Preparation and Characterization of Poly (urethane amide) Resins from Soybean Oil for Surface Coating Applications as Renewable Recourses

N. A. Alian

Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.
dr_ossama22@yahoo.com

Abstract: Poly(urethane amide) PUA resins with varying ratio of NCO/OH (0.5: 1 – 2:1) were synthesized from Soybean oil (S.O) with 2,4 toluene diisocyanate (TDI) using dibutyl tin dilaurate (DBTDL) as catalyst in order to tune the final properties of the materials. Methyl esters of soy oil were first prepared by reacting soy oil with dry methanol in presence of sodium methoxide (NaOMe) as catalyst, then the obtained methyl esters were reacted with diethanolamine to give N, N-bis (2-hydroxyethyl) soy fatty amide. The resins have been characterized by FT-IR and ^{1}H NMR spectroscopic analysis. The physicochemical characterization like hydroxyl value, iodine value saponification value and viscosity of poly(urethane amide) resins were carried out by standard methods. The coating performance of the resins was evaluated for film thickness, drying time, adhesion, flexibility, pencil hardness, impact resistance, gloss and chemical resistance properties.

The results show good performance of the poly(urethane amide) resins that hold promise for use as effective surface coating materials.

[N. A. Alian. **Preparation and Characterization of Poly (urethane amide) Resins from Soybean Oil for Surface Coating Applications as Renewable Recourses.** *J Am Sci* 2016;12(10):96-102]. ISSN 1545-1003 (print); ISSN 2375-7264 (online). http://www.jofamericanscience.org. 14. doi:10.7537/marsjas121016.14.

Keywords: Soybean oil; poly(urethaneamide) resins; coating performance; Renewable resource.

coatings vegetable oils are good feed stock for chemical industry due to existence of moieties for chemical conversions, physical and chemical stability, reduced toxicity, biodegradability, eco-friendliness and flexibility. [6-8]

Soy plant is cultivated in Egypt. The seeds contain about 22% oil. This oil possesses mainly triglycerides of linolenic, linoleic, oleic and saturated acids. Soy bean oil is one of the most widely used drying oils in coatings and varnishes [9]. The reactivity of drying oil is determined by the linoleic and the linolenic acid content, and thereby can be quantified from the drying index:

D.I = linoleic % + 2 linolenic %

Where D.I. is the drying index and linoleic % and linolenic % are expressed in weight percentages.

The design of polymers from renewable resources is currently receiving increasing attention and interest has focused on the use of cheap, biodegradable and annually renewable starting materials to reduce petroleum dependence and the negative impact on the environment.

The long fatty acid chains of vegetable oils import desirable flexibility and toughness to some brittle resin system such as epoxy, urethane and polyester resins. Trighlyceride oils are one of the most important sources for biopolymers. Triglycerides from plants, such as soybean, palm, rapeseed or sun flower, can be utilized. Triglycerides are composed of three fatty acid chains joined by a glycerol center, with a typical structure shown in Figure 1 [10].

1. Introduction

Sustainable development had become the key ideal of the 21st century. In the research for sustainable chemistry, considerable importance is being attached to renewable raw materials, which exploit the synthetic capabilities of nature and may eventually substitute for fossil, depleting feed stocks[1]. The encouragement of environmentally sound and sustainable use of renewable nature resources is an important aim of agenda 21[2]. Oils and fats of vegetable and animals origin make up the greatest proportion of the current consumption of renewablenature raw materials is the chemical industry because they offer to chemistry a large number of possibilities for applications that can be rarely met by petrochemistry. In this regard, vegetable oils have a number of excellent properties, which could be utilized in production for variable polymeric materials such as alkyd, epoxy polyesteramide, polyurethane, etc. in addition to many applications in other fields.[3-5]

Vegetable oils are converted into derivatives, for instance, alkyd resins and alkyd based polyols. Polyols are then reacted with different disiocyanates to obtained PU coatings polyurethane are synthesized from vegetables oils obtained from various plant seeds such as neem, caster, cotton, rapes seed palm, soybean other biorenewable resources are also used to make PU coatings along with vegetable oils.

