test, there was no detachment of coatings within the square lattice as well as at the edges. This indicated that the coatings encompassed very good adhesion strength may be due to balance molecular structure of resin along with numerous terminal functional groups. The PUPEAPM coatings showed better adhesion, scratch resistance, and pencil hardness on mild steel than PUPEAPI and PUPEAH. This may due to hydrogen bonding and van der wal bonding in between mild steel and the resin molecules. Also the PU-COHBP coatings show high crosslink density. It was clearly observed that the PUPEAPM coatings has secondary pi bond interaction with metal which, that would have enhanced the adhesion strength of the coating than their counterpart. [13,15,16]

All coatings were pass flexibility test due to the presence of oil based soft segment.

Table 1: Gloss and Cross cut adhesion test PU coating

Sr. no.	Sample	Gloss at 60°	Cross cut adhesion (%)	Flexibility test	Pencil hardness	Scratch resistance (Kg)
1	PUPEAPM	-58.72	100	Pass	4B	2.5
2	PUPEAPI	70.03	70	Pass	2B	0.5
5	PUPEAPH	75.25	35	Pass	2B	0.5

Chemical resistance study

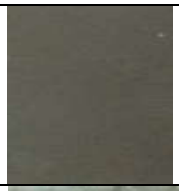
In chemical resistance test were carried in 2N HCl, 2N NaOH, 3.5% NaCl, Water, and xylene. The sample panels were tested initially for 24 h and further extended for a total exposure time of 168 h (7 days). Panel specimens were continuously examined for corrosion inside and at the crossed area of substrate from time to time by visual inspections and recorded using a digital camera (Nikon, 16 megapixels). [13], [15], [16]

The observations are given following table.

Table 2: Chemical resistance study

Sample	2 N HCl (120 hrs)	2N NaOH (168 hrs)	3.5 % NaCl (168 hrs)	Water (168 hrs)	Xylene (168 hrs)
PUPEAPM	f	b	c	a	b
PUPEAPH	e	d	c	a	e
PUPEAPI	f	d	e	b	a
Note: a) Not affected, b) slightly gloss loss, c) complete loss of gloss, d) blistering, e) slightly blistering, f) film completely removed					

Table 3: Illustration of Chemical resistance study

Sample	2 N HCl	2 N NaOH	3.5% NaCl	Xylene	Water
Blank					
PUPEAPM					
PUPEAPH					
PUPEAPI					

5. Conclusion

Castor oil was used as renewable as well as bio-based precursor for preparation of fatty amide successfully. Fatty Amide was characterized by acid value, hydroxyl value, and FTIR analysis. Fatty

amide was used in polyurethane coatings. In this project we studied the polyurethane coatings properties like cross cut adhesion, pencil hardness, scratch resistance, gloss, and chemical resistance study. The coatings are effective to corrosive protective on metal surface for long time. Hence we successfully prepared Bio-based resin from renewable resources.

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