

PART-2/CHAPTER-4

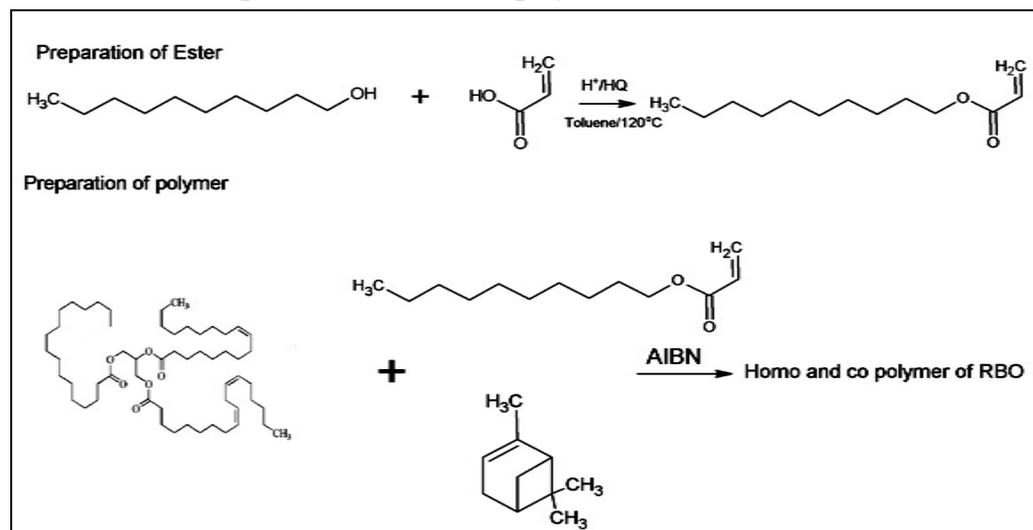
RICE BRAN OIL-BASED HOMO AND COPOLYMERS AS POTENTIAL LUBE OIL ADDITIVES

2.4.1 INTRODUCTION

Lubricating oil additives are the substances which when added to the oil, can either improve the properties already present or incorporate some new feature in it[2]. The most important categories of additives are surface protective additive like friction modifier, antiwear, extreme pressure, detergent, dispersant additive. Performance additive like viscosity improver, pour point depressant. Antioxidant additives protect lubricants from being auto oxidized hence they are lube protective additives of base lube. Additives synthesized from vegetable oils are less toxic and more environmentally benign due to their biodegradable property and low toxicity [3]. Moreover, they exhibit high viscosity index (VI), low pour point, and good antiwear property. Though vegetable oil itself exhibits high viscosity index, low pour point, high dispersant activity, high-temperature stability but unsaturation present in their fatty acid moiety makes them vulnerable to aerial oxidation. After performing certain chemical modifications they can act as a multifunctional lube oil additive. Therefore, more focus has been laid on the research of lube oil additives from vegetable oils. Rice bran oil contains a high percentage of unsaturated triglycerides and can be used as a monomer in free radical polymerization [4]. There are many research papers based on rice bran oil in the field of food[5], pharmaceutical[6], cosmetics[7], industries, etc. However, reports regarding the application of acrylate and alpha-pinene copolymers of rice bran oil as a multifunctional additive for lubricant are very scanty. A recent study in the lubricant industry has given special

attention to the application of plant oil-based additives in lube due to their biocompatibility and enhanced additive performances compared to those toxic chemicals available in the market. In this case, we have prepared a homopolymer of rice bran oil (RBO) and copolymers with decyl acrylate and alpha-pinene at different percentage ratios using a conventional thermal pathway in presence of azobisisobutyronitrile (AIBN) as a free radical initiator[1]. Characterization of the polymers was recorded by spectral technique (FT-IR and NMR spectroscopy). The gel permeation Chromatography method (GPC) was used to determine the average molecular weight of the prepared polymers. Thermogravimetric analysis (TGA) was used to study the thermal stability of the prepared polymers. Standard ASTM methods were used to investigate the performance of all the prepared polymers in two types of base oil as viscosity index improver (VII) and pour point depressant (PPD). Disc diffusion method(DD) and soil burial method(SBT) were used to ascertain the biodegradability of prepared polymers [1].

Scheme 2.4.1:-Preparation of ester and polymer.



Percentage composition(w/w) of major fatty acids in Ricebran oil, Palmitic acid (16:0) 15%, Oleic acid (18:1) 42.5%, Linoleic acid (18:2) 39.2%, Other(saturated or unsaturated) 3.3%[10].

