

CHAPTER-II

Biodegradable vegetable oil polymer as a multifunctional lubricating oil additive

3.1.1. Introduction

Modern lubricants are formulated from a range of base fluids and chemical additives. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. Viscosity index improvers, detergent dispersant, antioxidant, anti-wear agent, antifoaming agents, emulsifiers, demulsifiers, pour point depressants etc. are examples of different kinds of additives. Among them most important are PPDs^{1, 2} and VMs.^{3, 4}

There are many additives used as PPDs^{5, 6} and VMs.⁷⁻⁹ Most of the present day additives are synthetic acrylate¹⁰⁻¹² based, but because of potent toxicity environment prevents them from becoming noble additives. Therefore, the development of eco-friendly lubricants has become the primary concern of the present decade. Plant oils are substituted as base fluid for biolubricants¹³⁻¹⁹ because of their excellent lubricity, viscosity-temperature characteristics and mainly for their biodegradability.

Concerning this background the present work involves the synthesis of homopolymer of rice bran oil (RBO) and copolymers of rice bran oil with dodecyl acrylate (DDA) and styrene respectively followed by characterization of them (by thermogravimetric, gel permeation chromatography [GPC], and spectral analysis) and evaluation of their biodegradability, additive performance (as PPDs and VMs) in lubricating oil by standard ASTM methods.

3.1.2. Experiments

3.1.2.1. Materials

Toluene, hydroquinone, and H₂SO₄ were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (GC Purity 99%) and dodecyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Hexane and styrene were purchased from S D Fine Chem. Ltd. Rice bran oil was collected from local market and methanol was purchased from Thomas Baker Pvt. Ltd. and were used as

received. Benzoyl peroxide (BZP) obtained from LOBA chemical was recrystallized from CHCl_3 -MeOH before use. Specifications of the chemicals are depicted in **Table 3.1**. Two different base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in **Table 3.2**.

3.1.2.2. Preparation of rice bran oil polymer

Synthesis of homopolymer of RBO by thermal method (named as P-0) was performed at 90°C in a three necked round bottom flask for 6 h without adding any solvent. The flask was fitted with a magnetic stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. 10 g of the monomer was introduced in it and heated at 90°C for 30 min. Then, 0.1 % BZP was added to it as an initiator and the mixture was heated at 90°C with continuous stirring. The reaction occurs via radical mechanism. After the desired time, the flask was cooled to room temperature, and to terminate the polymerization the reaction mixture was poured into methanol with stirring until the precipitation was completed. It was then purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 40°C .

3.1.2.3. Preparation of DDA (dodecyl acrylate) ester

The preparation and purification of DDA from acrylic acid and dodecyl alcohol was carried out by following the method (Chapter II of Part I, Page No. 27-28) reported earlier from our laboratory.¹¹

3.1.2.4. Preparation of copolymers

The rice bran oil+DDA and rice bran oil+styrene copolymers were prepared by using different concentrations of DDA and styrene (10%, 20%, and 30% [w/w]) with rice bran oil, P-1 to P-3,

and P-4 to P-6, respectively. The radical polymerization was carried out following the method (Chapter II of Part I, Page No. 28-29) as reported elsewhere.¹⁵

3.1.3. Measurements

3.1.3.1. Spectroscopic measurements

The IR spectra of the samples were recorded on a Perkin Elmer FT-IR 8300 spectrophotometer using 0.1 mm KBr cells at room temperature. The NMR spectra were recorded in a 300 MHz Bruker Avance FT-NMR spectrometer using 5mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) was used as reference material.

3.1.3.2. Thermogravimetric test

The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of 10 K min^{-1} .

3.1.3.3. Molecular weight determination by GPC

The weight average and number average molecular weights (M_w and M_n) and poly dispersity indices of the polymers were measured in Waters' GPC equipment using polystyrene standards for calibration in THF phase. Details of the experimental procedure followed were mentioned in an earlier publication.¹⁵ The results are tabulated in **Table 3.3**.

3.1.3.4. Pour point determination

The pour point of the polymers in base oils was tested according to the ASTM D97-09 method on a Cloud and Pour Point Tester model WIL-471 (India).

3.1.3.5. Photographic measurement

The photomicrograph analysis for wax behaviour of lube oil (BO2) without and with polymers at

3% (w/w) concentration has been recorded. A Banbros polarizing microscope model BPL-400B was used for photographic analysis.