Vegetable oils are also used in coating formulations and as a binder for different kinds of

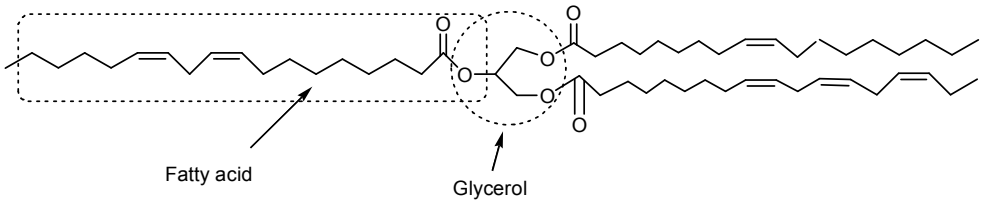


Figure 1. Molecular structure of a typical triglyceride molecule

poly(urethane amide) (SOPUA) were recorded onFourier transform IR (FT-IR) Nicolet Magna – IR 750 spectometer (Madison, WI) using KBr pellet and on a FX-100 NMR spectrometer (Polo Alto CA), using tetramethyl. Silane as the internal standard and $CDCl_3$ as the solvent. (Table 3).

The physico-chemical properties of the resins such as hydroxyl value, iodine value, saponification value, viscosity were determined by the standard methods[17]the drying time and chemical resistance of the cured resins as well as the impact resistance, pencil hardness, adhesion and gloss were determined according to the standard methods[18] (Tables 4, 5).

2.3 Preparation of the resins

2.3.1 Preparation of methyl ester of the soy bean oil[19]

Methyl ester from soy bean oil was prepared by acid catalyzed esterification method in which 100g oil was taken in 500 ml round bottom flask and 300 ml methanol and 1 ml concentrated sulfuric acid were added. The contents were refluxed for 4h. on water bath. At the end of reaction, excess methanol was distilled off and 50 ml distilled water was added. The contents were then transferred to a separating funnel and lower aqueous layer was withdrawn. The upper organic layer was washed 2-3 times with sodium carbonate solution to remove un-esterified fatty acids. The esters were purified by distillation under 4-5 mm Hg pressure.

2.3.2. Preparation of diethanol amide from the methyl ester of the oil (DEASO):

Diethanol amide of the fatty acids of the oil were prepared using the method of Mahapatra S.S.*et al.*[19] 3.45g diethanol amine with 0.5% sodium methoxide (with respect to the ester) was heated to 110-115°C, then the methylester of the oil was added over a period of 1h and heating was continued for another 3h. N,N'-Bis (2-hydroxyethyl soy oil amide)(diethanol amide of the fatty acids) was then purified. The yield was 75%.

2.3.3 Synthesis of soy oil poly(urethane amide) (SOPUA).

A three-necked round-bottomed flask was fitted with a mechanical stirrer, a nitrogen inlet and a dropping funnel. 2.5 g (6.87 mmol) diethanol amide of the fatty acid was added to the calculated amount of polyethylene glycol (PEG) as chain extender and 0.05 wt% DBTDL, as the catalyst (with respect to the diol)

Polyurethane coatings based on vegetable oil with linolenic acid content show better physical properties and vegetable oil based palmitic acid was used as a starting material for biobased polyurethane films and coatings with high transparency.[11]

Polyurethene polymers are a versatile class of polymers which are used in a wide range of applications, and their structure can be tailored to specific requirements. Depending on the hydroxyl value and other characteristics two of the polyol, it can be applied in the development of adhesives, coatings, and flexible or rigid foams. In combination with isocyanates, vegetable oil-based polyols produce polyurethanes that can be compete in many ways with polyurethanes derived from petrochemical polyols, and their preparation for general polyurethane use has been the subject of many studies.[12,15]

Most of the polyurethanes synthesized from vegetable oils are usually based on either polyester polyols to impact sufficient rigidity to the resin or polyether polyols to impact improved flexibility.[14]

This work reports the synthesis and characterization of poly(urethane amide) resins based on soy bean oil by using amide polyols, as it may give better performance in many respects due to the presence of amide bonds instead of ether or ester linkages. The work also hopes to give a good start to produce (not import) polyurethane amide resin based on vegetable oil in Egypt.

2. Experimental

2.1. Materials

The oil used in this work was procured from local market and analyzed for physico-chemical characteristics by standard BIS methods[15](Table 1). Diethanolamine, polyethylene glycol, toluene diisocyanate (TDI), and dibutyl tin dilaurate (DBTDL) (E-Merck, Germany) were used without further purification. All other chemicals used in the study were of reagent grade and used without any purification.

