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Research Article

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Determination of Physico Chemical Properties of Biopolyester Resins from cardanol and castor oil

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ABSTRACT

Biopolyesters based on the fumarate ester of castor oil and methylolated cardanol such as poly(castor oil fumarate) biopolyester resin and poly(cardanol fumarate) biopolyester resin were prepared using naturally available byproducts like castor oil and cashew nut shell liquid (cardanol).The Physico Chemical Properties of these biopolyester resins were studied under standard conditions.

INTRODUCTION

The use of renewable resources as starting materials for the synthesis of various polymers has been at the centre research activity for more than 20 years [1-5]. These renewable resources hold beneficial characteristics for being non-toxic, biodegradable and environmentally friendly. Natural polymers are formed in nature during the growth cycles of all organisms and are available in large quantities from renewable sources. These facts have helped to stimulate interest in biodegradable polymers and in particular biodegradable biopolymers. Designing these materials to be biodegradable and ensuring that they end up in an appropriate disposal system is highly relevant to protect the environment and ecology.

Plant oils containing hydroxyl fatty acids are important raw materials for the polymer production. They can be polymerized to form elastomeric networks and are used as alternative material resources to petro-chemical derived resins. The polymers obtained from plant oils are biopolymers; they are often biodegradable as well as non-toxic**.** [6,7].

One of the most naturally and abundantly occurring plant oil is castor oil (Ricinus oil). It is a triglyceride of fatty acids which occurs in the seed of the castor plant, Ricinus Communis. It is produced by cold pressing the seeds and subsequent clarification of the oil by heat. In comparison with other oils, it presents high viscosity, high polarity, very low vapour pressure and optical activity. The ester linkages, double bonds and hydroxyl groups in castor oil provide reaction sites for the preparation of many useful derivatives. Castor oil plasticizes a wide variety of natural and synthetic resins. Castor oil has become a important raw material for the production of polyurethanes, IPNs, biodegradable polyesters etc. Castor oil can generate high polymer with limited crosslink density and offers toughening characteristics to brittle and highly cross linked composite materials. [8, 9]

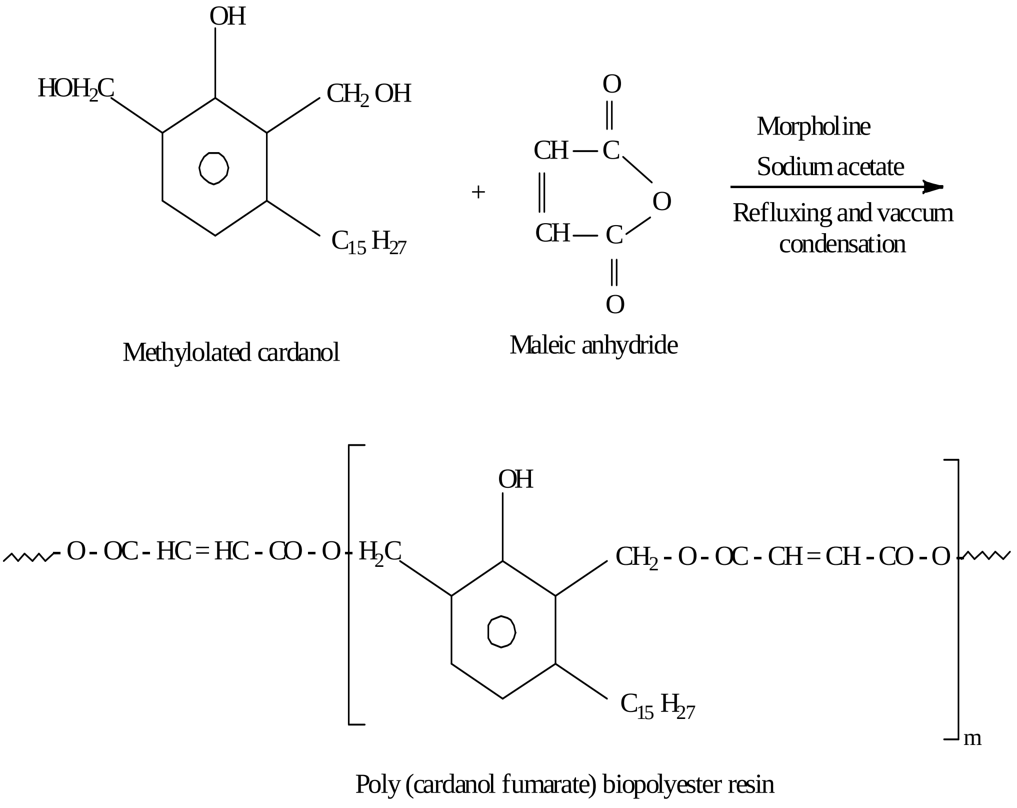
Cashew nut shell liquid (CSNL), an agricultural renewable resource contained in the spongy mesocarp of the cashew nut shell (Anacardium occidentale L). It holds considerable importance, because it is a source of unsaturated hydrocarbon phenol and behaves as an excellent monomer for thermosetting polymer production. Cardanol, a major constituent of CNSL is a meta substituted phenolic compound. Cardanol is obtained by distilling the cashew nut shell liquid (CSNL). The unique feature that makes cardanol as an interesting monomer is the presence of a meta substituent of a C_{15} unsaturated hydrocarbon chain with 1-3 double bonds and the phenolic character of the cardanol. Compared with conventional polymeric materials, cardanol based polymers can have improved functional characteristics (such as toughness, process ability and hydrophobicity) due to the long meta substituent alkyl chain and rigid phenyl group. [10-12].

