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Synthesis and Characterization of Urethane Modified Polyestreamide

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ABSTRACT

In recent years application of renewable resources has become the matter of choice in the field of coating and paint industries.. Jatropha curcas seed oil having suitable unsaturation in the fatty acid chain, low color values and also has low viscosity provide an opportunity to utilize in making urethane polyesteramide resin. Polyesteramide resins contain sufficient amide linkages in addition to ester linkages as a repeating unit and known for improve water and chemical resistance performances. With a view towords the use of Jatropha curcas seed oil, as a precursor for the synthesis of polyesteramide resins and to cure at ambient temperature, toluene diisocyanate (TDI) was incorporated into polyesteramide in varying proportions to obtain urethane modified polyesteramide. It has been found that TDI could be incorporated into polyesteramide upto 6 wt% beyond this wt% the resin loss their fluidity and forms lumpy aggregates.The latter resins were found to cured at room temperature. The synthesized resins were characterized by determination of acid, saponification, iodine and hydroxyl values. The broad structural feature of the polyesteramide and urethane modified polyesteramides were assigned by FTIR, ^{1}HNMR,^{13}CNMR spectroscopies.

Key words: Jatropha curcas seed oil, polyesteramide, urethane

INTRODUCTION

In recent years synthesis of the polymers from renewable resources has attracted considerable attention of the research scientists and academia through out the world, because of the continuous hike in price of petroleum and high rate of depletion of natural mineral resources [1-7]. Furthermore, it has also been forecasted that petroleum stocks moving of the point of exhaustion by the late of 21st century [8-10] consequently much attention is focused in the development of materials from forest product which could be grown again and again. This has inspired investigation of the natural renewable sources as an alternative for the polymer industry[1, 3, 11-13]. These polymers are having great application in different areas such as in adhesive, varnishes, coatings materials, encapsulating materials and surgical equipments etc [5, 6, 14-16].

India possess vast forest resources and crowned with various herbs, plant and farm land, yielding variety of oil bearing seeds such as castor[17-18], linseed[19], vernonia [20] anona squamossa[21], pungamia glabra [22], soybean [23-24], cocos[25], sunflower[25-26], tung oil[27-28] safflower [29-30], canola [30]etc . The advantage of these polymeric starting materials include their low cost, ready availability and annual renew ability of resultant polymer material after the targeted use [4-5, 31].

JATROPHA tree yielded non edible seeds which contain about 48% oil into appropriate percentage of fatty acid. Although the *Jatropha* oil is of significant importance, but very little work has been reported in the literature regarding its utility in synthesizing polymers[30, 34]. Keeping the fact that ***Jatropha curcus*** will be going to one of the most abundant oil bearing plant. In present work we have utilized the seed oil of the Jatropha curcas in making urethane modified polyesteramide resin with the objective of using a precursor obtained from of a non-conventional seed oil in making polymeric materials cured at room temperature and reduce the pressure on utilization of petrochemicals.

EXPERIMENTAL

Materials

Oil was extracted from crushed seed of *Jatropha curcas* through soxhlet apparatus, petroleum ether (b.p 60-80^{0}C) was used as solvent. The fatty acids composition of the oil is given in Table-1. Phthalic acid, oxalic acid, acetic acid glacial, pyridine, methanol, carbon tetrachloride, sodium hydroxide, were used of analytical grade (Merck India). Diethanolamine of analytical grade (S.d.Fine chemicals) was distilled under redused pressure before use. Toluene 2,4 diisocynate was obtained from s.d.Fine Chemicals.

Synthesis of n.n-bis (2-hydroxy ethyl) jatropha curcas oil fatty amide (HEJCA)

Diethanolamine 0.32 mol and sodium methoxide 0.007 mol were taken in four necked round bottom flask fitted with an electrical stirrer, thermometer, dropping funnel and condenser. The reaction mixture was heated to 140±5^{0}C. The Jatropha curcas oil (0.1 mole) was added drop wise into the reaction mixture over a period of one hour. The progress of reaction was monitored by TLC .The reactant was further heated for 2-21/2 hour to ensure the conversion of oil into HEJCA. After the completion of reaction the product was dissolved in diethyl ether and washed with dilute aqueous sodium chloride solution. The ethereal solution was filtered and evaporated in a rotatory vacuum evaporator to obtain HEJCA.