2.4.2 EXPERIMENTAL

2.4.2.1 SYNTHESIS OF THE POLYMERS

The homopolymer of RBO was synthesized by the free radical polymerization method taking the monomers of RBO in presence of the AIBN initiator (Scheme:-2.4.1) The polymerization was carried out in an RB, fitted with a thermometer, magnetic stirrer, condenser, and an inlet for the introduction of air. The monomer was heated to 90° C in presence of toluene as solvent. Initiator AIBN (0.5% w/w, considering total monomer weight) was then added and continuously heated for 5 hours keeping the temperature constant at 90°C. After the completion of the reaction, the product was poured into methanol with continuous stirring, filtered off, and dried. Decyl acrylate was synthesized at 120°C using 1-decanol and acrylic acid in a Dean stark apparatus using H₂SO₄ as the catalyst. The copolymers of RBO with decyl acrylate (DA) (P-1 to P-3) and another set of copolymers of RBO with alpha-pinene (P-4 to P-6) at different percentages ratios were also prepared in a similar procedure. hydroquinone as a free radical quencher, and toluene as solvent [1]. Percentage composition of different monomers in polymers arranged in the following table

Composition in different polymers.

Polymer Code	Specification
P-0	Homopolymer of RBO
P-1	Copolymer ,RBO:DA=9:1 (w/w)
P-2	Copolymer, RBO:DA=8:2 (w/w)
P-3	Copolymer ,RBO:DA=7:3 (w/w)
P-4	Copolymer, RBO:α pinene=9:1 (w/w)
P-5	Copolymer, RBO:α pinene=8:2 (w/w)
P-6	Copolymer, RBO:α pinene=7:3 (w/w)

2.4.3 MEASUREMENTS

2.4.3.1 INSTRUMENTATION

- **SPECTROSCOPIC MEASUREMENTS**

Bruker Avance 300 MHz FT-NMR spectrometer was used to record the NMR spectra by using CDCl_3 as solvent. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wavenumber range of 400 to 4000 cm^{-1} [1].

- **MOLECULAR WEIGHT DETERMINATION**

The average molecular weight was recorded by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at 35° C at a flow rate of 1 mL/min [1].

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

TGA data were recorded on the Shimadzu TGA-50 system, at a heating rate of 10° C/min [1].

2.4.3.2. PERFORMANCE EVALUATION

- **EVALUATION OF VISCOSITY INDEX**

Viscosity index (VI) is an important parameter that determines the change of viscosity of the lubricant at high temperatures. A higher value of VI indicates the small change in viscosity at high temperatures. It was calculated according to standards ASTM protocol[12]. The kinematic viscosities of the lubricant composition were determined at 40° C and 100° C which are required for the calculation of VI.

- **EVALUATION OF POUR POINT**

Pour point values of the lubricant composition were determined according to the ASTM D 97-09 method[13] using the cloud and pour point tester model WIL-471 (India). A good pour point depressant additive decreases the pour point of the lubricant composition to a larger extent.

- **BIODEGRADABILITY TEST**

- (a) **DISC DIFFUSION METHOD (DD)**

The biodegradability test was carried out for the prepared polymers against *Calletotricheme camellia* (CC), *Fusarium equisetae* (FE), *Alterneria alternate* (AA), *Colletrichum gleosproides* (CG), and *Curvularia eragrostidies* (CE) pathogens. A suitable amount of potato extract, dextrose, and agar powder was mixed to prepare the culture media strain. All the experiments were completed in Petri dishes and were kept incubated at 37° C for 90 days after the addition of about 1g of the polymer sample. The fungal progression was studied by a yellow to blackish color change. After 90 days, the polymer samples were recovered from the fungal media by chloroform, purified, and dried. The dried samples were weighed[14].

- (b) **SOIL BURIAL METHOD (SBT)**

The SBT method was carried out as per ISO 846:1997 standard method. A thin film of polymer sample was prepared by taking 1.5 g of each of the samples separately and then buried in the soil. Then the soils with the samples were incubated in a Bacteriological Incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) at 30° C with a relative humidity of 60% for 90 days and thus subjected to the action of microorganisms present in the soil. After 90 days, the polymer samples were recovered by chloroform and weighed[14].