Unsaturated polyester resins are typically used as the resin component in the manufacture of fiber reinforced thermoset plastics for a variety of applications, including structural automotive parts, building and construction components. [13-15].The resins generally consist of unsaturated polyesters synthesized by the condensation of saturated and unsaturated anhydrides with glycols and dissolved in a polymerizable ethylenically unsaturated monomer such as styrene. Unsaturated polyester resins exhibit excellent physical properties as well as good weather ability. These deficiencies are thought to be caused by the high polymerization shrinkage from the copolymerization of the unsaturated polyester resin with the cross linking agent. The polyesters prepared by condensation of saturated and unsaturated anhydrides with glycols lead to generation of water/methanol and consequent formation of voids. The inhibition of vinyl free-radical initiated curing of unsaturated polyester resins by the presence of oxygen is well known. Achievement of a tack-free cross linked surface with appreciable mar resistance, solvent resistance and resistance to bacterial attack during the use is also a major problem in the polyester resin field. Hence it is relevant to explore the use of cardanol and castor oil to develop novel addition-curable resins for high performance biopolyester materials.

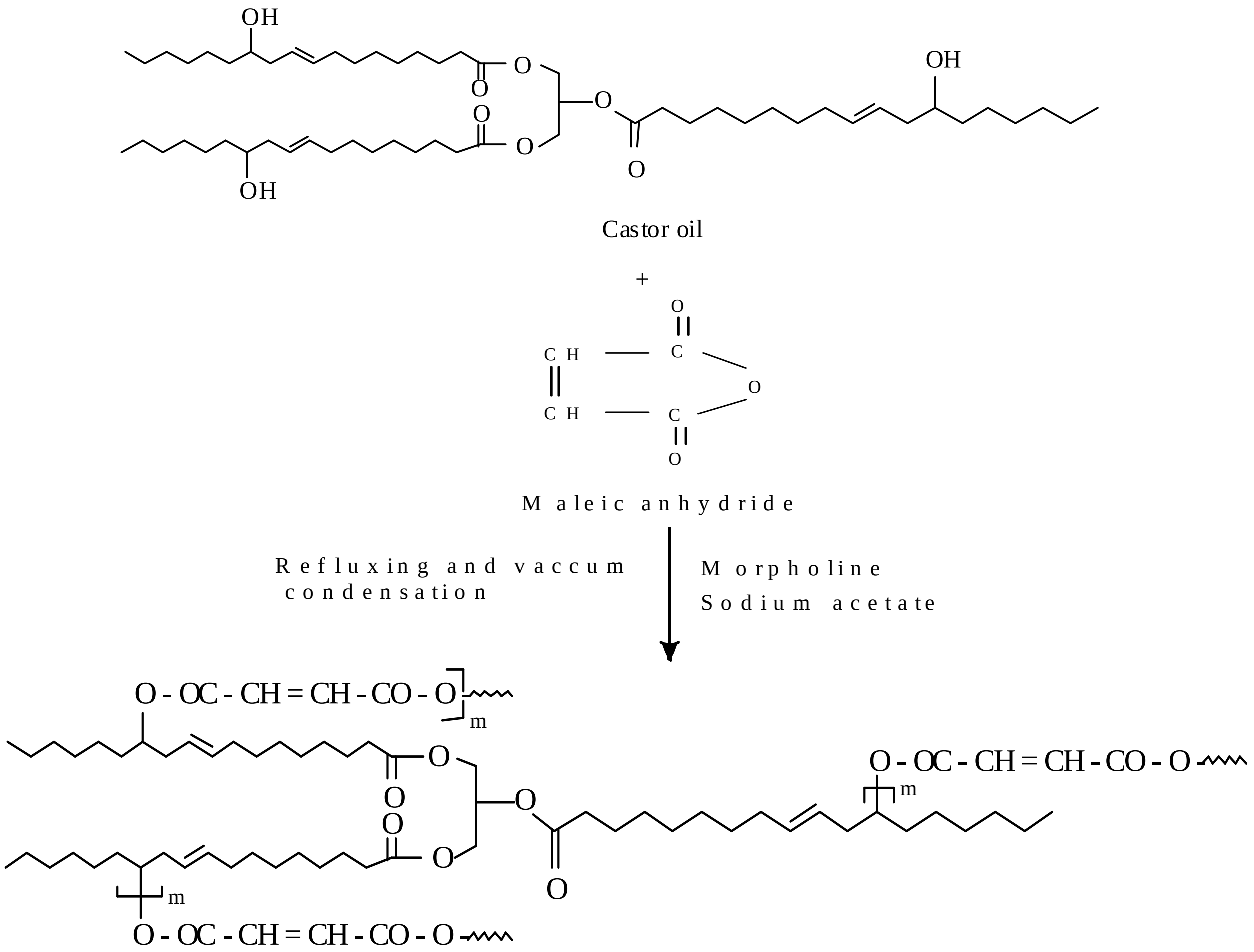
EXPERIMENTAL SECTION

2.1 Synthesis of Poly (cardanol fumarate) biopolyester resin and Poly (castor oil fumarate) biopolyester resin

The poly cardanol fumarate resin (MCFR) was prepared by heating 1 mole of methylolated cardanol with 2 mole of maleic anhydride using morpholine and sodium acetate catalyst. .The poly castor oil fumarate resin (CFR) was prepared by heating 3 moles of castor oil with 1 mole of maleic anhydride using morpholine and sodium acetate as catalyst. [16] (Reaction scheme1, 2).



Reaction Scheme 1: Synthesis of Poly (Cardanol Fumarate) Biopolyester Resin