2.2. Instruments and methods

High performance liquid charomatography (HPLC)[16] analysis was made on a Buchi 688 chromatograph with UV detector (Table 1).

The FT-IR and ^1H NMR spectra of diethanolamide of soy oil (DEASO) and soy oil of

bending test using 10-20% poly(urethane amide) resin solution in xylene. The thickness of the coating was measured by pentest, coating thickness gauge (model 1117, Sheen Instrument Ltd. U.K.). The results are given in Table (4) the determination of bending test, adhesion (tape test), impact, gloss and pencil hardness were determined by standard method[21-25] Table (4).

2.4.3. Determination of chemical resistance properties[26,27]

The following solutions with their respective concentrations were used for chemical test.

(1) For acid resistance :20% H_2SO_4 solution
(2) For alkali resistance : 10% NaOH solution
(3) For water resistance : distilled water.
(4) For solvent resistance : benzene/turpentine
(5) For salt resistance : 3.5% NaCl solution

The results of chemical resistance test are furnished in Table 5.

3. Results and Discussion

The reaction steps for the synthesis of the fatty acids methyl ester, the fatty acids diethanolamideand polylurethane amide) resins of the Soybean oilare shown in scheme 1.

Xylene was added to the mixture, and stirring was continued for 10 min at room temperature.

The calculated amount of toluene disocyanate (TDI) (0.5: 1, 1.0:1 1.5: 1, and 2.0: 1) was added dropwise over a period of 15-30 min to the reaction mixture. The mixture was then heated to 40-50°C with stirring until the solution become viscous.

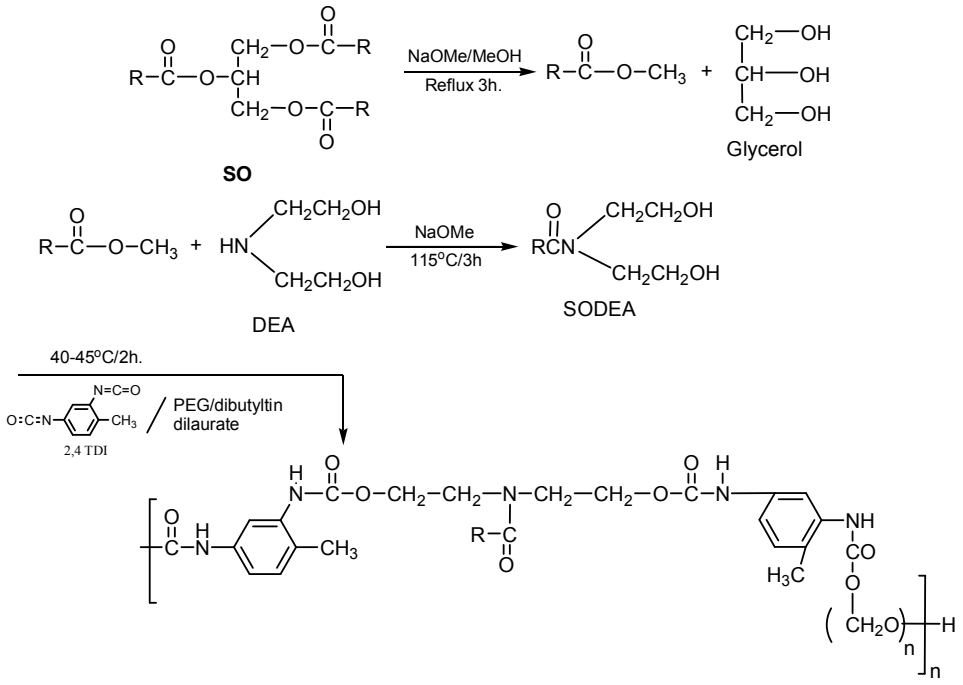
2.4. Performance study

2.4.1 Panel preparation

The mild steel and aluminium panels were first degreased in alkali solution and subsequently swabbed with xylene to remove any type of oily material or contaminant. After the xylene has evaporated, panels were burnished with emery paper as Indian Standards [20]. Panels were again washed with xylene after burnishing to remove any trace of emery paper particles or metal particles. As soon as the panels were dry, coatings were applied on them without any delay.

