

STRUCTURAL AND THERMAL CHARACTERIZATION OF SYNTHESIZED POLYESTER RESIN BASED ON A NEW LINSEED VARIETY (SHUATS-ALSI 2)

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ABSTRACT

In recent times, industrial as well as academic researchers are trying to develop bio-based polyesters as a better alternative for petroleum-based ones. Their main goal is to synthesize materials that can lead to biodegradation with comparable performance. Plant oil serves as an eco-friendly, renewable natural resource and exhibits some remarkable properties. They are readily available in nature, sustainable and inexpensive. Vegetable oil-based polyesters are almost equally applicable as petroleum-based polyester. Vegetable oil-modified polyesters have been studied over a long period. Continuous researches are undertaken to utilize the commonly used vegetable oils and new oils are also explored for their possibility to be used in producing polymers. In the present work, unsaturated polyester resin (UPRs) based on new linseed variety (SHUATS-ALSI 2) was synthesized. Structural and thermal properties were studied and compared with commercially available resins. FT-IR and ¹H-NMR spectroscopy was applied to explore the chemical structure of synthesized resin. TGA analysis reveals comparable thermal stability of both resins i.e. synthesized and commercial. TGA curve was further considered to evaluate Ts and IPDT parameters.

Keywords: Vegetable Oil, Linseed Oil, Unsaturated Polyester Resin, Thermal Decomposition, Renewable Resource, Biodegradable Polymers.

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INTRODUCTION

Numerous varieties of unsaturated polyesters are known to exist, exhibiting even greatly numbered potential applications, an enlistment of which could exhaust several reams. Industries related to construction, transportation and marines accommodate the major categories of such ubiquitous utilities.¹ The most attractive property which makes unsaturated polyester resin (UPRs) as one of the essential polymers is their price to property ratio.² Due to the proportional thermo-mechanical and chemical properties, these materials extensively finds applications in coating and composite industries.³ Almost 7% of all oil and gas used worldwide is utilized for synthesizing non-renewable polymeric materials.⁴ Mostly used raw materials in industries of UPRs are generated from petroleum resources such as propylene glycol, maleic anhydride and phthalic anhydride.³

However, due to environmental and sustainability issues, a growing concern in our modern society is to replace these fossil fuel-based monomers. In this respect, renewable raw material such as vegetable oil will be a better substitute for synthesizing UPRs.⁵ Due to their biodegradable nature, easy availability and low toxicity it is an interesting renewable source for such synthesis.⁶ Vegetable oils are triglycerides that play a major role in the synthesis of various polymeric structures like linear and cross-linked.⁷ Several studies have been focused on the substitution of such natural materials for synthetic ones. Thermoset resin based on epoxidized linseed oil was developed and further, their thermo-mechanical properties were studied and compared with castor oil and commercial resin-based materials.⁸ Linseed oil-based alkyd resin was utilized in paint formulation.⁹ Glass fiber-reinforced composite based on photosensitive

thermoset resin from linseed oil were developed and its mechanical, as well as biodegradable behavior, was compared with natural fiber-based composites.¹⁰ *Chaulmoogra* and *Alexandrian* Laurel seed oil was used to produce polyol through solvent-free glycerolysis technique; its structural and thermal properties were further evaluated.¹¹ Thermomechanical properties of UPRs based on soybean and coconut oil were studied³. Synthesis of *Broccoli* seed oil-based polyester was carried out through two steps process: C=C was oxidized to produce oxiranes that underwent ring-opening with dicarboxylic acids.¹² *Karanja*¹³, *Yellow oleander*¹⁴, *Jatropha curcas*¹⁵, *Nahar*¹⁶ seed oil-based polyester resins were prepared and tested for coating applications. Such contributions of scientists assure vegetable oil-based polymers as a useful material for various applications. Linseed (*linum usitatissimum* L.) oil is an attractive resource for various industries because of its high unsaturation index which makes its properties superior to other oils.⁵ In the present work, unsaturated polyester resin (UPRs) based on new linseed variety (SHUATS-ALSI 2) was synthesized. Structural and thermal properties were studied and compared with commercially available resins. FT-IR and ¹H-NMR spectroscopy was applied to explore the chemical structure of synthesized resin. TGA analysis reveals comparable thermal stability of both resins i.e. synthesized and commercial. TGA curve was further considered to evaluate Ts and IPDT.

