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Synthesis of Biodegradable Crosslinkable Poly (Castoroil Fumerate) Polyester Resin Blends on Vinylacetate

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Abstract

Biodegradable hydroxyl terminated – Poly (castor oil fumarate) resin was synthesized by the malination of castor oil ,an excellent naturally occurring renewable resource in the presence of morpholin catalyst and further cross linked with Vinyl acetate (VA) by benzoyl peroxide initiator and dimethyl aniline accelerator to yield biodegradable polyester, containing the ratio of resin blend and VA ,1:1,1:0.75,1:0.5,1:0.25, set fast with tolerable exothermic temperature as a cross linked toughened sheets CFRVA-I,CFRVA-II,CFRVA-III,CFRVA-IV.

Keywords: Castor oil, Poly (castor oil fumarate), Polyester, Maleic anhydride, Benzoyl peroxide.

Introduction

The use of renewable resources as starting materials for the synthesis of polymers has been at the center of our research activity for more than 20 years (1-5).In recent past years a remarkable research has been carried out to the synthesis of biodegradable polymers from renewable resources[6].The use of renewable resources in the preparation of various industrial materials has been revitalized because of the environmental concerns. Natural oils are now considered as the most important class of renewable sources[7]. Natural oil and their derivatives are used due to their availability, renewability and biodegradability[8].Natural oils have attracted renewed attention as raw materials for the preparation of resins and polymeric materials[9]. Polymers from renewable resources have been attracting ever-increasing attention over being environmental concerns[10].

In the present study biodegradable Poly(Castoroil Fumerate) Polyester Resin has been synthesized from the natural oil, castor oil. Castor oil is obtained from extracting the seed of a plant which has the botanical name Ricinus communis of the family Eurphorbiacae .The oil is not only a naturally occurring resource, it is inexpensive and environmentally friendly. Castor oil (ricinus oil) is a viscous, pale yellow, non-volatile and non-drying oil with a bland taste, that occurs in all tropical and subtropical regions and India is the world"s largest exporter of castor oil[11].It is a triglyceride of fatty acids that contains 87-90% of ricinoleic acid (cis-12-hydroxy octadec-9-enoic acid) with a hydroxyl number of163mg KOH/g, and average functionality of about 2.7.Ricinoleic acid is an unsaturated omega-9-fatty acid has 18-carbon on its backbone with one hydroxyl group on the 12th carbon atoms and it also has a cis double bond between 9th and 10th carbon atoms[12].

However several reports concerning agronomics marketing, processing and application aspects of this oil have been already published[13-22]. Castor oil is mostly used in the form of its modified derivatives such as dehydrated, hydrogenated, alkoxy-lated, sulphated and the halogenated derivatives. Castor oil is a natural oil polyol and there is substitute in nature for its unique biochemical structure. Castor oil and castor derivatives are bio-renewable biostainable and where necessary bio degradable. The hydroxyl groups in castor oil account for a unique combination of physical properties like relatively high viscosity and specific gravity. Since it contains higher polar hydroxyl groups, it is not only compatible with, but will plasticize a wide variety of natural and synthetic resins.

The ester linkages, double bonds and hydroxyl groups in castor oil provide reaction sites for the preparation of many useful derivatives. The hydroxyl functionality of castor oil has been widely utilized to synthesize CFR, Castor oil fumarated resin[23].In the present study, CFR is made to react with the cross linking agent, vinyl acetate in different molar proportions, and is cured to form rigid biodegradable poly esters.

Materials

Castor oil Acid value-2.0mg KOH/g, hydroxyl value-162 KOH/g ,iodine value (wij method) Specific gravity 0.957-0.961 was obtained from Sriram industries, Madurai. Sodium acetate. Benzoyl peroxide and

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dimethyl aniline were received from Ranbaxy-Newdelhi, Maleic anhydride (CDH, Bombay),Morpholine (Paxmy chemicals, Chennai) and vinyl acetate (Loba chemic Pvt.Ltd.Mumbai). The chemicals were used as received.