2.4.4 RESULTS AND DISCUSSION

2.4.4.1 SPECTROSCOPIC ANALYSIS

The homopolymer of RBO (P-0) showed an IR absorption band for the ester carbonyl group at 1745.03 cm^{-1} . The peaks at 2852.4 cm^{-1} and 2924.2 cm^{-1} are the stretching vibration of the $\text{CH}_3\text{-CH}_2\text{-}$ group. (Fig:-2.4.7.1) In the ^1H NMR spectra of homopolymer, the peaks in the range of $4.120\text{-}4.314\text{ ppm}$ indicate the protons of -COOCH_2 group (Figure:-2.4.7.2). In the ^{13}C NMR spectra of homopolymer, the peaks in the range of 174.35 ppm indicate the carbons of an ester carbonyl group. (Figure:-2.4.7.3) The carbons of the -OCH_2 group appear in the range $62.77\text{-}64.71\text{ ppm}$. The IR spectra of three copolymers (P-1 to P-3) are almost similar. The absorption band at 1732 cm^{-1} is due to an ester carbonyl group. (Figure:-2.4.7.4) In the ^1H NMR spectra, peaks at $4.020\text{-}4.124\text{ ppm}$ indicate the protons of -OCH_2 of decyl acrylate moiety. The peaks in the range of $4.311\text{-}4.374\text{ ppm}$ indicate the protons of -COOCH_2 group of RBO. No peaks in the range of $5\text{-}6\text{ ppm}$ indicate that polymerization was carried out successfully. (Figure:-2.4.7.5) In the ^{13}C NMR spectra, peaks ranging from $165.65\text{-}173\text{ ppm}$ confirm the presence of carbons of ester groups (Figure:-2.4.7.6). There is no peak in the range of $120\text{ - }150\text{ ppm}$ and it indicates that polymerization was carried out successfully. The IR spectra of the three copolymers (P-4 to P-6) are almost similar. The absorption at 1745.28 cm^{-1} is due to the ester carbonyl group of RBO moiety. The absence of any peak in the range of $4\text{ - }6\text{ ppm}$ in ^1H NMR and $120\text{ - }150\text{ ppm}$ in ^{13}C NMR spectrum indicated the formation of the copolymer of RBO with α -pinene (Figure:-2.7.4.8-Figure:-2.4.7.9).

2.4.4.2 MOLECULAR WEIGHT DATA ANALYSIS

The experimental value of the number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymers (P-0 to P-6) are shown in Table:- 2.4.7.1. From the experimental data, it was observed that among the seven polymers, the homopolymer of RBO (P-0) and the copolymer P-3, have the lowest and highest molecular weight respectively. Moreover, it is also observed that with increasing the percentage of DA moiety (P-1 to P-3) and alpha-pinene moiety (P-4 to P-6) in the copolymers, the molecular weight increases. A better molecular weight is obtained in the copolymers of RBO and DA than RBO and alpha pinene[1].

2.4.4.3 ANALYSIS OF TGA DATA

From the experimental TGA values of the seven polymers, it was observed that the thermal stability of the homopolymer of RBO (P-0) is less than copolymers. This indicates that when DA or alpha-pinene moiety is introduced in the backbone of RBO oil, the thermal stability increases[1]. Two major decompositions have been observed at 160 ° C and 330 ° C with 23% and 85% weight loss respectively in the case of P-0. The thermal stability of copolymers P-1, P-2, and P-3 are almost identical where two major decompositions were observed at 220 ° C and 482 ° C with 22% and 78% weight loss respectively. The thermal stability of copolymers P-4, P-5, and P-6 is less than other copolymers P-1, P-2, and P-3 but higher than the homopolymer of RBO (P-0).

2.4.4.4 ANALYSIS OF VISCOSITY INDEX (VI) VALUES

VI was calculated at different concentrations ranging from 1% to 5% (w/w) in two types of base oil and the values are listed in Table:- 2.4.7.2. The viscosity of lube oil decreases with increasing temperature but when lube oil is blended with the polymeric additives, the decrement of viscosity stops. At high temperatures,

expansion of additive molecules takes place and as a result, the size of the micelle increases. This increased in micelle size prevents the reduction of the viscosity of the lubricant composition. It is also observed that with the increasing concentration of the lubricant composition, the VI values increase. It may be due to an increase in the total volume of polymer micelle and hence improves the VI property[3]. It was found that the VI value increases by incorporation of DA and alpha-pinene moiety in the backbone of the homopolymer of RBO. This may be due to the higher molecular weight and higher crosslink density of the copolymers[8]. The copolymer P-3 has the highest VI value than the other prepared polymers in both types of base oil. It may be due to higher molecular weight compared to others.

2.4.4.5 ANALYSIS OF POUR POINT (PP) VALUES

The pour points of the base oil containing additives at concentration levels ranging from 1%–4% (w/w) are listed in Table:- 2.4.7.2 for two types of base oil which indicate that the prepared lubricant compositions have lower PP than base oil and hence the prepared additives can be used as PPD. From the experimental data, it is observed that the efficiency as PPD increases up to 3% concentration. The reason may be, at this concentration the interaction between the additive and paraffinic wax of base oil is more effective and decreases the shape of crystals of the paraffinic wax[9-10]. Among the seven polymers, P-3 showed best performance as PPD than the others in both types of base oil.

2.4.4.6 ANALYSIS OF BIODEGRADABILITY TEST RESULTS

Biodegradability test results obtained by using the disk diffusion and soil burial test method are presented in Table:- 2.4.7.3. All the polymers showed significant biodegradability against the pathogens *Calletotricheme camellia* and *Alterneria alternate* only. The mass loss after biodegradation of the prepared

polymers was further confirmed by shifting of IR frequency of the ester carbonyl (Figure:-2.4.7.10) along with other shifted peaks and determining the GPC molecular weight after biodegradation is shown in Table:-2.4.7.1. Among the prepared seven polymers, the homopolymer of RBO (P-0) showed better biodegradation both in disk diffusion as well as soil burial test method[14].