2.4.2 Film characterization

The coating was prepared at ambient temperature on 75 mm x 25 mm X1.39 mm glass strips for drying air and stove drying and for chemical resistance tests, and on mild steel strips 150 mmx 100 mm x 1.44 mm for gloss, impact, pencilhardness test and on 150 mm x 50 mm x 0.19 mm aluminum strips for adhesion and



DEA : diethanolamine SODEA: Soyoil diethanolamide
SO : Soy oil 2,4TDI: 2,4 toluene diisocyanate
PEG : Polyethylene glycol

Scheme 1. Synthesis of poly(urethaneamide) resin from Soy oil

(DEASO) and the resins of the oil. The formation of the fatty acid methyl ester is indicated by very low

Table 2 illustrates the physicochemical properties of the intermediate, the fatty acids diethanolamide

soybean oil is linoleic acid (18:2) which is the most abundant fatty acid followed by oleic, palmitic linolenic and stearic acids. No attempt was made to separate on purify these products as the goal of the research was to demonstrate the suitability of soy oil for the planned synthesis as its naturally occurring mixture.

3.2. Coating properties

The coated films on the strips were cured at ambient temperature (30 ± 2)°C under atmospheric conditions without using any driers or curing agent.

The results of evaluation of films properties of PUASO resins are shown in Table 4 and 5. From the results given in Table 4 it suggests that these films give good tack-free dry properties. The drying time reduces on increasing the amount of the NCO/OH ratio in the resins. The good drying time can be attributed to the presence of increasing amount of reactive free NCO groups in the resins that react with moisture and subsequently form cross linked products. The dried films were further post cured at 100°C for 1 h and then the coating performance was studied. The best curing performance of PUASO 2.0 resin can be attributed to the high degree of crosslinking formed by the reaction between the free hydroxyl group in the amide and free isocyanate groups. The isocyanate help to link the polymer molecules together and a higher degree of crosslinking occurred because of the presence of free isocyanate groups in the polyurethane resin which react with moisture to form the corresponding aminesthat react further with active hydrogen of the polymer and form crosslinking structure.

The coating performance characteristic of the poly(urethane amide) resins are shown in Table 4. It has been found that the gloss at 60 angle, and adhesion for the resin are very good. Hardness of poly(urethane amide) resins coating showed excellent results because of polyurethane – linkage and aromatic content present in PUASO. The films formed hard structure due to di-functional isocyanate cross linker. Flexibility is the ability of material to be bent or flexed without a cracking or undergoing any failure.

The bending test indicates that all the resins are highly flexible due to the presence of flexible ether linkages in PEG as well as the flexibility of the hydrocarbon chains of the fatty acids of the oil.

PUASO resins showed excellent mechanical properties since it has proper balance of hardness and flexibility due to aromatic linkage. Impact resistance was also excellent because the film passed the flexibility test without any cracking. This may be attributed to adequate contribution of the linear structure of PUASO resins.

The chemical resistance data (Table 5)revealed that the PUASO resins have excellent chemical acid value (0.6 mg KOH/g) and the formation of the fatty acids diethanolamide is evident from their high hydroxyl value as shown in Table 2. It has been found that with the progressive increasing of TDI to the fatty acids diethyanolamide of soy oil, the hydroxyl value of SOPUA decreases, which confirms the reaction of hydroxyl group with TDI. However, the presence of free hydroxyl group indicated that the reaction was not complete.

On the other hand, the decrease in saponification value with the progressive increasing of TDI to the fatty acids diethanolamide of soy oil indicates the increase of molecular weight as supported by viscosity measurements of the resins as shown in Table 2.

3.1. Characterization of fatty acids diethanolamide and poly (urethaneamide) resins for Soy oil.

Thestructure of the intermediate, fatty acid diethanolamide was supported by FT-IR and ^{1}H NMR spectral data as shown in Figures (2,3).

In FT-IR spectrum (Fig. 2), all the important peaks and corresponding groups for DEASO are shown. The appearance of characteristic bands of amide group at 1734 cm^{-1} for (C=O), at 1620cm^{-1} for (–C=C–), at 3375 cm^{-1} [–OH (alcoholic)] and at 2856-2925cm^{-1} for [CH_2(chain)].