EXPERIMENTAL

Material and Methods

SHUATS ALSI-2 is a novel linseed (flax) variety developed at Sam Higginbottom University of Agriculture, Technology and Sciences, Prayagraj. This variety is well suited to irrigated farm conditions, matures in 123-125 days, is found resistant to powdery mildew and rust with an average yield of 11.10 q/ha, oil content 37-40% suitable for cultivation throughout the state of Uttar Pradesh.¹⁷ The seeds of SHUATS -ALSI 2 were collected from the field of the Department of Genetics & Plant breeding of Sam Higginbottom University of Agriculture, Technology & Sciences. (SHUATS), Allahabad (India). Phthalic anhydride (PA) and Hexane was purchased from Merck, India. Adipic Acid (AA) and Maleic anhydride (MA) were purchased from Central drug house (P) Ltd and Propylene glycol (PG) was purchased from Rankem and was used without further purification in the synthesis of UPRs. Styrene 98% was purchased from Avra synthesis Pvt. Ltd, Hyderabad, India. Methyl ethyl ketone peroxide (MEKP) and cobalt-octoate were used as received from Lilha & company, Varanasi, India.

Oil Extraction

Soxhlet extractor was used to extract oil from the crushed seeds with hexane as a solvent. Hexane was then removed by distillation.

Determination of Physicochemical Properties

An idea can be obtained about quantity, type of glycerides and mean weight of acid through the use of saponification value along with the acid value for a given sample of oil.¹⁸ Iodine value determines the characteristic nature of oil. These values express the degree of unsaturation in oils.¹⁹ Based on iodine value, oils can be further classified as drying (200-130), semi-drying (130-100) and non-drying (lower than 100).²⁰ Various physicochemical properties like acid value, saponification and iodine value of the extracted oil was evaluated as per standard methods.²¹⁻²³

Determination of the Fatty Acid Composition

Perkin Elmer autosystem XLGC with Turbomass was used for the analysis of the fatty acid methyl esters. Helium was used as a carrier gas and total run time for 35min. MS was scanned from 20 to 620 Da. NIST library was used for the identification of esters in fatty acid methyl esters of SHUATS ALSI-2.

Synthesis of UPRs

The Alcoholysis-polyesterification method was applied to synthesize UPRs.²⁴ Table-1 shows the amounts of various ingredients used. The above-mentioned process was carried out in a Dean & Stark type condenser.

In the first stage, oil was transformed into a monoglyceride by heating with continuous stirring a mixture of oil and PG. Methanol solubility test confirms the formation of monoglyceride, in which resin and

methanol are mixed in a ratio of 1:3 at ambient temperature. The resin completely solubilized in methanol indicated the formation of monoglyceride.²⁵

Table-1: Composition of the Synthesized Resin

Oil	PG	AA	MA	PA
0.05M	0.24M	0.10M	0.28M	0.11M

In the second stage finely divided form of AA and acid anhydride (PA and MA) was added after cooling the reaction mixture. The mixture was again heated continuously until a minimum constant acid value was attained.

Styrene (35 wt%) was dissolved in the synthesized resin. To cure the resin, MEKP (2wt%) and cobalt-octoate (0.2 wt%) were added as initiator and accelerator respectively with continuous.³

Characterization and Evaluation of Synthesized UPRs

Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectra of the resin were recorded on Perkin Elmer spectrum RX-I. The absorption peaks in between 4000 cm⁻¹ to 400 cm⁻¹ were studied.

Nuclear Magnetic Resonance Spectroscopy (¹H)

¹H- NMR spectra of the synthesized polymer samples were scanned on a Bruker Avance II spectrometer working at 400 MHz at 293 K in CDCl₃. Chemical shifts (δ) were expressed in ppm.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out with an EXSTAR TG/DTA 6300. Alumina crucible was used to place samples (10 ± 0.2 mg). An empty alumina crucible was used as a reference. All materials were heated from 35° C to 1000° C in a 200ml/min flow of air at a heating rate of 10 ° C/min. Continuous recording of sample temperature, weight and heat flow were performed.