3.1.3.6. Viscosity index determination

Kinematic viscosity (KV) of the polymers was determined separately at 40 °C and 100 °C by counting the time of flow of polymer solution in base oil using viscometer apparatus and measuring the density of it. According to ASTM D-7042 method and also by using the method of viscosity index calculation⁴ the viscosity index of each polymer solution was determined.

3.1.3.7. Biodegradability test

Biodegradability of the polymers was tested (a) by the disc diffusion method against five different fungal pathogens, namely, *Colletotrichum camelliae*, *Fusarium equiseti*, *Alternaria alternata*, *Colletotrichum gloeosporioides*, and *Curvularia eragrostidis* following the method as reported earlier²⁰ taking homopolymer of dodecyl acrylate (HDDA) as reference and (b) by the soil burial degradation test²¹ of polymer sample films as per ISO 846:1997 as per the earlier literature report.²⁰⁻²²

3.1.4. Results and discussion:

3.1.4.1. Spectroscopic data

FT-IR spectra (**Figure 3.1**) of rice bran oil homopolymer showed absorption at 1745.03 cm⁻¹ due to ester CO stretching vibration along with other peaks. In its ¹H NMR spectra (**Figure 3.2**), the polymer showed a broad singlet ranging between 4.12 to 4.31 ppm due to the -OCH₂ protons of rice bran oil and in ¹³C NMR spectrum (**Figure 3.3**) it showed peak at 174.35 ppm of ester carbonyl carbon.

FT-IR spectra of rice bran oil+DDA (**Figure 3.4**) exhibited absorption at 1732.0 cm^{-1} due to ester CO stretching vibration along with other peaks at 1456.2 , 1260 , 1164 and 1112.9 cm^{-1} and peak at 723.3 cm^{-1} was appeared due to C-H bending. In its ^1H NMR spectra (**Figure 3.5**), the polymer showed a broad singlet ranging between 4.02 and 4.31 ppm due to the $-\text{OCH}_2$ protons of rice bran oil and DDA along with the $-\text{CH}_3$ protons ranging between 0.86 and 0.90 ppm together with $-\text{CH}_2$ protons ranging between (1.26 and 1.60) ppm. The formation of the copolymer was further indicated by the absence of sp^2 hydrogen in its ^1H and sp^2 carbon in ^{13}C NMR spectrum (**Figure 3.6**), respectively.

FT-IR spectra of rice bran oil+styrene copolymer (**Figure 3.7**) exhibited absorption at 1732 cm^{-1} for the ester CO stretching vibration along with other peaks at 1456 , 1378 , 1244 , 1174 , and 724 cm^{-1} . In its ^1H NMR spectra (**Figure 3.8**), the polymer showed a broad singlet ranging between 4.11 and 4.3 ppm due to the proton of $-\text{OCH}_2$ group of RBO along with the $-\text{CH}_3$ protons at 0.88 ppm and $-\text{CH}_2$ protons ranging between 1.26 and 1.62 ppm. In its ^{13}C - NMR spectra (**Figure 3.9**) the ester carbonyl carbon showed peak at 172 ppm and the carbon of phenyl part of styrene showed peak in the region 127 - 130 ppm. The extent of incorporation of styrene in the polymer chain was also determined through a comparison of area of $-\text{OCH}_2$ group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports²³ as well as on the basis of our earlier paper.²⁴

3.1.4.2. Thermogravimetric analysis

Plot of TGA data in **Figure 3.10** presents a comparison between the thermal stability of the homopolymer of rice bran oil and its copolymers with DDA and styrene respectively. The analysis reveals that copolymers are more stable than that of homopolymer and for both set of copolymers, thermal stability increases with increasing concentration of DDA and styrene in the

feed and the rice bran oil + DDA copolymers are more stable than the corresponding rice bran oil + styrene copolymers.

3.1.4.3. Performance evaluation of the prepared polymers as PPD

The pour point (PP) values of the polymers in both the base oils are tabulated in **Table 3.4**, which indicates that their PPD efficiency increases (up to a certain limit) with increasing concentration of the polymer in base oils. Comparison among the PP values indicates that the efficiency of the polymers as PPD is greater for DDA copolymers than the styrene copolymers. Again, the efficiency in base oil, BO1 is greater than that of in BO2.

