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Synthesis and Evaluation of Polyesters from Rice Bran Oil

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Abstract - This research aims to study the synthesis and evaluation of rice bran oil based polyesters. Rice bran oil is readily available, low cost and used for the synthesis of various polymers. Rice bran oil based polyester sheet was synthesized by the treating rice bran oil with peroxyacetic acid followed by the addition of acrylic acid. The obtained acrylated epoxidised rice bran oil resin was cured in the presence of vinyl acetate, methyl methacrylate, benzoyl peroxide and dimethylaniline. The spectral analysis such as FT-IR, swelling, crosslink density, solvent absorptivity percentage, thermal and mechanical properties were evaluated. This result found that the RPSVA possess maximum swelling, good thermal and mechanical properties due to high crosslink density.

***Keywords: Rice bran oil, acrylated epoxidised rice bran oil resin, polyesters, chemical resistance, swelling, thermal and mechanical properties*.**

I. INTRODUCTION

Polymers are complex and giant molecules composed of numerous repeated smaller molecules. Polymers and polymeric materials possess excellent mechanical properties, high corrosion resistance and low assembly costs [1].

Several polymeric materials have been synthesized using renewable resources such as starch, lignin, protein, wool, fiber, vegetable oils and many others. They fine plentiful applications such as plasticizers, adhesive, biodegradable packaging materials, biological appliances, biomedical engineering, coatings and binder for paints [2]. Now a days, there is a rising interest to produce biopolymers. Triglyceride oils are one of the most significant sources for biopolymers. Oil-based biopolymers comprise many advantages compared with polymers prepared from petroleum based monomers. They are biodegradable and in many cases, cheaper than petroleum polymers [3].

Triglycerides are known as triacyl glycerol (TAG), glycerol molecule is attached to the fatty acid chains of unsaturated and saturated fatty acids. The saturated fatty acids contain only single bond between two carbon atoms. The unsaturated fatty acids present in vegetable oils are oleic acid, lioleic and linolenic acid containing one, two and three double bonds between two carbon atoms [4]. 90-95% of the total weight of triglycrerides accounts for the fatty acids and their content is specific of each plant oil [5].

RBO is used extensively as premium edible oil in many Asian countries like Japan, Korea, China, Taiwan and Thailand. It is also called as “Heart Oil”. Current world production of rice is approximately 500 million tons per annum. When paddy is milled, the germ and bran layer is separated from the endosperm. The milling process of paddy produces about 20% husk, 8-10% bran, 2% rice germ and approximately 70% starch endosperm (white rice). Rice bran with about 15-30% lipids is a good source of protein, minerals, vitamins, phytin, trypsin inhibitor, lipase and lectin [6].

Epoxy resin is a compound or prepolymer undergoes ccationic or anionic homopolymerization with curing agents, frequently called hardners or crosslinkers [7]. Among different hardners, carboxylic acid, polyamines and anhydride is the most important curing agents used for the conversion of epoxy resin to highly crosslinks, glassy and three dimensional networks [8].

Although epoxidised vegetable oil based polymers suitable as a polymeric matrix further modification involves acrylation of the epoxides. Reaction of epoxy functional triglyceride with acrylic acid incorporates acrylate chemical groups on to the triglycerides, attaching vinyl functionalities to its structure [9].

Polyester is a long-chain polymer with chemically composed of an ester, dihydric alcohol and terphthalic acid formed by the esterification condensation of polyfunctional alcohols and acids [10]. Polyester used as the major binder since 19^{th} century because of their

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excellent auto- oxidative, chemical and mechanical properties [11].

Life cycle of polymer based on triglyceride oil is shown in Figure 1.

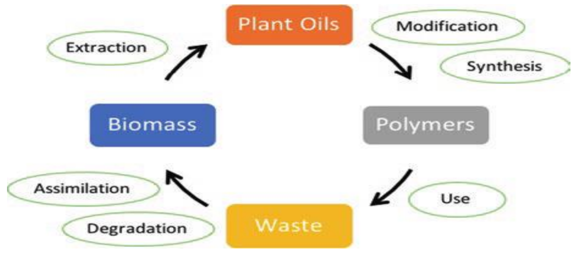

Figure 1 Life cycle of polymer based on triglyceride oils

Triglyceride structure of rice bran oil is presented in Figure 2.