Statistic heat-resistant index (Ts)

The statistic heat resistant index temperature (Ts) was calculated by equation 1.^{26,27,28} values of T_{d5} & T_{d30} from the TGA data are used to calculate Ts.

$$Ts = 0.49[T_{d5} + 0.6 \times (T_{d30} - T_{d5})] \quad (1)$$

Integral Procedural Decomposition Temperature (IPDT)

Doyle's method as proposed earlier^{28,29,30} was used to calculate the IPDT.

$$IPDT (^{\circ}C) = AK * (T_f - T_i) + T_i \quad (2)$$

$$A = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad K = \frac{S_1 + S_2}{S_1}$$

Where,

A- Area ratio of total experimental curve divided by total TGA thermogram

T_i- Initial temperature (500°C)

T_f- Final temperature (800°C)

S₁ S₂ & S₃ values were determined by earlier studies

K is the coefficient of A

RESULTS AND DISCUSSION

Physicochemical Properties of Oil

The physicochemical properties of the oil are depicted in Table-2. Oil with higher iodine value can be called a drying oil as it signifies the presence of unsaturation; applications in the areas like paints, surface coating production thus become possible because a higher iodine value (177) renders drying capability to the thin film of oil to produce a hard film through auto-oxidation. The saponification value of 204 is

indicative of its applicability for soap production. The physical and chemical properties are in close approximation to the data provided by other researchers.³¹

Table-2: Physicochemical Properties of Oil

Physiochemical Properties	Mean Value
Acid Value(mg KOH/g of oil)	1.5
Saponification Value(mg KOH/g of oil)	204
Iodine Value (g I ₂ /100g of oil)	177

Fatty Acid Composition

Table-3 represents the fatty acid composition of the seed oil. The fatty acid profile confirms that the major acid is linolenic acid (49.97%) accompanied by other components viz. oleic acid (26.38%), linoleic acid (13%), palmitic acid (5.72%) and stearic acid (4.03%). SHUATS ALSI-2 consists of 9.75% of saturated and 89.35% of unsaturated fatty acids.

Table-3: Fatty Acid Composition of the Seed Oil

Fatty Acids	Retention Time	Percentage(%)
Palmitic acid	14.49	5.72
Stearic acid	18.25	4.03
Oleic acid	18.57	26.38
Linoleic acid	19.47	13.00
Linolenic acid	21.05	49.97
Unknown fatty acids		0.90

Synthesis of UPRs

Transesterification reaction occurs when Linseed oil (SHUATS ALSI-2) is heated with propylene glycol and yields a mixture of products referred to as monoglyceride. The mixture contains monoglyceride, diglyceride, triglyceride and propylene glycol.³²

The mixture further undergoes polyesterification reaction on the addition of MA and PA and produces unsaturated polyester resin. The polyesterification reaction can be checked and was done by evaluating the acid value at a distinct interval of time.

With the progression of the polyesterification reaction, there was a decrease in acid value. The decrement in acid value was found to be fast in the initial phases of the reaction in comparison to the later phases. This alteration in the change in acid value during this reaction is supported by the theory of difference in reactivity of primary hydroxyl group and the secondary hydroxyl group of propylene glycol³³, the former group being more reactive than the latter. It is assumed that the fast decrement in acid value during initial phases is due to reaction of the primary hydroxyl group and the slower decrease in acid value during later stage corresponds to the reaction of secondary hydroxyl group.³⁴

The duration when the decrement in acid value is slow, which is contributed by the reaction of the secondary hydroxyl group of propylene glycol, supposedly specify the start of the development of three-dimensional networks as a result of cross-linking of polyester chain.³⁵

The crosslinking of the alkyd chain causes an increase in the viscosity of the reaction medium. Furthermore, the rate of reaction reduces towards the final stages of reaction due to a decrease in free acids.³⁵

Fourier Transform Infrared Spectroscopy (FTIR)