2.4.5 CONCLUSION

A consideration of the chemical structures of DA and alpha-pinene may be taken into consideration to explain the differences of performance between the copolymers of RBO with DA and RBO with alpha-pinene. The average molecular weight of copolymers of RBO with DA is better than RBO with alpha-pinene. A viscosity index value of homopolymer of RBO is lower than copolymers and viscosity index value increases with increasing the percentage of DA or alpha-pinene in copolymers. The pour point of the lubricant compositions is found to be better for the copolymers of RBO with DA than the copolymers of RBO with α -pinene and the values decrease with the increasing concentration of the lubricant composition. The homopolymer of RBO and copolymers of RBO with alpha-pinene showed significant biodegradability than copolymers of RBO with DA.

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for Base Oil.

2.4.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-4 of Part-2**”.

2.4.7 TABLES AND FIGURES

TABLE 2.4.7.1

THE WEIGHT AVERAGE AND NUMBER AVERAGE MOLECULAR WEIGHTS (M_w AND M_n) AND POLYDISPERSITY INDEX OF THE POLYMERS BEFORE AND AFTER THE BIODEGRADABILITY TEST

Polymer samples	Before biodegradability test			After biodegradability test		
	M_n	M_w	PDI	M_n	M_w	PDI
P-0(10:0)	11352	16547	1.45	9321	14536	1.55
P-1(9:1)	20503	27323	1.33	17865	24895	1.39
P-2(8:2)	25953	33523	1.29	21712	31247	1.43
P-3(7:3)	38362	46264	1.2	34231	43135	1.26
P-4(9:1)	14274	19213	1.34	12115	17426	1.43
P-5(8:2)	16936	22721	1.34	14487	20147	1.39
P-6(7:3)	18932	24365	1.28	16548	22335	1.34
P-0 (homopolymer of RBO), P-1 to P-3 (RBO: DA) and P-4 to P-6 (RBO: alpha pinene) w/w, M_n = number average molecular weight; M_w = weight average molecular weight; PDI = polydispersity index.						

TABLE 2.4.7.2

POUR POINT AND VISCOSITY INDEX VALUE OF DIFFERENT POLYMERS AT DIFFERENT CONCENTRATIONS

Property/base oil/(PP/VI)	Con., %	Sample						
		P-0	P-1	P-2	P-3	P-4	P-5	P-6
PP/BO1(-3)	1	-6	-6	-12	-15	-6	-9	-12
	2	-9	-9	-15	-18	-9	-12	-15
	3	-9	-12	-18	-21	-12	-15	-18
	4	-9	-12	-18	-21	-12	-15	-18
PP/BO2/(-6)	1	-9	-9	-15	-18	-9	-12	-15
	2	-12	-12	-18	-21	-12	-15	-18
	3	-12	-15	-21	-24	-15	-18	-21
	4	-12	-15	-21	-24	-15	-18	-21
VI/BO1(80)	1	86	98	100	112	96	98	107
	2	90	101	104	118	98	102	115
	3	96	107	116	125	104	110	123
	4	100	109	120	136	107	116	129
	5	105	119	126	140	115	123	137
VI/BO2(85)	1	94	115	119	121	104	116	120
	2	98	118	123	129	107	117	126
	3	102	128	133	135	110	119	132
	4	109	131	138	142	121	130	138
	5	115	135	141	148	129	133	139
BO = base oil; PP = pour point; VI = viscosity index.								

TABLE 2.4.7. 3

RESULTS OF BIODEGRADABILITY TEST BY THE DISC DIFFUSION METHOD AND SOIL BURIAL TEST METHOD & GRAPHICAL REPRESENTATION

sample	Weight loss in disc diffusion method (in g)					Weight loss in soil burial test (in gm)
	CC	FE	AA	CG	CE	
P-0	0.39	0	0.59	0	0	0.38
P-1	0.35	0	0.51	0	0	0.33
P-2	0.27	0	0.46	0	0	0.29
P-3	0.26	0	0.38	0	0	0.24
P-4	0.35	0	0.56	0	0	0.37
P-5	0.34	0	0.56	0	0	0.35
P-6	0.32	0	0.52	0	0	0.35

CC = Calletotricheme camellia; FE = Fussarium equisitae; AA = Alterneria alternata; CG = Colletrichum gleosproides; CE= Curvularia eragrostidies