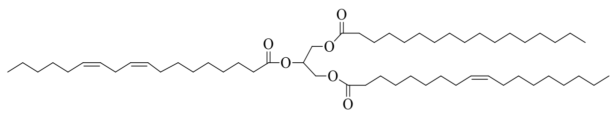

Figure 2 Triglyceride structure of rice bran oil

II. EXPERIMENTAL

A.MATERIALS

The raw materials used for the synthesis of polyesters were Acetic acid (glacial), Hydrogen peroxide (30%), Sulphuric acid (Merck), Acrylic acid, Triethyl amine (Sigma-Aldrich), N, N-Dimethyl aniline, Benzoyl peroxide were purchased from Merck, Vinyl acetate and Methyl acrylate were obtained from Sigma-Aldich.

B. Synthesis of crosslinked polyesters

Rice bran oil was epoxidised using glacial acetic acid and hydrogen peroxide solution at 160^{0}C for about 8 hrs. The prepared epoxidised resin with acrylic acid and triethylamine at 160^{0}C for about 2 hrs and allowed to vacuum oven at 80^{0}C for about 1 hr to produce acrylated rice bran oil resin. Which is treated with vinyl acetate as the monomer, benzoyl peroxide was used as the initiator and N,N-dimethylaniline as the accelerator. The mixture was poured into silicon spreaded glass plate and cured in oven at 180^{0}C for 6 hrs. The obtained sheet was coded as RPSVA. The above same procedure was followed for the methyl acrylate monomer based polyester sheet codes as RPSMA (Figure 3).

C. FT-IR spectral analysis

Infrared qualitative analysis of all polyester sheets were carried out using Shimadzu FT-IR 8400S spectrometer based on KBr pellet method.

D. Determination of swelling and molecular weight between crosslinks

The accurately weighed polyesters were allowed to swell in the solvents having different solubility parameters such as ethyl methyl ketone, toluene, tetrahydrofuran (THF), chloroform, acetone, dimethyl acetamide (DMA), ethanol, n-butyl alcohol, ethylene glycol and dimethyl formamide (DMF) in diffusion test bottles for 2 days at room temperature. After immersion of the solvents, the sheets were removed from and the wet surfaces were dried quickly using tissue paper.

E. Determination of solvent absorptivity percentage

The polyester sheet was put in 3 ml of different solvents for 24 hours. After 24 hours, excess of the solvent present on the surface of the polyester sheet was removed by using filter paper. Then it was weighed and the solvent absorptivity percentage (%) was calculated using the following equation,

$$\text{Solvent absorptivity percentage} = \frac{W2 - W1}{W1} \times 100$$

Where,

W_1 = Weight of the dry sample

W_2 = Weight of the sample after absorption of the solvent

F. Determination of mechanical properties

Tensile strength of the newly prepared polyester sheets were determined in Universal Testing Machine at across head speed of 100 mm / minute using rectangle shaped specimens (10 × 1 cm) punched out from sheets as for ASTM D6100. The gauge length was fixed at 3 cm in each test. The tensile strength, Young's modulus and elongation at break were calculated using standard formulations. Shore A hardness of polyesters were tested by using Durometer type A shore instrument according to ASTM D2240 standard.

G. Determination of thermal properties

Thermal properties are used to study thermal stability of the polyesters, which are influenced by the molecular weight between crosslinks and the degree to which segments from stiff sequences and elastically dynamic branch points [12]. Thermal properties of new polyesters were studied by TGA and DTA. TGA carried out a heating rate of 100C/min ambient to 500^{0}C under nitrogen atmosphere, the weight loss was noted for all the polyesters. In DTA, the decomposition checked for all the polyesters.

III. RESULTS AND DISCUSSION

A.FT-IR spectral analysis of crosslinked polyesters

The FT-IR spectra of vinyl acetate and methyl acrylate based polyester sheets (Figure 3 & 4) shows the peak at 1727.64 & 1734.14 cm^{-1} is corresponds to the C=O stretching of ester carbonyl group. The peaks at 2924.09 & 2929.12 cm^{-1} indicates the extra hydrogen bonding interaction with the hydroxyl groups.