3.1.4.4. Photomicrographic analysis

The photo micrographs of lube oil (BO2) with and without different additives are shown in **Figure 3.11(a–h)**. **Figure 3.11a**, the photograph of the fresh lube oil showed large number of crystalline and some needle shaped wax crystals. But by the addition of polymers the wax crystal size [**Figure 3.11(b–h)**] is significantly decreased from large crystal structure (base oil) to very small dots dispersed in the oil phase of the lube oil, and the polymer which acts as better PPD (reveals by PPD data), decreases the wax size more compared to other. Therefore, a correlation between the depression of pour point and degree of wax structure modification has been verified.

3.1.4.5. Performance evaluation of the prepared polymers as VMs

The VI values in two base oils (measured in five different concentrations) tabulated in **Table 3.4** indicates that in both the base oils the values for homopolymer are lower than that of copolymers. Among copolymers the values are greater for rice bran oil+DDA copolymers than that for respective rice bran oil+styrene copolymers. Both for DDA and styrene copolymers, the VI value increases with decreasing RBO concentration in the copolymer feed. This result may be

explained on the basis of the molecular weight of the polymers. Again, with increase in concentration of the polymers in solution, VI increases. The reason may be that although the viscosity of the lube oil gets decreased at higher temperature, the polymer molecules may effectively offset this reduction in viscosity by thickening the oil changing its shape from tight coil to expanded one due to increased polymer-solvent interaction. The result is increase in viscosity of the solution. Again, a higher polymer concentration means increase in total volume of polymer coils in the solution which imparts a higher VI compared to a low concentrated polymer solution.²⁵

3.1.4.6. Analysis of biodegradability test results

Biodegradability test results (**Table 3.5**) with both set of copolymers showed significant biodegradability against the fungal pathogens, *Colletotrichum camelliae* and *Alternaria alternata*, though the result is better for the rice bran oil+DDA copolymers. Soil burial test results also indicated similar extent of biodegradability. Change in molecular weight also supported the biodegradable nature of the polymers (**Table 3.3**). It was further confirmed by the shift of IR frequency of the ester carbonyl after the test is over (**Figure 3.12, 3.13 and 3.14**). HDDA does not show any weight loss under identical experimental conditions and thus confirmed its non-biodegradable nature.

3.1.5. Conclusions

1. The rice bran oil + DDA copolymers are thermally more stable than the rice bran oil + styrene copolymers and in turn more stable than homopolymer of rice bran oil. Again thermal stability increases with increasing concentration of styrene and DDA in the copolymers.

2. Evaluation of performance of the additives indicates that the rice bran oil + DDA copolymers act as better PPD and viscosity modifiers compared to the RBO + styrene
3. Investigation also indicates that although the homopolymer of rice bran oil is considerably biodegradable but it gains poor thermal stability and average performance as a PPD and VM. On the other hand copolymers showed biodegradability in addition to the multifunctional additive performance (PPD and VM), and so are considered as being more useful in field applications compared to the existing additives.

3.1.6. References

References are given in Bibliography under Chapter-II of Part-III (Page No. 206-208).

Table 3.1. Specification of the chemicals used

<i>Chemical name</i>	<i>Source</i>	<i>Mole fraction purity</i>
Toluene	Merck Specialities Pvt. Ltd.	0.995
Hydroquinone	Merck Specialities Pvt. Ltd.	0.990
H ₂ SO ₄	Merck Specialities Pvt. Ltd.	-
Acrylic acid	SRL Pvt. Ltd.	0.990
Dodecanol	S. D. Fine-Chem Ltd.	0.980
Hexane	S. D. Fine-Chem Ltd.	0.995
Styrene	Across Organics.	0.950
Methanol	Thomas Baker Pvt. Ltd.	0.980
Benzoyl peroxide	LOBA chemicals	0.980
Rice bran oil	Local Market	-

Table 3.2. Base oil properties

Properties	Base oils	
	BO1	BO2
Density at 313 K, kg.m ⁻³	836.98	868.03
Viscosity at 313 K, Pa-s	5.97 ×10	20.31×10
Viscosity at 373 K, Pa-s	1.48 ×10	3.25 ×10
Cloud point, °C	-10	-8
Pour point, °C	-3	-6
Viscosity index	80	85

Table 3.3. The weight average and number average molecular weights (M_w and M_n) and polydispersity of the polymers before and after 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	1.20	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: DDA) and P-4 to P-6 (RBO:styrene) w/w, Mn = number average molecular weight; Mw = weight average molecular weight; PDI = poly dispersity index.