Poly (castor oil fumarate) Biopolyester Resin
Reaction scheme 2: Synthesis of Poly (Castor Oil Fumarate) Biopolyester Resin

2.2Physico Chemical Characterization of Addition Curable Poly (Cardanol fumarate) Biopolyester Resin and Poly (Castor oil fumarate) Biopolyester Resin

2.2.1 Determination of Specific Gravity

The specific gravity bottle was used to determine the specific gravity of resins. The specific gravity bottle was filled with pure resin until it overflows by inserting the stopper. Then it was immersed in the water bath (maintained at 30.0±0.20^0 C) and held for 30 minutes. The capillary opening was thoroughly wiped off, cooled to room temperature and weighed. The process was then repeated with distilled water. Then using formula the specific gravity of cardanol was calculated,

$$\text{Specific gravity (g/cc at } 30/300^0\text{ C)} = (A-B) / (C-B)$$

Where, A = Weight (g) of the specific gravity bottle with cardanol at 300^0 C
B = Weight (g) of empty specific gravity bottle
C = Weight (g) of specific gravity bottle with water at 300^0 C

2.2.2 Determination of Viscosity

The viscosity of resins was determined with a U-tube viscometer as per standard procedure A-3, IS: 840-1986. The following formula was used to calculate the kinematic viscosity (centistokes) from each efflux time.

$$V = Ct$$

Where, V = Kinematic viscosity (centistokes)

C = Calibration constant for the instrument
t = Time of flow in seconds
The dynamic viscosity (cp) was calculated using the equation,

$$\text{Dynamic Viscosity (cp)} = \text{Kinematic viscosity} \times \text{Specific gravity}$$

A U-tube viscometer at 30^0 C is used to measure the relative viscosities (ηr) of resins at different concentrations with toluene solvent. The specific viscosity (ηsp) and reduced viscosity (ηred) values were calculated from the relative viscosity. The intrinsic viscosity (ηi) value was determined from the point of intercept from the plotted graph of reduced viscosity versus concentration.