Existence of major linkages such as olefinic double bonds, ester groups and other specific peaks are indicated by the FT-IR spectra of the developed resin. FT-IR analysis confirms the polyesterification reaction. Figure-1 shows the FTIR spectra of the synthesized resin. The presence of -OH group is confirmed by the broad singlet peak at 3444 cm⁻¹. Aromatic C-H stretching as well as olefinic C-H stretching is confirmed by the peak at 3082.2 cm⁻¹. Peaks around 2855.9-2927.7 cm⁻¹ represent aliphatic C-H stretching vibrations. The presence of ester linkages (C=O) is confirmed by the characteristic peak at 1731.2 cm⁻¹. Peaks around 1601.9-1580 cm⁻¹ confirm the presence of aromatic C=C. Stretching (-C-O-C-) is confirmed by the peaks around 1261.3-1074.9 cm⁻¹. C-O stretching frequency of ester is confirmed by

The infrared spectrum of poly(2-vinylpyridine) displays transmittance (%T) on the y-axis (0.0 to 55.0) against wavenumber (cm⁻¹) on the x-axis (4000 to 400). The spectrum shows a broad absorption band around 3400 cm⁻¹, sharp peaks in the 3000-3100 cm⁻¹ region, a strong carbonyl absorption at 1731.2 cm⁻¹, and multiple peaks in the fingerprint region between 1600 and 600 cm⁻¹.

Wavenumber (cm⁻¹)
3444.2
3082.2
3007.7
1731.2
1602.4
1581.6
1261.2
1183.5
1074.0
983.4
844.2
700.7

Fig.-1: FTIR Spectra of the Synthesized Resin

Figure-2 depicts the ^1H NMR spectra of the synthesized resin. The peak at 1.01 ppm is for the H^1 of the terminal CH_3 group of the fatty acid chains. The peak at 1.76-1.78 ppm corresponds to the H^1 of CH_2 groups attached beside to above terminal CH_3 group. The peak at 1.31-1.35 ppm is mentioned for all the internal CH_2 groups available in the fatty acids chains.

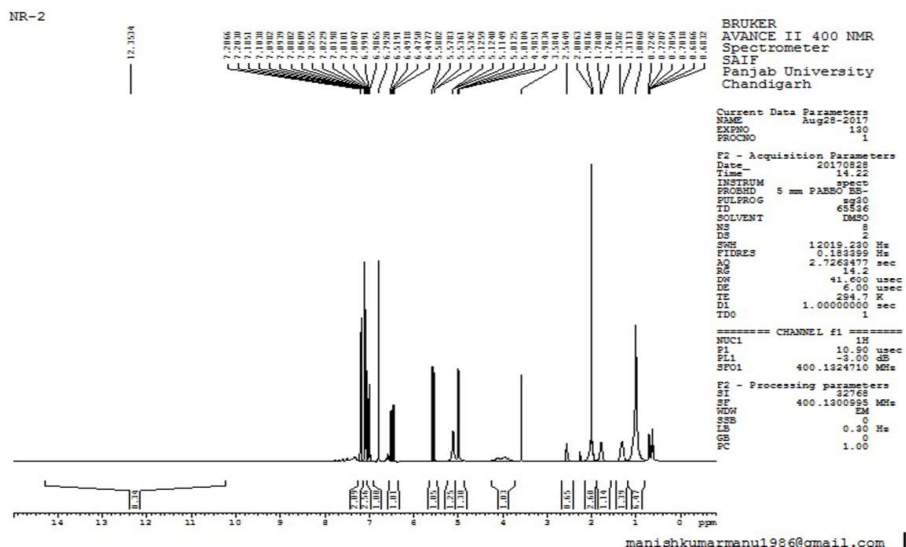


Fig.- 2: ^1H NMR Spectra of the Synthesized Resin

The characteristic peak at 5.1-5.5 ppm is for protons of unsaturated carbon. For methylene protons of propylene, glycol moiety is observed at 3.58ppm. The characteristic peaks at 6.98-6.99 ppm are for the protons for CH of propylene glycol moiety. The peaks at 7.10-7.20 ppm are observed for aromatic protons of phthalic anhydride.^{14,37,38}

Thermo-oxidative stability is a key determining factor in the applicational aspects of UPRs.³⁹ Thermal stability of the cured unsaturated polyester resin has been measured in an air atmosphere by thermogravimetric analysis at the heating rate of 10 ° C/min. Figure-3 represents the TGA curve of the commercial resin (CR-1) and synthesized resin (CR-2).