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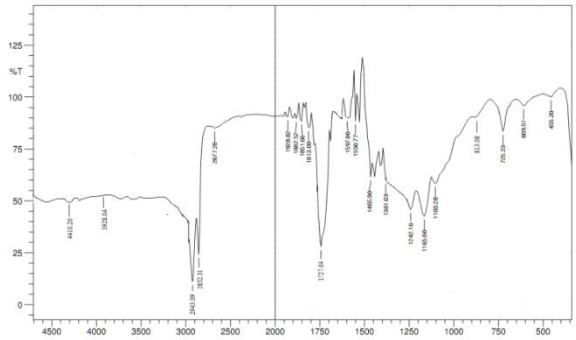

Figure 3 FT-IR spectrum of RPSVA

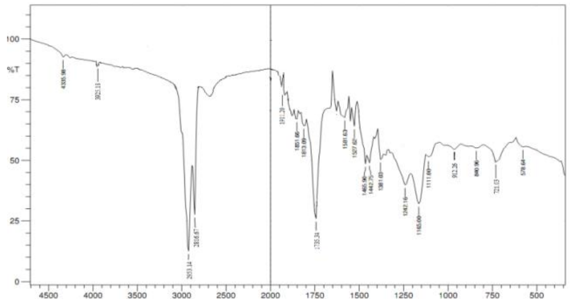

Figure 4 FT-IR spectrum of RPSMA

B. Swelling properties

Swelling coefficient of polyesters are presented in Table 1. The solubility parameter of the solvents in the x-axis was plotted against swelling coefficient in the y-axis shown in Figure 5. This shows that the synthesized polyesters are should be crosslinked. Then the prepared polyester sheets were maximum swelled in dimethyl acetamide (DMA).

Table 1 Swelling coefficient of crosslinked polyesters

Swelling coefficient 'Q'	Polyesters	
	RPSVA	RPSMA
EMK	0.24	0.20
Toluene	0.22	0.24
THF	0.29	0.25
Acetone	0.25	0.23
DMA	1.28	1.26
Chloroform	0.33	0.29

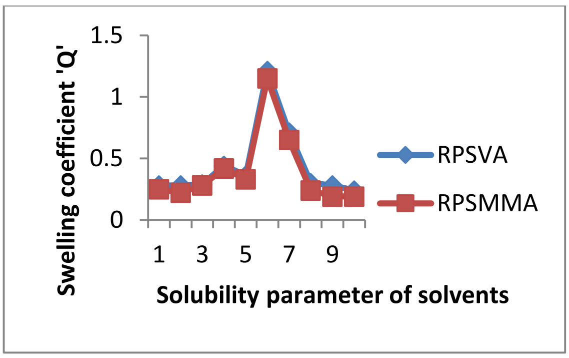

Figure 6 Swelling coefficient of crosslinked polyesters

Table 2 Crosslink density of polyesters

Polyesters	Density (g/cc)	Swelling coefficient in DMA (Q)	Crosslink density ($\times10^{-3}$)	Molecular weight between crosslinks (mol^{-1})
RPSVA	1.25	1.30	1.427	680.23
RPSMA	1.19	1.21	1.230	582.02

C. Solvent absorptivity percentage

In the present investigation, solvent absorptivity percentage is carried out in different solvents such as EMK, Toluene, THF, Acetone, DMA and Chloroform. These values are presented in Table 3. From the data, it is found that the solvent absorptivity percentage of polyesters increases from non-polar to polar solvents. This shows these polyesters are hydrophobic in nature. Maximum swelling is observed for polar aprotic solvent like dimethyl acetamide (DMA).