2.2.3 Determination of Moisture Content

The percentage of moisture content of the resins was determined as per the standard procedure A-4 and A-5 of IS: 840-1986. The percentage of moisture content and the insoluble matter in toluene were calculated using the formula,

$$\text{Moisture, percent by weight} = 100\ V\ D / W$$

Where, V = Volume (ml) of water
D = Specific gravity of water at the temperature at which the volume of
Water is read

W = Weight (g) of castor oil taken

2.2.4 Determination of Acid Value

Acid value of resins was determined as per the method described elsewhere [17]. One gram of resin was weighed accurately in a conical flask and added with 50 ml of the acid-free alcohol. The content was boiled and cooled. One ml of phenolphthalein indicator was added and titrated against standard potassium hydroxide solution.

Acid value was calculated using the formula,

$$\text{Acid value} = 56.1\ V\ N / W$$

Where, V = Volume (ml) of KOH
N = Normality of KOH
W= Weight of cardanol (g)

2.2.5 Determination of Hydroxyl Value and Number Of Hydroxyl Groups

Hydroxyl value was determined by acetylation method as per the method of Goodman [18]. About one gram of resin was mixed with 10 ml of a mixture of dry pyridine and acetic anhydride in 3:1 volume ratio in an Erlen Meyer flask. Then it was refluxed on a water bath for 40-50 minutes using an air condenser with occasional swirling. After this process 10 ml of distilled water was added through the air condenser carefully and heated for another 5 minutes. The entire mixture was cooled and washed down the sides of the flask with 10 ml of n butyl alcohol. One ml of phenolphthalein was added and titrated against 1 N sodium hydroxide to a slightly pink end point. A blank titration was performed. Using the equations Hydroxyl number and Number of hydroxyl groups were calculated,

$$\text{Hydroxyl number} = (B\text{-}S)\ N\ 56.1/W$$
$$\text{No. of hydroxyl groups} = (B\text{-}S)\ NM/W1000$$

Where, B = Volume (ml) of std. NaOH solution required for the blank
S = Volume (ml) of std. NaOH solution required for the sample
N = Normality of std. NaOH solution
W = Weight of cardanol (g)
M = Molecular weight of cardanol

2.2.6 Determination of Iodine Value

As per the standard IS: 840-1964, Wij's method was used to determine the Iodine value. About 50 g of resin was taken in a 250 ml beaker and heated slowly to 205 ± 50^0 C on an electric hot plate with continuous stirring. The content was cooled and filtered through a filter paper to remove any impurities. 0.1 g of the filtered sample was weighed in a clean dry 250 ml iodine flask to which 25ml of carbon tetra chloride was added to dissolve the content.

25ml of the Wij's solution was added and replaced the glass stopper after wetting with potassium iodide solution. The entire content was swirled for intimate mixing and allowed to stand in the dark for one hour. Then 15 ml of potassium iodide solution was added. The liberated iodine was titrated immediately with standard sodium thiosulphate solution using starch indicator. A blank test was carried out simultaneously under similar experimental conditions. Using the formula Iodine value was calculated,

$$\text{Iodine value} = 12.69\ (B\text{-}S)\ N / W$$

Where, B = Volume (ml) of standard sodium thiosulphate solution required for the blank
S = Volume (ml) of standard sodium thiosulphate solution required for the sample
N = Normality of the standard sodium thiosulphate solution
W = Weight (g) of cardanol taken.

2.2.7. Determination of Molecular Weight

Molecular weight is an important characteristic of polymers because it can significantly affect polymer properties. GPC is by far the most widely used method of determining molecular weight distribution [2-4]. A gel permeation chromatography technique, GPC may be used preparative to obtain narrow molecular weight fractions. A phenomenon often referred to as 'molecular sieving' was used, in which the separation was accomplished on a column packed with a highly porous material that separates the polymer molecules according to size. Present thought on the phenomenon is that the separation is based on the hydrodynamic volume of the molecules rather than on the molecular weight per second [5]. Small molecules are able to diffuse into the pores of the column packing more efficiently and hence they travel through the column more slowly. Higher molecular weight fractions are thus eluted first. A typical gel permeation chromatogram plots detector response against the volume of dilute polymer solution that passes through the column (the elution volume). To obtain molecular weights at a given retention volume, the chromatogram may be compared with a reference chromatogram obtained with fractions of known average molecular weight in the same solvent and at the same temperature.