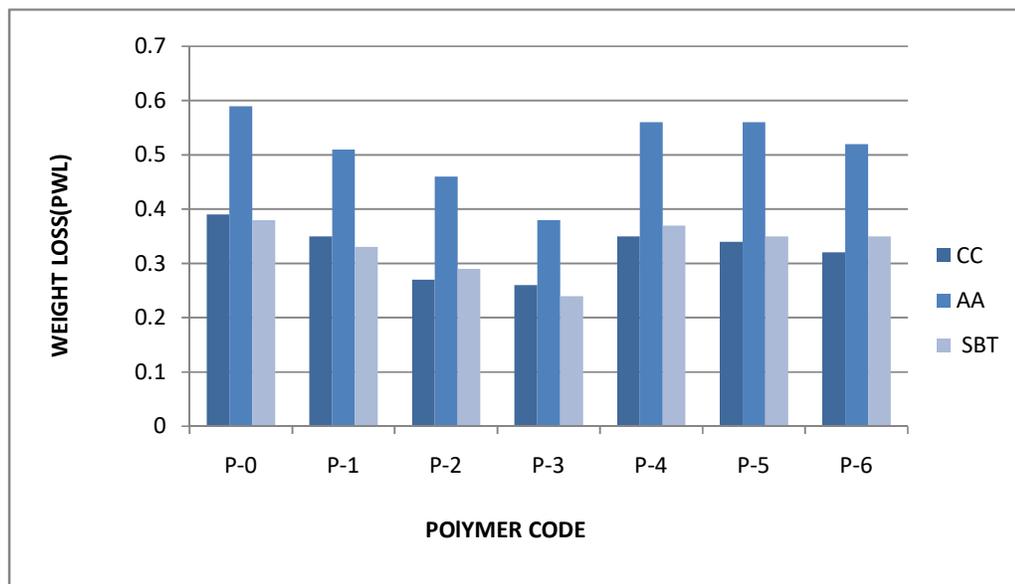


FIGURE 2.4.7.1

FT-IR SPECTRA OF RICE BRAN OIL HOMOPOLYMER

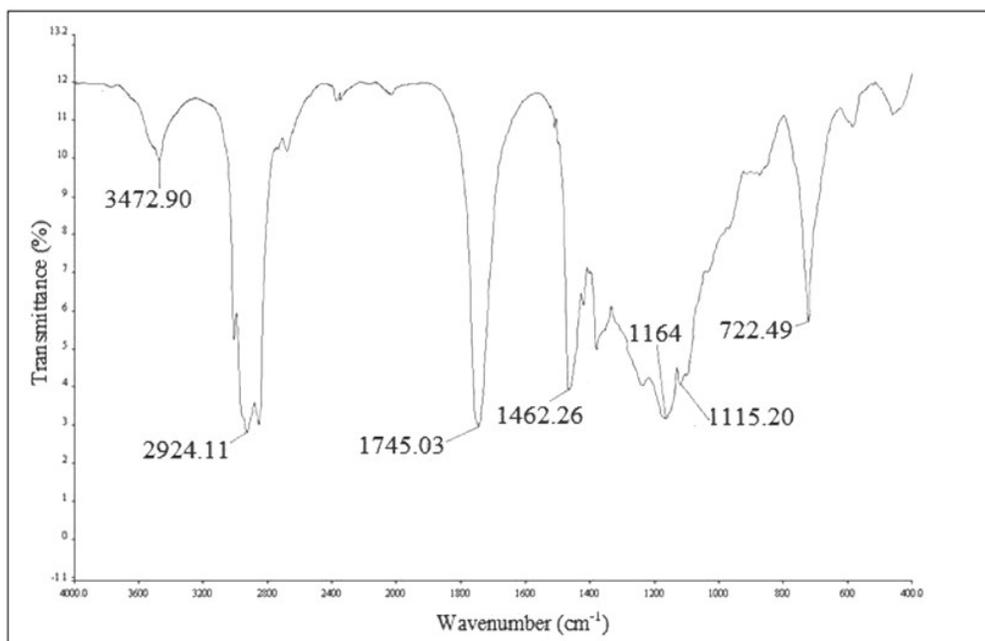


FIGURE 2.4.7.2

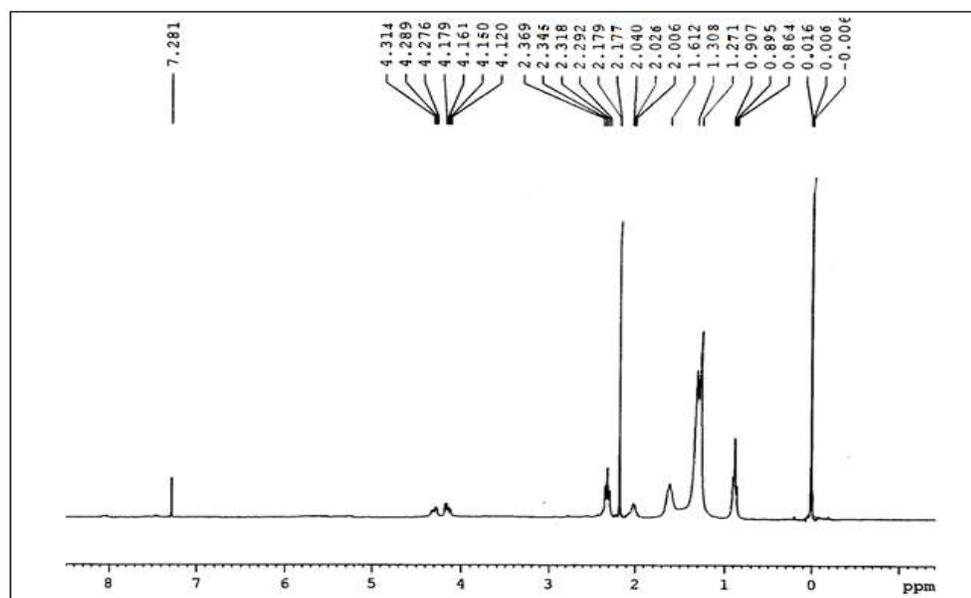
¹H NMR SPECTRA OF RICE BRAN OIL HOMOPOLYMER.