Table 3 Solvent absorptivity percentage of crosslinked polyesters

Solvent absorptivity percentage (%)	Polyesters	
	RPSVA	RPSMA
EMK	15.82	13.19
Toluene	17.58	16.29
THF	24.52	19.16
Acetone	30.71	26.10
DMA	73.1	70.29
Chloroform	37.00	29.77

D. Mechanical properties

The data on the mechanical properties of polyesters such as tensile strength, elongation at break, young's modulus and shore A hardness are given in Table 4. Among two polyesters, RPSVA shows higher tensile strength, young's modulus and hardness due to its higher crosslink density. Crosslinking increases the more rigid network of polymer with better mechanical properties [13].

Table 4 Mechanical properties of crosslinked polyesters

Properties	RPSVA	RPSMA
Tensile strength (MPa)	16.8	15.1
Elongation at break (%)	138	127
Young's modulus (MPa)	9.3	8.13
Shore A hardness	38	35

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E. Thermal properties

Thermal properties are used to study the thermal stability of the polyesters [15]. In TGA curves of the polyesters have two different temperature regions were obtained, the samples experienced significant weight loss at 100-250 ^{0}C (stage I). On the other hand, the insoluble substances were found to be highly crosslinked thermosets that decompose at 240-450^{0}C (stage II). The polyesters decomposes at 440-500^{0}C (stage III) this may be due to the completed decomposition of polyester moiety results the char residue.

DTA thermogram of the polyesters shows two exotherms and mild softening temperature between 30-120 ^{0}C, which may be due to disruption of physical crosslinks. TGA & DTA of crosslinked polyesters are shown in Figure 7 & 8 and the data's are tabulated in Tables 5 & 6.

Table 5 TGA data of polyesters

Polyesters	TGA data		
	Temperature (^{0}C) at the each stage of degradation weight loss (%)		
	I (Tstart)	II	III
RPSVA	247.10 (11.01%)	379.41 (76.12%)	496.12 (99.10%)
RPSMA	245.07 (9.41%)	384.02 (88.20%)	492.34 (98.30%)

Table 6 DTA data of cpolyesters

Polyesters	Endothermic response (^{0}C)			Exothermic response (^{0}C)	
	Softening	I	II	Iexo	IIexo
RPSVA	86.3	374.5	429.6	402.0	491.4
RPSMA	84.1	372.3	425.4	392.5	452.7

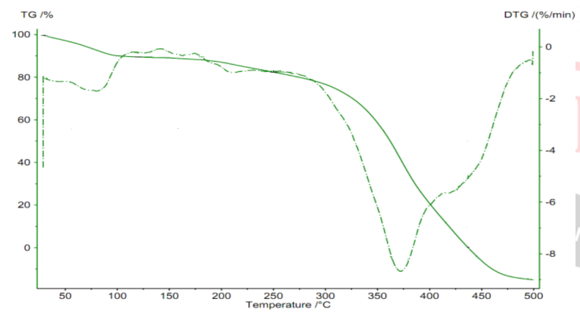

Figure 7 TGA/DTA curve for RPSVA

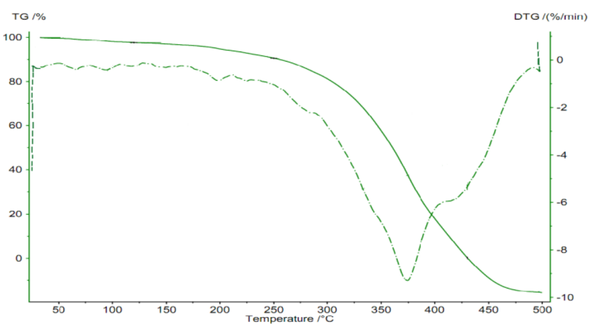

Figure 8 TGA/DTA curve for RPSMA

IV. Conclusions

The outcome of this study revealed that the RPSVA based polyester has high crosslink density than the RPSMA based polyester sheet. Crosslinking increases the more rigid network and reduces the molecular mobility of the chains between the junctions. Both polyesters have maximum swelled in dimethyl acetamide (DMA).

Thermogravimetric analysis shows the prepared polyesters are hydrophobic in nature and RPSVA based polyester possesses good thermal stability due to high crosslink density. RPSVA based polyester possesses high tensile strength, Young's modulus and hardness due to its higher crosslink density. Crosslinked polyesters are potential used for various consumer applications such as sporting goods, packaging materials and agrochemical applications.

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