Table 3.4. Pour point (in °C) and VI values of polymers in different concentration

Property/base oil/(PP/VI)	Conc., %	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
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
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 3.5. Result of biodegradability test by the disc diffusion method and soil burial degradation

sample	Weight loss in disc diffusion method, g Pathogens used					Weight loss in soil burial degradation, g
	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	0.25	0	0.35	0	0	0.20
P-5	0.18	0	0.29	0	0	0.17
P-6	0.13	0	0.28	0	0	0.13
HDDA	0	0	0	0	0	0

CC = Colletotrichum camelliae; FE = Fusarium equiseti; AA = Alternaria alternata; CG = Colletotrichum gloeosporioides; CE= Curvularia eragrostidis.

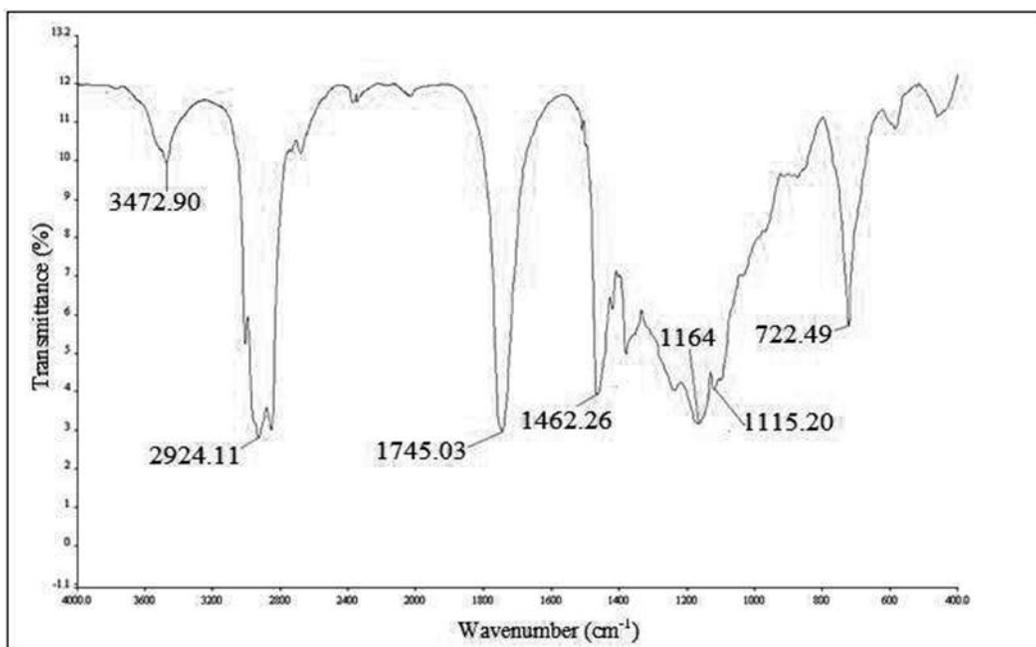


Figure 3.1. FT-IR spectra of rice bran oil homopolymer