FIGURE 2.4.7.3

¹³C - NMR SPECTRA OF RICE BRAN OIL HOMOPOLYMER

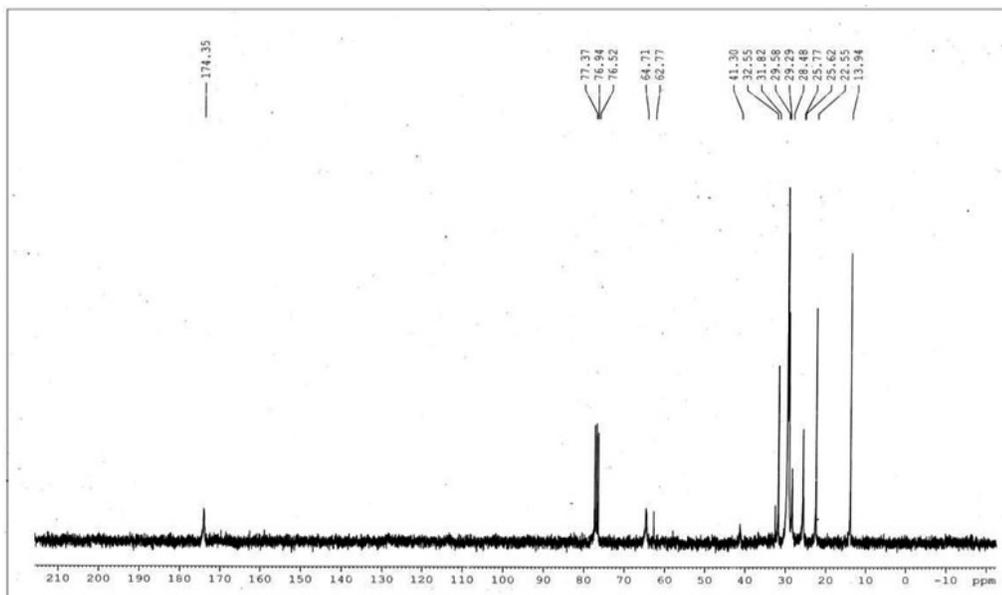


FIGURE 2.4.7.4

FT-IR SPECTRA OF RICE BRAN OIL + DA COPOLYMER

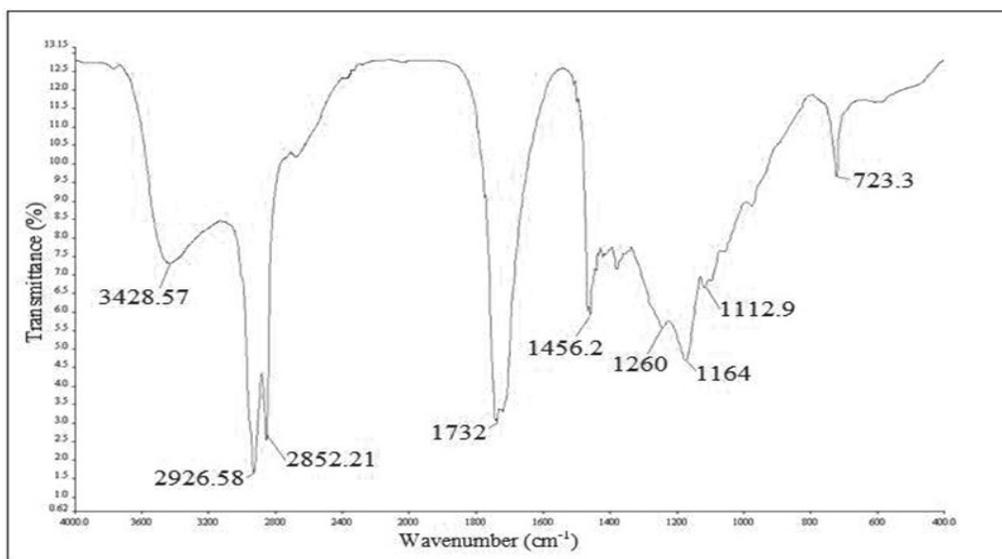


FIGURE 2.4.7.5

¹H NMR SPECTRA OF RICE BRAN OIL + DA COPOLYMER.