Cured polyester resin usually shows two main temperature ranges for weight loss. Low molecular weight oligomeric component degraded in the range of 100-250°C whereas ester linkages and the oil degrades around 250-450 °C.^{3,40,41} Thermal degradation temperatures of the resin are tabulated in Table-4.

The onset thermal degradation temperature (T_{onset}) of CR-1 is around 97.4°C whereas for CR-2 it is at 136°C which may be due to loss of water and other volatile substances.⁴² The earlier degradation of CR-1 can be explained by the assumption that the solvent used is more volatile than the one used for CR-2.⁴³ The temperature of 5% weight loss (T_{d5}) is at 180.5°C for CR-1 and 207°C for CR-2. 30% weight loss (T_{d30}) temperatures are almost comparable for both CR-1 and CR-2 i.e 354.4°C and 345°C respectively which correspond to degradation of ester linkages.

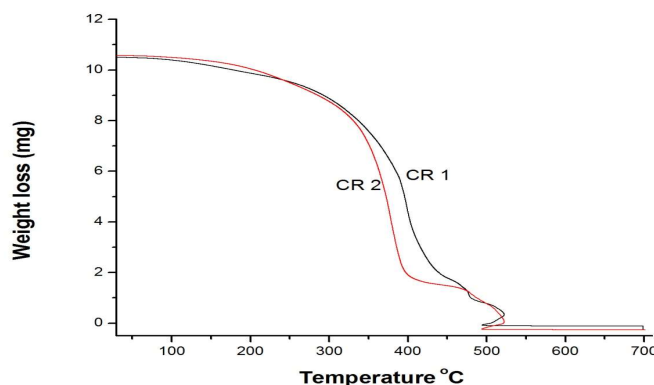


Fig.-3: TGA Curve of the Commercial Resin (CR-1) and Synthesized Resin (CR-2)

Table-4: Thermal Stability Data of CR-1 and CR-2

Sample Code	T_{onset} °C	T_{d5} °C	T_{d30} °C
CR-1	97.4	180.5	354.4
CR-2	136	207	345

Where, T_{onset} - Onset Temperature, T_{d5} - Temperature of 5% weight loss
 T_{d30} - Temperature of 30% weight loss, T_s -Statistic heat resistant index temperature

The T_s and IPDT are specific parameters to explain the thermal stability of the cured resins.²⁸ Parameters of thermal stability of cured resins are shown in Table-5.

Table-5: Parameters of Thermal Stability of Cured Resins

Sample Code	IPDT (°C)	T_s (°C)
CR-1	525	140
CR-2	494	142

The value of T_s of CR-2 is 142°C which is at par with CR-1 i.e 140°C whereas IPDT for CR-1 is at 525°C and 494°C for CR-2. These data indicate that CR-2 is thermally more stable than CR-1.

CONCLUSION

Unsaturated polyester resin (UPRs) based on a new linseed variety (SHUATS-ALSI 2) and a mixture of PA, MA, PG and AA in varying amounts by a two-stage alcoholysis-polyesterification process have been successfully synthesized. The FTIR and ^1H -NMR spectra confirmed the structure of the resin and TGA studies along with the values of IPDT and T_s confirms its thermal stability. On comparison, it is being found that the values of T_{onset} and T_{d5} for synthesized resin (CR-2) is higher than the commercial resin (CR-1) while the T_{d30} value of the CR-2 is higher than the CR-1. Even the values of IPDT and T_s are almost comparable for both resins. Based on these results, it can be concluded that UPRs based on new linseed variety SHUATS-ALSI 2 is thermally stable and has tremendous potential to be a good alternative for fossil fuel-based polymers.

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