Synthesis of jatropha curcas polyesteramide (JCPEA)

HEJCA, phthalic acid in equal molar ratio and xylene as a solvent were placed in four necked round bottom flask fitted with a Dean Stark Trap, thermometer and mechanical stirrer. Reaction mixture was heated up to 160^o C. The progress of reaction was monitored by taking acid value at regular intervals. After the completion of reaction, the product was taken out from the reaction flask and xylene was removed under reduced pressure to obtain JCPEA.

Synthesis of polyesteramide urethane (PEAU)

Polyesteramide of *Jatropha curcas* seed oil dissolved in xylene, and treated with varying amount of toluene-2, 4 diisocyanate (TDI) monomer in three necked round bottom flask fitted with mechanical stirrer and thermometer. The extent of loading of toluene-2, 4 diisocyanate (TDI) is given in Table-2. The reaction mixtures were heated at 130±5^{0}C under continuous stirring. The progress of reaction was monitored by thin layer chromatography (TLC) and also by determination of the hydroxyl value and acid value. The drying time continuously decreases on increasing the amount of TDI upto 6 wt% no signified reduction in time was noticed after this wt%. In addition to this resins losses fluidity and form lumpy aggregates.

characterization

HEJCA, JCPEA, , and PEAU were characterized by FTIR, ^{1}HNMR and ^{13}CNMR spectroscopies. FTIR spectra of these resins were taken on a Perkin Elmer 1750 FTIR spectro photometer (Perkin Elmer Cetus instrument Norwalk, CT, USA) using NaCl cell. ^{1}HNMR and ^{13}CNMR spectra were recorded on JEOL GSX 300MHZ FX 1000 spectrometer using deutrated chloroform as a solvent and tetramethylsilane as an internal standard.

The various physico-chemical characterizations like specific gravity, refractive

Table 1: Characterization of JCSO, HEJCA and JCPEA

Characteristic	JCSO	HEJCA	JCPEA
Oil content	40%	-	-
Gardener color no.	4.0	5	8
Specific gravity	0.927	0.938	0.948
Refractive index	1.475	-	-
Iodine value	96	30	24
Acid value	7	4	10.6
Saponification value	9	144	132
Yield	80.68	85.16%	
Fatty acid composition			
Myristic	0.5		
Palmitic	12-17		
Stearic	5-6		
Arachidic	0.3		
Oleic	37-63		
Linoleic	19-40		

Table 2: Physico-chemical characterization of polyesteramide urethane resins

Resin	Wt % of TDI	Acid value (mg KOH)	Hydroxyl value (%)	Saponification value	Iodine value	Specific gravity	Refractive index	Viscosity (dl/g)
PEAU	2	7.42	7.82	132	32.0	0.948	1.512	0.652
PEAU	4	7.26	7.74	124	30.0	0.952	1.515	0.664
PEAU	6	7.22	7.66	118	28.2	0.955	1.517	0.674
PEAU	8	7.06	7.52	113	27.8	0.957	1.518	0.728