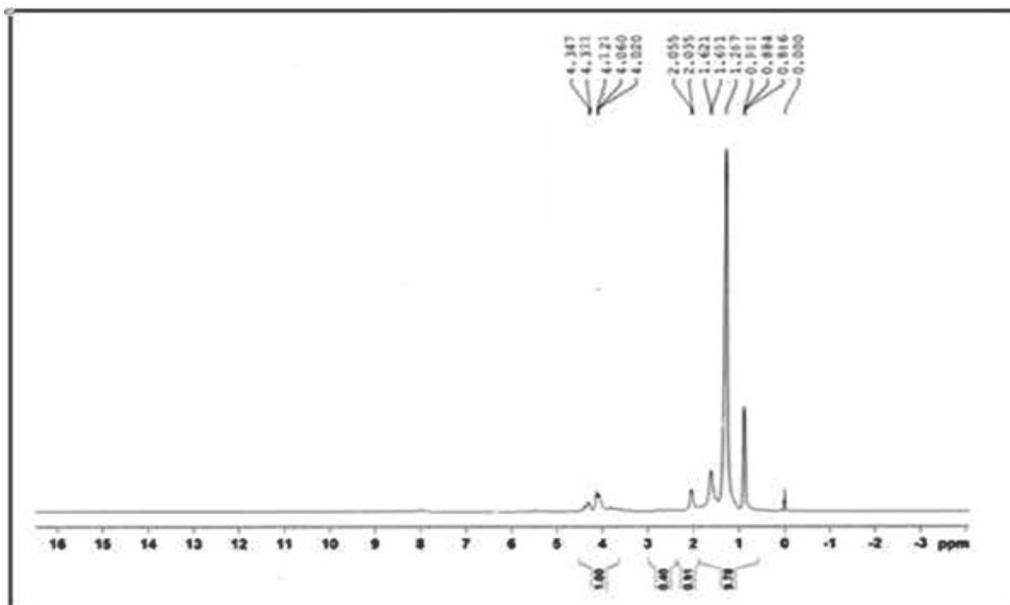


FIGURE 2.4.7.6

¹³C- NMR SPECTRA OF RICE BRAN OIL + DA COPOLYMER

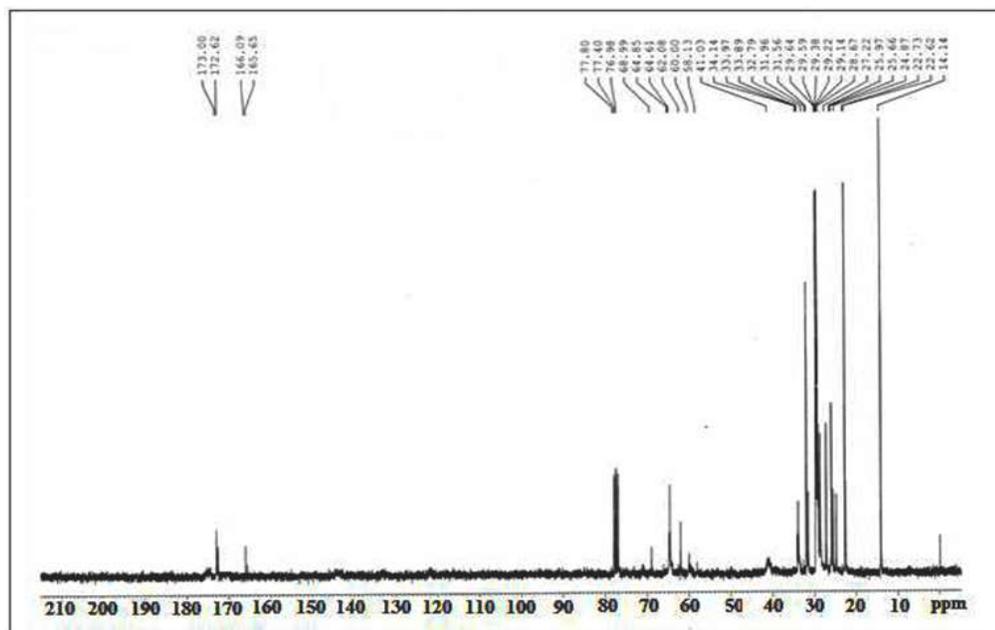


FIGURE 2.4.7.7

FT-IR SPECTRA OF RICE BRAN OIL + ALPHA PINENE

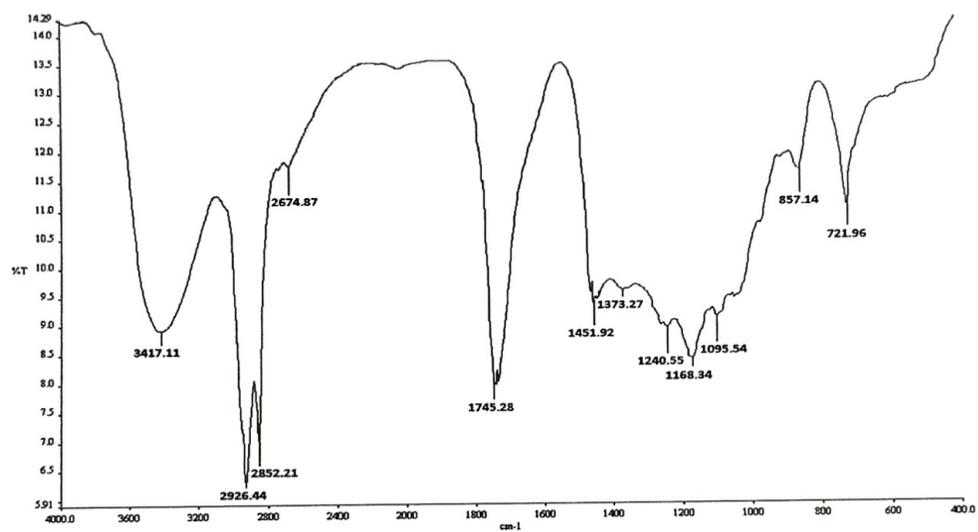


FIGURE 2.4.7.8