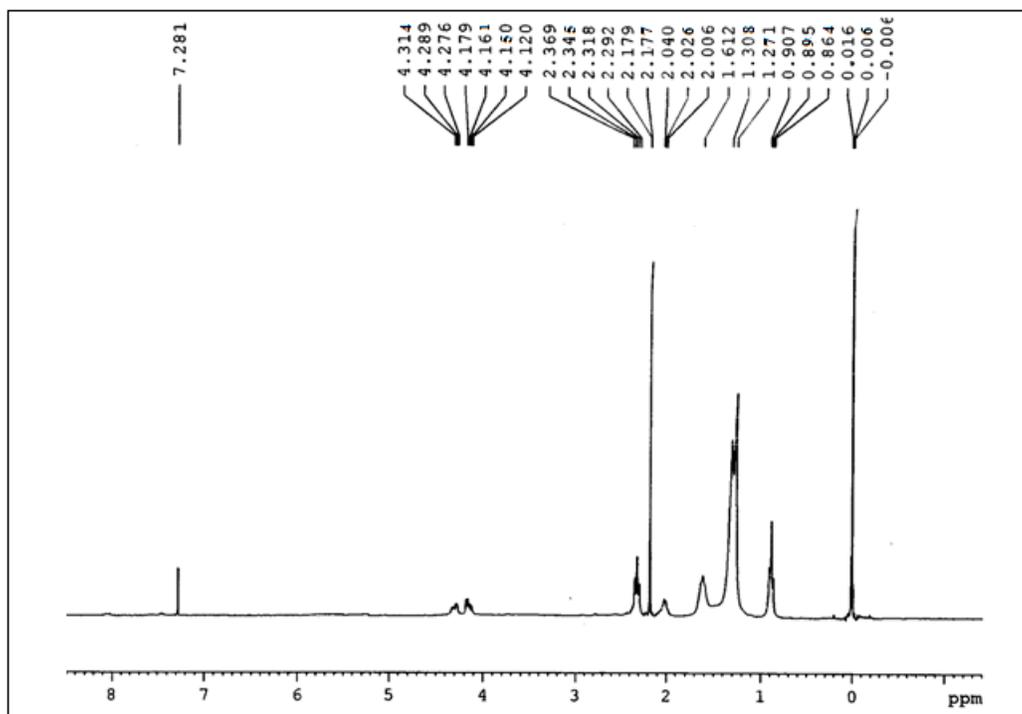


Figure 3.2. ¹H NMR spectra of Rice bran oil homopolymer

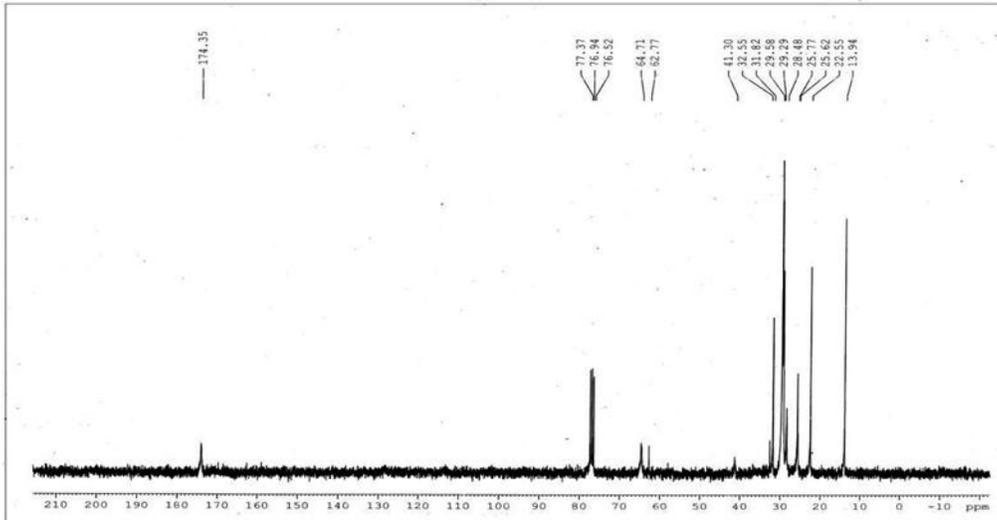


Figure 3.3. ^{13}C - NMR spectra of Rice bran oil homopolymer

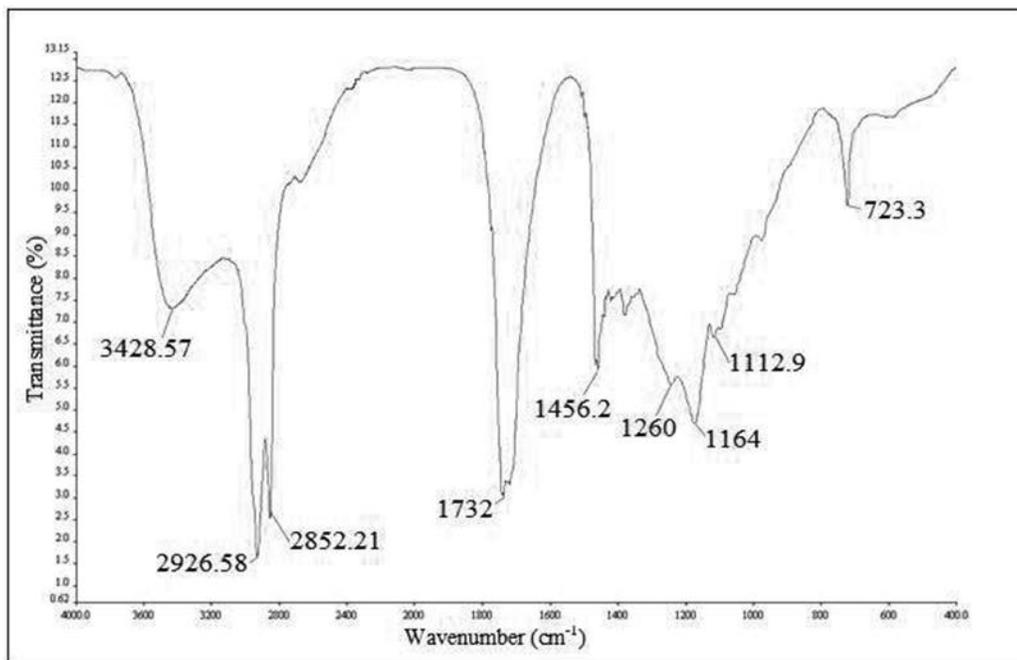


Figure 3.4. FT-IR spectra of rice bran oil + DDA copolymer (P-2)

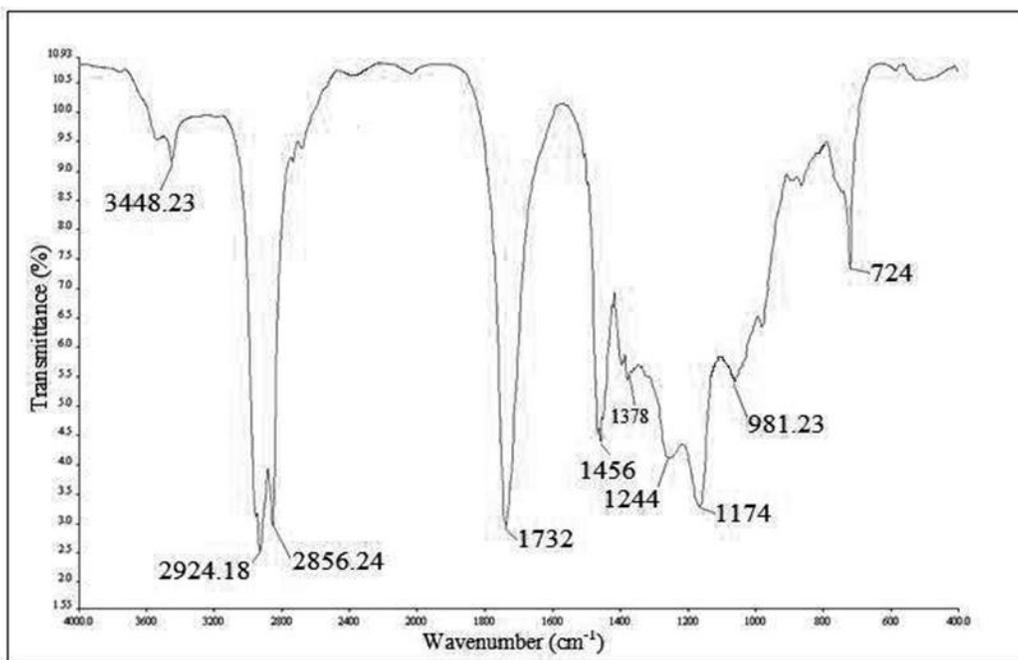


Figure 3.7. FT-IR spectra of rice bran oil + styrene copolymer (P-5)