In the present study the analysis was carried out using Waters GPC System involving 600 series pump and Waters Styragel HR-5E/4E/2/0.5 columns in series, 2414 Refractive index detector and Waters 717 plus auto sampler. The samples were treated with 3 ml tetra hydro furan. The volume of injection was 20µL. Tetra hydro furan was used as the mobile phase and the flow rate was 1ml/min. Polystyrene standards of Mp 100000, 34300, 162 were used for relative calibration. Viscometry is a useful technique for determining the molecular size of polymers [19] using intrinsic viscosity.

RESULTS AND DISCUSSION

The physico chemical properties of the addition curable biopolyester resins have been determined. Intrinsic viscosity [η] was measured using an Ubbelohde viscometer at 30°C. Toluene solvent was used. Intrinsic viscosity was obtained from the intercept of a plot of reduced-viscosity versus concentration. The addition-curable poly (cardanol fumarate) biopolyester resin possesses higher intrinsic viscosity than the cardanol due to higher degree of substitution of cardanol with fumarate linkages at ortho positions.

In methylolated cardanol, the presence of ortho substitution allows intra molecular hydrogen bonding between hydroxyl groups and releases hydrogen ions which contribute to the acidity of methylolated-cardanol. In comparing with methylolated cardanol, the acid value of poly (cardanol fumarate) is increased due to the presence of –COOH end groups of fumarate linkages. Hydroxyl value represents the concentration of hydroxyl groups in a molecule of definite molecular weight. The higher iodine value is due to the presence of fumarate linkages at the two ortho positions of the cardanol. The data of physico chemical properties are given in Table.1.

The castor oil is characterized by high viscosity and specific gravity; this is due to the hydrogen bonding of its hydroxyl groups. The lower specific gravity of the resin is due to the esterification occurs over the hydroxyl groups. Acid value gives the measure of the free acid present in the oil. The lower acid value of the addition curable poly (castor oil fumarate) biopolyester resin indicates the esterification of the maleic anhydride takes place with a formation of carboxyl end groups. The analysis of molecular weight of polyester resin reveals Mn 2090 and Mw 2450 with polydispersity 1.17 which also indicate the oligomeric nature of the resin. The Physico chemical properties of castor oil and poly (castor oil fumarate) resin are given in the Table 2.

Table 1.Physico Chemical Properties of Poly (Cardanol Fumarate) Biopolyester Resin

Properties	Methylolated- cardanol	Poly(cardanal fumarate) biopolyester resin
Colour	Dark reddish brown	Dark reddish brown
Smell	Phenolic	Phenolic
Intrinsic viscosity ($x10^{-2}$) (dL/g)	2.24	3.39
Iodine value	219	258
Acid value	158	194
No. of hydroxyl groups	3	1
Hydroxyl value	157.9	115.6
Molecular weight	395	Mn 3007, Mw 3780 polydispersity 1.2

Table 2.Physico Chemical Properties of Poly (Castor Oil Fumarate) Resin

No	Properties	Poly (castor oil fumarate) resin
1.	Colour	Yellowish
2.	Intrinsic viscosity ($x10^{-2}$) (dL/g)	3.86
3.	Specific gravity(g/c.c at 30^0c)	1.1
4.	Iodine value	265
5.	Acid value	145
6.	Iodine value (Wij's method)	265
7.	Molecular weight	Mn 2090, Mw 2450 polydispersity 1.17

CONCLUSION

Cardanol moiety, 3-(n-pentadeca-8, 11-dienyl) phenol was used in the present synthesis of methylolated cardanol and addition-curable poly (cardanol fumarate) biopolyester resin. Cardanol was converted into methylolated cardanol. Methylolation of cardanol with 0.2 molar excess of cardanol over the formaldehyde and oxalic acid has resulted substitution at ortho positions with CH_2OH groups. The methylolated-cardanol on further esterification with maleic anhydride at high temperature results in the formation of addition-curable poly (cardanol fumarate) biopolyester resin.Unsaturated addition-curable poly (castor oil fumarate) biopolyester resin was prepared using castor oil and maleic anhydride. The final oligomeric resin contains fumarate ester linkages in all the three ricinoleic branches since the castor oil contains three hydroxyl groups. The analysis of molecular weight indicates the oligomeric nature of the resin since the poly (castor oil fumarate) biopolyester resin possesses Mn 2090 and Mw 2450 with polydispersity 1.17.

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