¹H NMR, SPECTRA OF RICE BRAN OIL + ALPHA PINENE

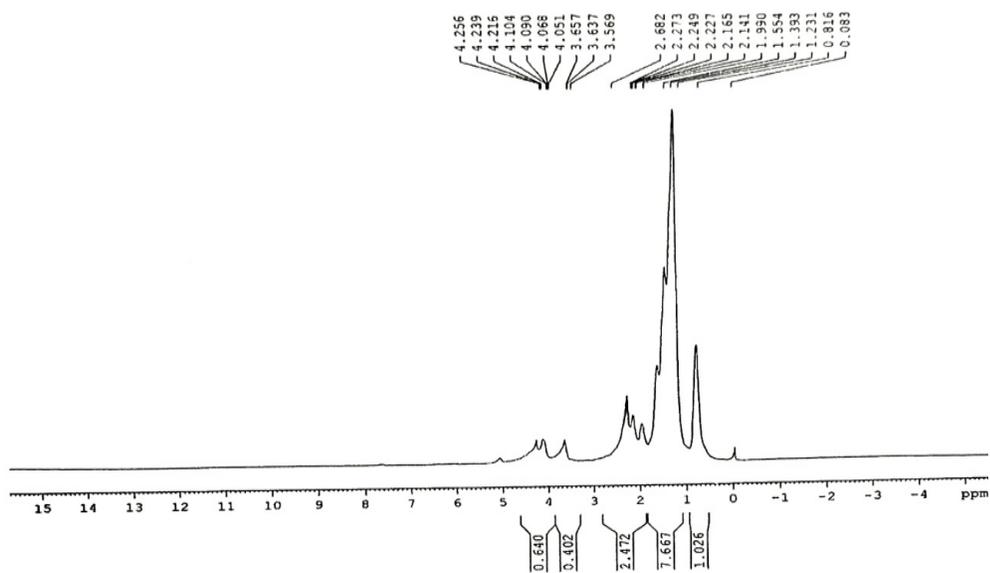


FIGURE 2.4.7.9

¹³C NMR SPECTRA OF RICE BRAN OIL + ALPHA PINENE

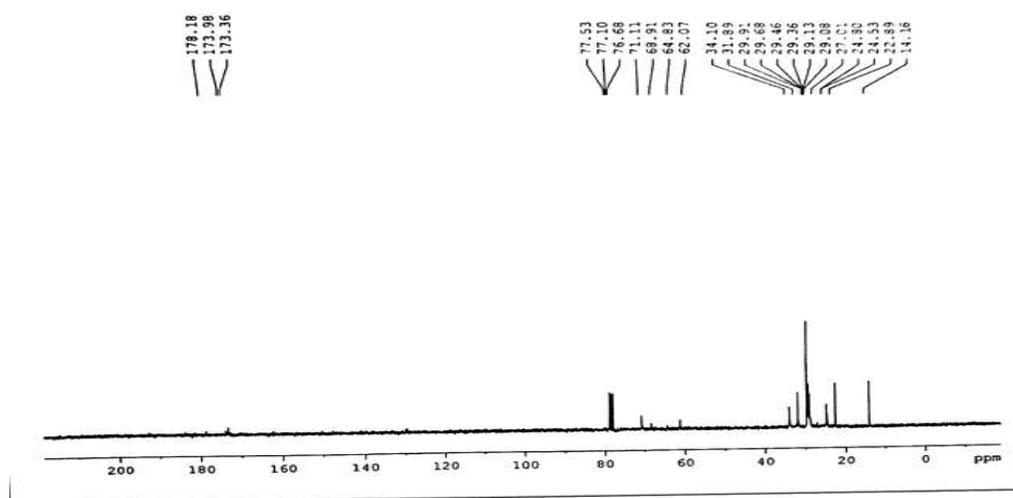


FIGURE 2.4.7.10

COMPARATIVE FT-IR SPECTRA OF RICE BRAN OIL HOMOPOLYMER BEFORE AND AFTER DISC DIFFUSION TEST