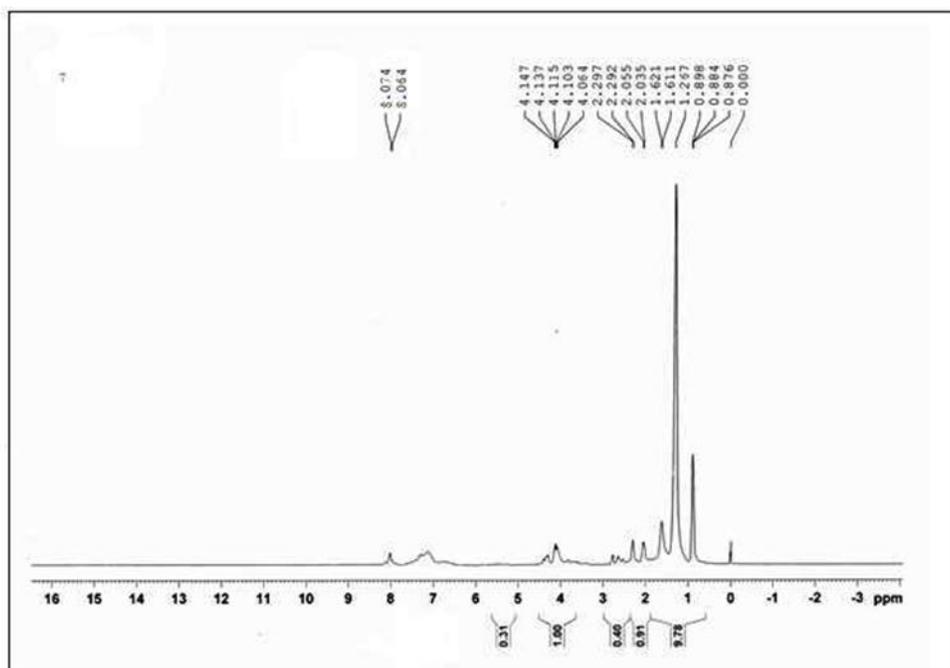


Figure 3.8. ^1H NMR spectra of Rice bran oil + Styrene copolymer (P-5)

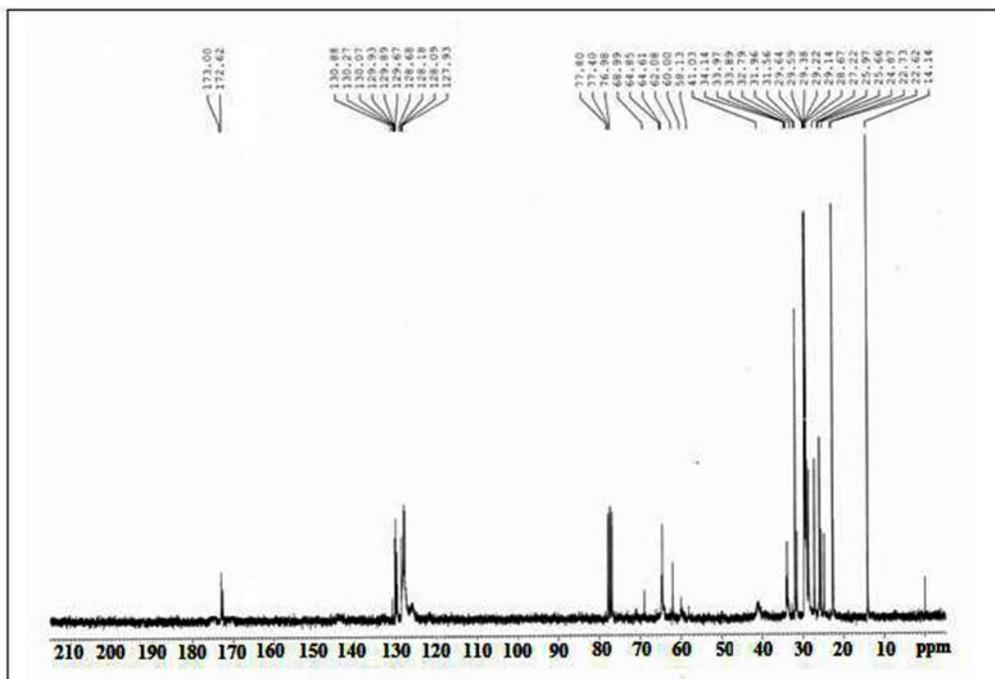


Figure 3.9. ^{13}C - NMR spectra of Rice bran oil + Styrene copolymer (P-5)