Methods

i)Preparation of Poly(Castor oil Fumerate) Polyester Resin

The Poly(Castoroil Fumerate) Polyester Resin was prepared by heating 3 moles of castor oil with 1 mole of maleic anhydride using morpholine as the catalyst.In a typical reaction45.8 g of castor oil,14.7g of maleic anhydride,1g of sodium acetate alon with few drops of morpholine were placed in a three necked flask with a stirrer.The reaction was carried out at$110^{o}c\pm5^{0}c$ for 60 minutes and then$180^{0}C \pm 5^{0}C$ for 10 minutes under vacuum condition using rota mantle to yield yellowish transparent liquid resin, CFR Poly(Castoroil Fumerate) Polyester Resin, the prepolymer.

ii) Synthesis of Poly (Castor oil Fumerate) Polyester Resin blend Vinyl acetate

The prepolymer, CFR is mixed with the cross linking agent, vinyl acetate (VA) in different molar proportions in presence of benzoyl peroxide (initiator) and dimethyl aniline(accelerator) and then casted on a clean silicone oil spreaded glass plate,cured in a hot air oven at $80^{0}c$ for 6 hours and the polyester blends CFRVAI,CFRVAII,CFRVAIII and CFRVAIV were obtained.

Results and Discussion

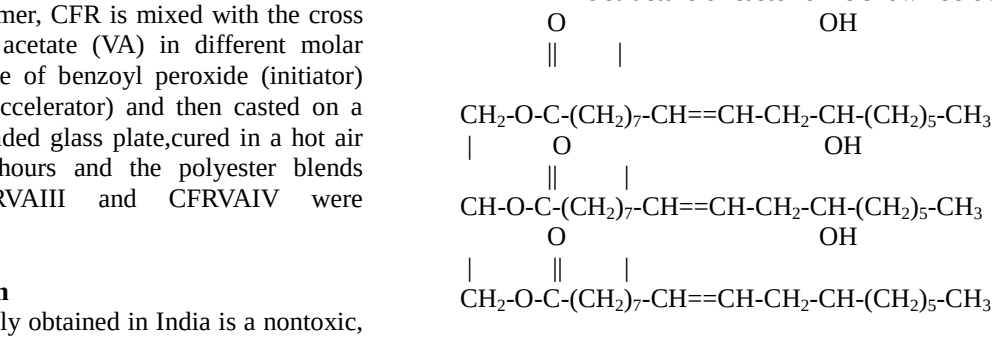
Castor oil easily obtained in India is a nontoxic, biodegradable, renewable resource. Because of its higher polar hydroxyl groups, castor oil is not only compatible with but will plasticize a wide variety of natural and synthetic resins, polymers and elastomers. The analytical data of castor oil and castor oil based resin are presented in table I , and the values are compared with that of standard castor oil.

The iodine value represents the degree of unsaturation. Castor oil has three olefinic bonds with varied degrees of unsaturation in the long aliphatic side chain. The lower iodine value of castor oil based resin indicates the lower degree of unsaturation in comparison to the castor oil. The higher viscosity and specific gravity of the oil is due to the hydroxyl groups in castor oil. The lower specific gravity of the resin is due to the esterification occurs over the hydroxyl groups.

Table I. Properties of castor oil and Poly (Castor oil Fumerate) Polyester

Properties	***Castor oil***	***Poly (Castor oil Fumerate) Polyester***
Colour	Light yellow	Dark yellow
Smell	Odorless	Odorless
Specific gravity	0.864g	0.736g
Viscosity	0.965 ps	1.264
Iodine value	204.54	197.24
Saponification Value	269.39	-
Acid value	16.8	268.24

The structure of castor oil is shown below.



Infrared spectrum of the Poly (Castor oil Fumerate) Polyester shown below.