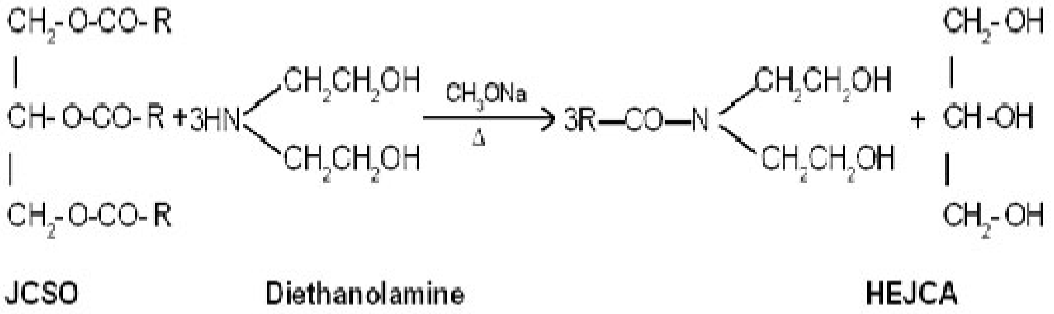

Fig. 1: Synthesis of HEJCA

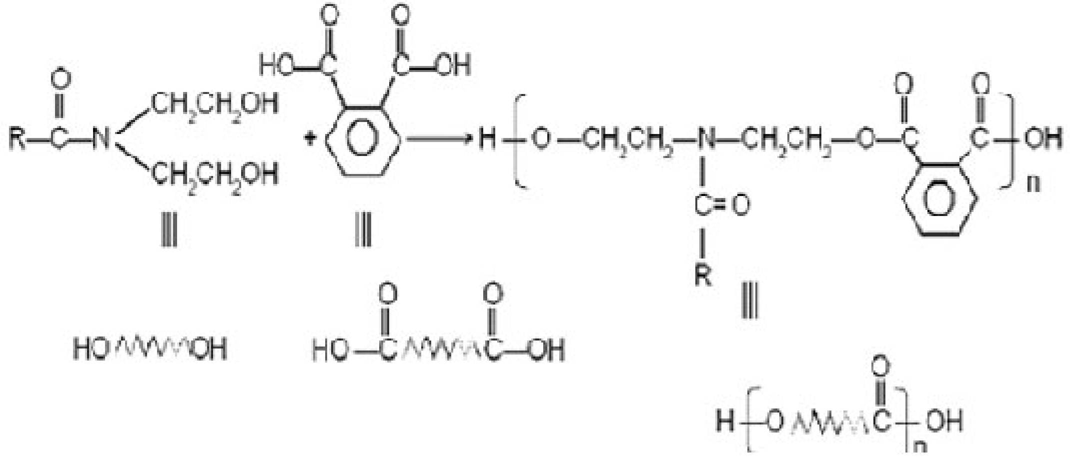

Fig.1(b): Synthesis of JCPEA

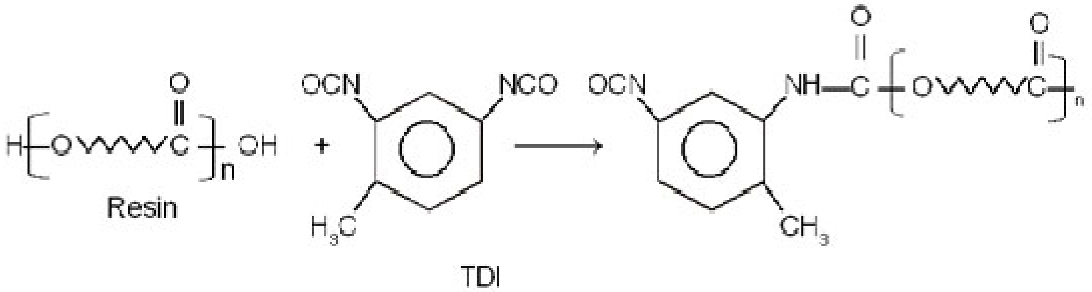

Fig.1(c): Synthesis of PEAU

value, acid value and saponification value of the same were determined as per standard laboratory methods and summarized in Table 1and 2.

Spectral Analysis

N.N-BIS (2-hydroxyl ethyl) jatropha curcas oil fatty amide (HEJCA)

The IR spectra of the HEJCA shows the band of alcoholic group at 3376 cm^{-1} (broad band of a primary alcohol), CH_2 asymmetric and symmetric stretching peak at 2927 and 2855 cm^{-1} respectively. The band for amide carbonyl was observed at 1622 cm^{-1} confirm the formation of amide linkages, while CH_2 bending appears at 1463 cm^{-1} and CN stretching peak (C-N group) at 1368 cm^{-1}.

The ^{1}HNMR spectrum of HEJCA shows the peak at ä = 0.862-0.89 ppm for terminal methyl group. A broad peak of chain CH_2 group appears at 1.26 - 1.60 ppm , CH_2 attached to amide nitrogen appears at ä = 3.46 ppm as a triplet. CH_2 attached to –OH group appears at 4.20 ppm, the alcoholic group appears at 5.3 ppm, the chain -CH=CH- appears at 5.282-5.35 ppm as a multiplet. These spectral datas are characteristic of structure of HEJCA Fig.1 (a).

^{13}CNMR spectra shows the characteristic signal of amide –CO group at 175.22 other signal such as terminal $–CH_3$ group appears at 13.9 ppm, the different CH_2 group of the fatty acid chain appears at 22-34 ppm. The CH_2 of adjacent to carbonyl group appears at 32.9, the CH_2 adjacent to –OH appears at 65.52, and CH_2 adjacent to amide appears at 50.75 ppm. The olefinic double bonded carbon of fatty acid chain appears at 127 and 129 ppm, respectively.