The DEASO structure is further confirmed by ^{1}H NMR analysis (Fig. 3) which shows characteristic peaks for –OH (alcoholic) at 5.3 ppm, CH_2 adjacent to amide carbonyl at 2.0-2.3 ppm, CH_2 attached to C=C at 2.0 ppm, CH_2 chain at 1.22-1.28 ppm and CH_3 terminal aliphatic at 0.86 ppm.

The FT-IR spectrum of PUASO 2.0 resin (Fig. 4), even though the OH and NH stretching frequencies are overlapping in the region 3300-3400 cm^{-1}, NH, deformation appears at 1538 cm^{-1}[28]. The other important characteristic peaks are supporting the structures of the resins as shown in the reaction scheme 1.

The appearance of characteristic bands at 1069cm^{-1} for (C–N) and at 763 cm^{-1} for aromatic. Moreover the structure was confirmed by ^{1}H NMR spectrum of the PUASO 2.0 (Fig. 5). Indicated the presence of TDI moiety at 2.7 ppm along with other characteristic groups as CH_3 terminal aliphatic at 0.87 ppm, chain CH_2 at (1.24-1.26) ppm CH_2 attached to C=C at 2.0 and the aromatic at 7.2 ppm, –OH alcoholic at 5.6 ppm and CH_2 adjacent to amide carbonyl at 2.0-2.3 ppm. These observations confirm the formation of PUASO resins through the steps as shown in scheme 1.

The HPLC analysis of the fatty acids found in the soy bean oil used in this work is summarized in Table 1. Soybean oil consists of approximately 12.84% saturated fatty acids that have no carbon-carbon double bond. Most fatty acids (91.39%) is soybean oil are unsaturated. The highest percentage of fatty acid in

not have any hydrolysable functionality as polyester or polyesteramide resins[26].

resistance in all test media except the alkali resistance improved by increasing the NCO/OH ratio in the resins. This may be due to the fact that these resins do

Table 1. Fatty acid weight composition of soybean oil determined by HPLC analysis

Soy fatty acids		Formula	Weight %
Saturated	Plamitic $C_{16:0}$ $CH_3(CH_2)_{14}COOH$	$C_{16}H_{32}O_2$	8.80
	Stearic $C_{18:0}$ $CH_3(CH_2)_{16}COOH$	$C_{18}H_{36}O_2$	2.90
Unsaturated	Oleic $C_{18:1}$ $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	$C_{18}H_{34}O_2$	30.42
	Linoleic $C_{18:2}$ $CH_3(CH_2\text{-}CH=CH)_2(CH_2)_7COOH$	$C_{20}H_{32}O_2$	50.88
	Linolenic $C_{18:3}CH_3(CH_2\text{-}CH=CH)_3(CH_2)_7COOH$	$C_{20}H_{38}O_2$	7.00

Table 2. Physicochemcial Characteristics of soy oil, diethanolamide and poly(urethane amide) resins.

Characteristic	Soy oil	DEASO	PUASO 0.5	PUASO 1.0	PUASO1.5	PUASO 2.0
Colour	Yellow	Transport	Transport	Pale yellow	Pale yellow	Pale yellow
Hydroxyl value (mg KOH/g)	20	255	92.1	85.2	50.2	39.9
Iodine value (giodine/100g)	135	80	60.2	55.5	45.5	43.4
Saponification value (mg KOH/g)	194	220	150.2	120.6	95.5	80.7
Inherent viscosity (dL/g)	--	0.057	0.20	0.25	0.41	0.56

a. Indicates the NCO/OH ratio of the resins

Table 3. FT-IR and ^{1}H NMR spectral data of the diethanol amide fatty acids and poly(urethane amide) resin of Soy oil.