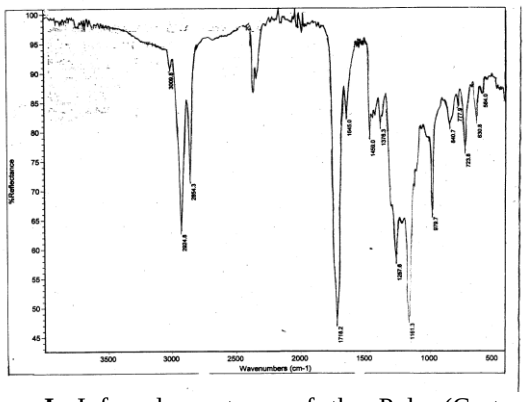


Figure I. Infrared spectrum of the Poly (Castor oil Fumerate) Polyester

Infrared spectrum of the Poly (Castor oil Fumerate) Polyester (figure 1) shows the responses $3009cm^{-1}$ (=C-H stretching),2854cm-1(-CO-CH3),1718cm-1(C=O stretching hydrogen bonded,1257 cm^{-1}(-OH bonding),1161 cm^{-1}(C-O-C linkage) indicates the esterification of castor oil.

Figure2 is the UV Spectrum of Poly (Castor oil Fumerate) Polyester, CFR. The major absorption peak is

at about 215nm (ester).

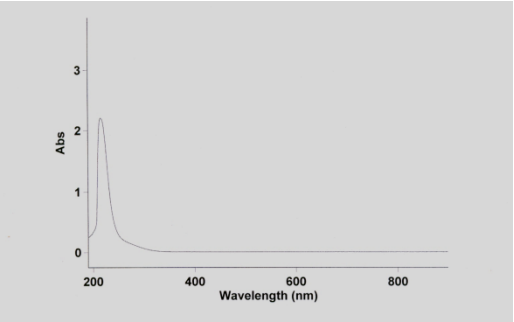


Figure II. UV Spectrum of Poly (Castor oil Fumerate) Polyester

The NMR Spectral studies of purified Poly (Castor oil Fumerate) Polyester,CFR indicates the appearance of peak at 4.35∂ due to the COOR group formed by Malination. The appearance of NMR signals and interpretation are as follows. The peaks at 6.9-6.15∂ are due to the olefinic linkage. The peaks at 5.6∂ indicates the presence of OH group. The peaks at 7.25∂ indicates the presence of aryl hydrogen. (Figure-3).

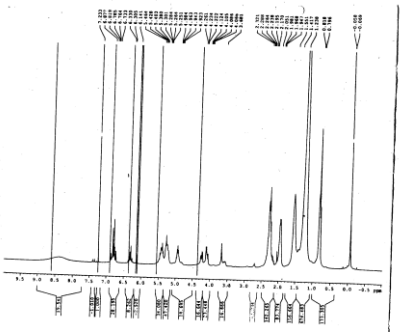


Figure III. NMR Spectral studies of purified Poly (Castor oil Fumerate) Polyester

The IR spectrum of the Poly (Castor oil Fumerate) Polyester Resin blend Vinyl acetate in different proportions (Figure 4) shows the responses 2925cm^{-1} (-CH stretching from methylene),2854cm-1(COCH3),1730cm-1(C=O stretch in esters),1454cm-1(CH2),1372cm-1(CH3),1226cm-1(OH group),1164cm-1(C-O-C linkage),802cm-1(CH=CH2),713cm-1(trisubstituted CH=CH2)

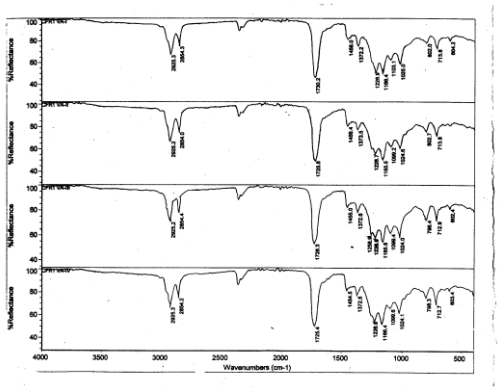


Figure IV. IR spectrum

Conclusion

Poly (Castor oil Fumerate) Polyester Resin blend Vinyl acetate is polyester obtained from the bio renewable resource and the setting and crosslinking of the polymer depends on the concentration of the monomer.

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