Jatropha Curcas Polyesteramide (JCPEA)

The IR spectra of the JCPEA shows the band of alcoholic group at 3378 cm^{-1} (broad band of a primary alcohol), CH_2 asymmetric and symmetric stretching band at 2921 and 2856 cm^{-1} respectively. The band for amide carbonyl and carbonyl group of ester are observed at 1634 and 1735 cm^{-1}. The CN stretching band (C-N group) at 1463 cm^{-1}; The C-O-C symmetric and asymmetric band are observed at 1275 and 1383 cm^{-1}.The band at 769.4 a characteristic of disubstituted benzene of a phthalic acid. The ^{1}HNMR spectrum of JCPEA shows the peak at ä=0.86-0.89 ppm for terminal methyl group. A broad peak of chain CH_2 group appears at 1.26-1.30 ppm , CH_2 attached to amide nitrogen appears at ä=1.60-1.61 ppm . The sharp peak of CH_2 adjacent to the ester group is observed at ä=2.02- 2.06 ppm, alcohol i.e proton at ä=4.33 ppm, -CH=CH- at ä = 5.29-5.36 ppm, and aromatic protons are observed at ä=7.30-7.48 ppm, supporting the structure of JCPEA as shown in Fig.1 (b).

^{13}C-NMR spectra shows the characteristic signal of carbonyl of ester at 177 ppm confirm the formation of ester linkages. The additional signal such as –CO of amide appears at 173 ppm . Various ring carbon of benzene ring appears at 133, 132, 129, 127, 123 ppm. The peak for different CH_2 groups of the fatty acid chain appears at 34-24 ppm the peak for double bonded carbon of a fatty acid chain appears at 127.8 and 127.2 ppm respectively . Terminal methyl group of fatty acid chain appears at 14 ppm.

Polyester AmideUrethane (PEAU)

The IR spectra of PEAU are more spread than PEA in the range of 3500-3150 cm^{-1} indicates the overlap of OH and NH groups. These characteristic bands indicate the introduction of NH group in addition to OH group. In case of PEA the peak is suppressed and appears as a solder 3378 cm^{-1}. In PEAU the NH deformation mode appears at 1560 cm^{-1}, CH_2 asymmetric and symmetric stretching peak appears at 2925.3 and at 2863 cm^{-1} respectively. The –CH=CH- appears at 3022.6 cm^{-1} where as aromatic double bond appears at 2963.3 cm^{-1}. The peak for amide carbonyl and carbonyl group of ester are observed at 1607 and 1727 cm^{-1}. The CN stretching peak (C-N group) appears at 1494 cm^{-1}. The C-O-C symmetric and asymmetric peaks are observed at 1378 and 1456 cm^{-1}. The band at 1456, 1378, 1229, 1038 are characteristic of disubstituted benzene of a phthalic acid.

The ^{1}HNMR spectrum of PEAU shows the peak at ä=0.86-0.88 ppm for terminal methyl group. The peak at ä=2.02-2.07 ppm for methyl group of TDI. A broad peak of chain CH_2 group appears at 2.23-2.37 ppm , CH_2 attached to amide nitrogen appears at ä=2.56-2.66 ppm . The new peak for –NH of urethane at 7-8.8 ppm. The different characteristic peaks for aromatic protons are observed at ä=6.93-7.28 ppm. These observations broadly confirm the proposed structure of PEAU as shown in Fig.1(c).

^{13}CNMR spectra show the characteristic signal of carbonyl of ester at 178 ppm and signal for carbonyl of amide at 174 ppm. Various ring carbon of benzene ring appears at 137, 136, 134, ppm. The peak for different CH_2 groups of the fatty acid chain appears at 22-19 ppm. The peaks for methyl group of TDI appear at 15- 14 ppm.

CONCLUSION

In this work Jatropha curcas seed oil a renewable resource used as a starting material for the synthesis of PEAU, cured at room temperature which reduce the consumption of petrochemical in making polymeric resins. The color of PEAU very low which provide avenue for utilization in paint industries. The broad spectral feature of the HEJCA, JCPEA and PEAU was confirmed by IR, ^{1}HNMR, ^{13}CNMR spectroscopies. The various physico-chemical properties were also investigated. These informations can be used in making high performance coatings and paints.

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