Functional group	**DEASO IR(cm^{-1})**	**DEASO ^{1}H NMR (ppm)**	**PUASO 2.0 IR(cm^{-1})**	**PUASO 2.0 ^{1}H NMR (ppm)**
–OH (alcoholic)	3375	δ5.3	3363	δ5.6
–NH deform	--	--	1538	--
–C=O amide carbonyl	1734	δ2.0-2.3 (CH_2 adjacent to amide carbonyl)	1725	δ 2.3(CH_2 adjacent to amide carbonyl
–C=C–	1620	δ2.0 (CH_2 attached to C=C	1619	δ 2.0 (CH_2 attached to C=C)
C–N	--	--	1069	--
Aromatic	--	--	763	δ7.2
CH_3(TDI)	--	--	--	δ2.7
CH_3 (terminal aliphatic)	1459	δ 0.86	1457	δ0.87
CH_2(Chain)	2856-2925	δ 1.22-1.28	2858-2925	δ

Table 4. Coating properties of cured Poly(urethane amide) resins of Soy oil films

Resin code	Film thickness (μm)	Drying[a] time (mim)	Adhesion	Scratchhardness (1kg)	Flexibility (l/8/in)	Impact Resistance (Ib/in)	Gloss at 60°
PUASO 0.5	55	120	5B	Passes	Passes	150	80
PUASO 1.0	60	60	5B	Passes	Passes	165	83
PUASO 1.5	70	40	5B	Passes	Passes	176	90
PUASO 2.0	80	10	5B	Passes	Passes	189	92

a: Ambient cured 5B: % none (Percent Area Removed)

Table 5.: Chemical resistance of poly(urethane amide) resins of Soy oil films.

Resin code	Alkali resistance 10% NaOH (24h)	Acid resistance (20% H_2SO_4 (30 days)	NaCl (3.5%) (30 days)	Distlled H_2O (30 days)	Solvent resistance (Benzene/turpentine) 30 days
PUASO 0.5	D	B	A	A	A
PUASO 1.0	C	B	A	A	A
PUASO 1.5	B	A	A	A	A
PUASO 2.0	A	A	A	A	A

A: Film unaffected B: Slighty loss in gloss
C: Film cracked and removed D: Film completely removed

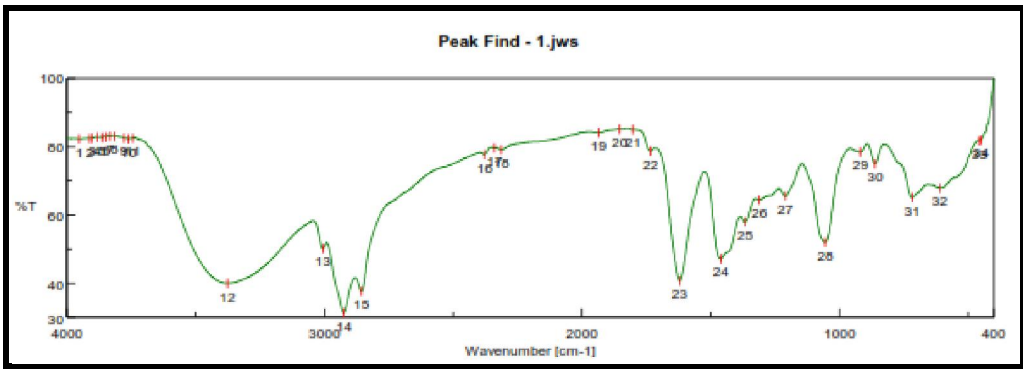


Fig. 2. FT-IR spectrum of diethanol amide of the fatty acids of soy oil (DEASO).

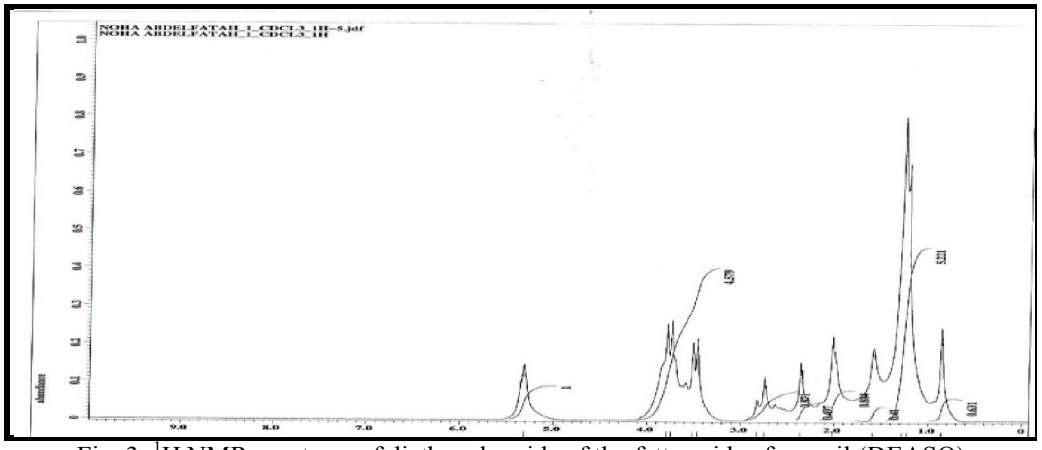


Fig. 3. ^{1}H NMR spectrum of diethanol amide of the fatty acids of soy oil (DEASO)

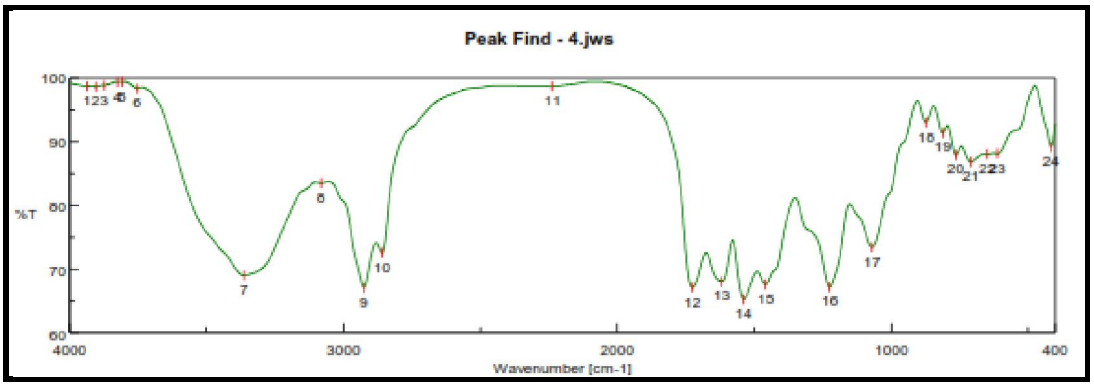


Fig. 4. FT-IR spectrum of soy oil poly(urethane amide (SOPUA).

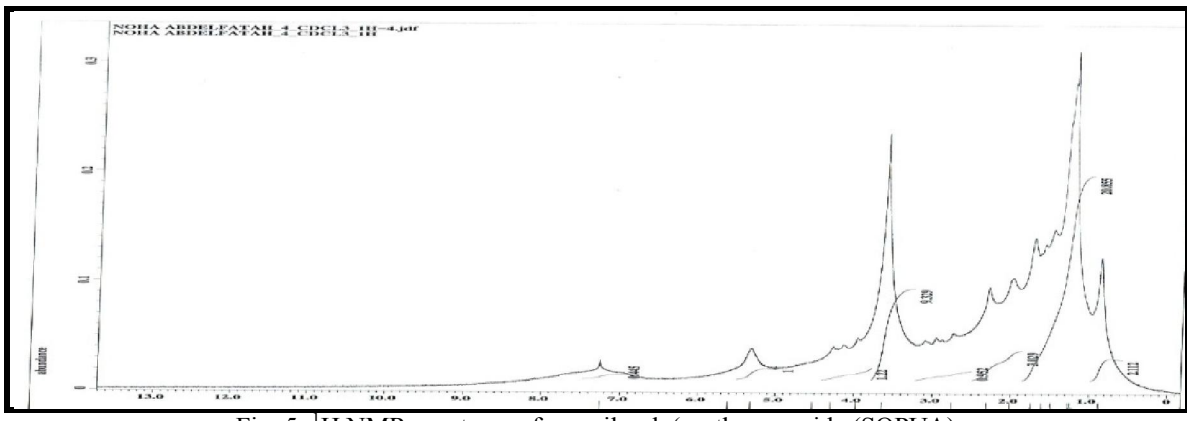


Fig. 5. ^{1}H NMR spectrum of soy oil poly(urethane amide (SOPUA)

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Conclusion

PUASO resin was successfully prepared through one-shot technique at ambient temperature. It was synthesized at much lower temperature (lower energy consumption) in comparison to those of polyesteramide urethane, alkyd and uralkyd. The steps of synthesis are easily carried out with no gaseous or liquid effluents and in one reactor; there is no need for vacuum application. Therefore, the overall synthesis is environmentally friendly, cheap, and very suitable for scale-up.

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