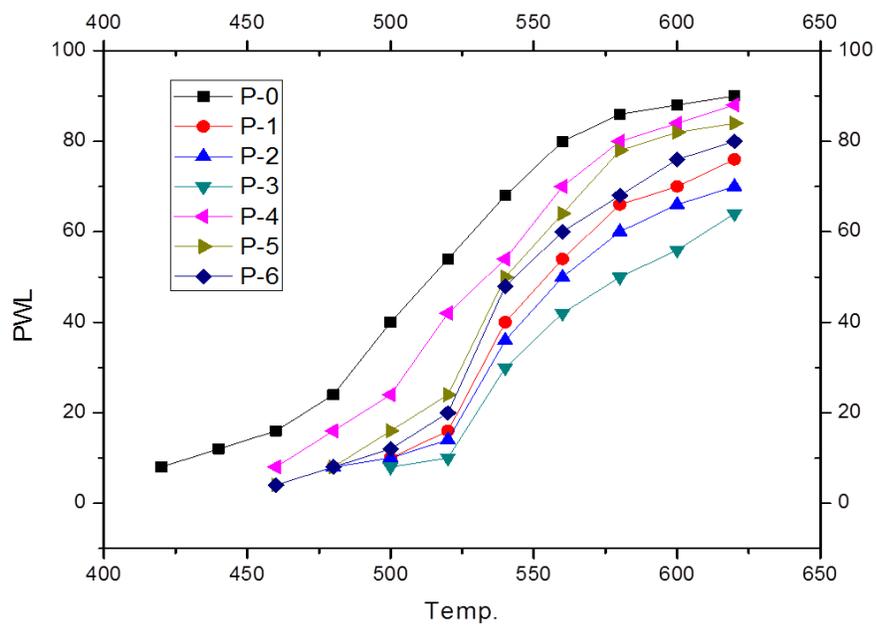


Figure 3.10. Plot of PWL (Percent Weight Loss) vs Temperature (in K)

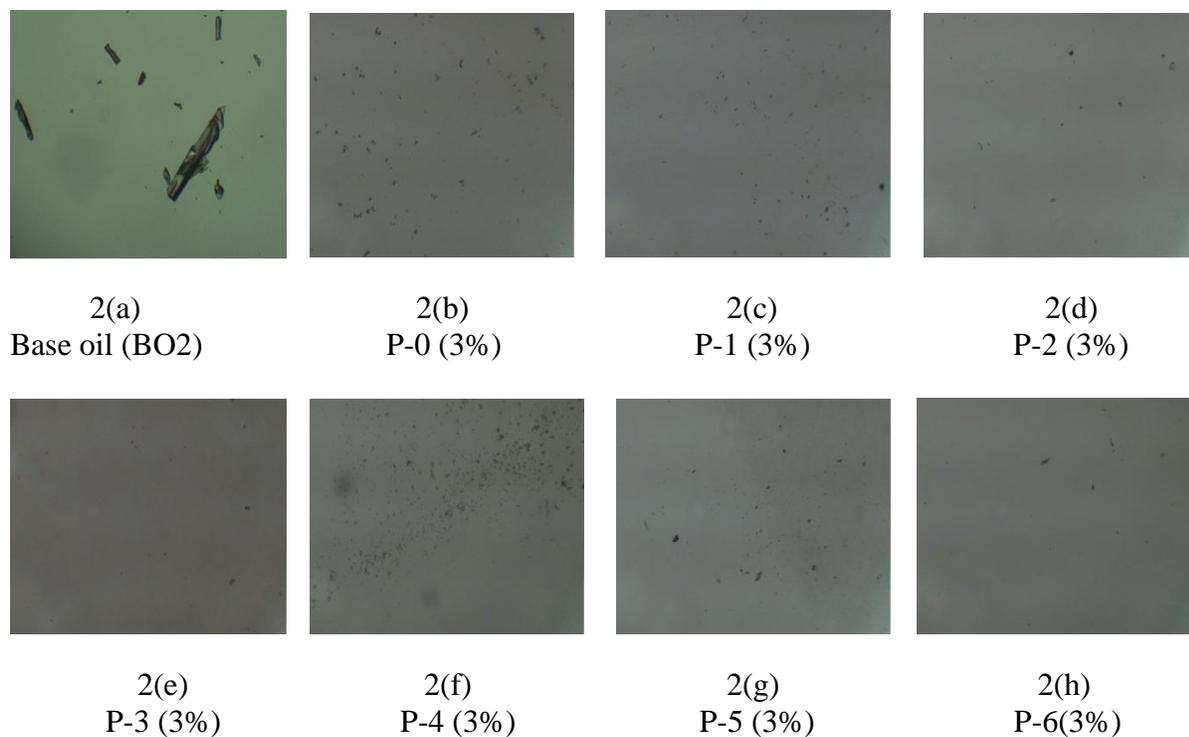


Figure 3.11(a-h). Plot of Photomicrographic images of base oil and additive (P-0, P-1, P-2, P-3, P-4, P-5 and P-6) doped base oil

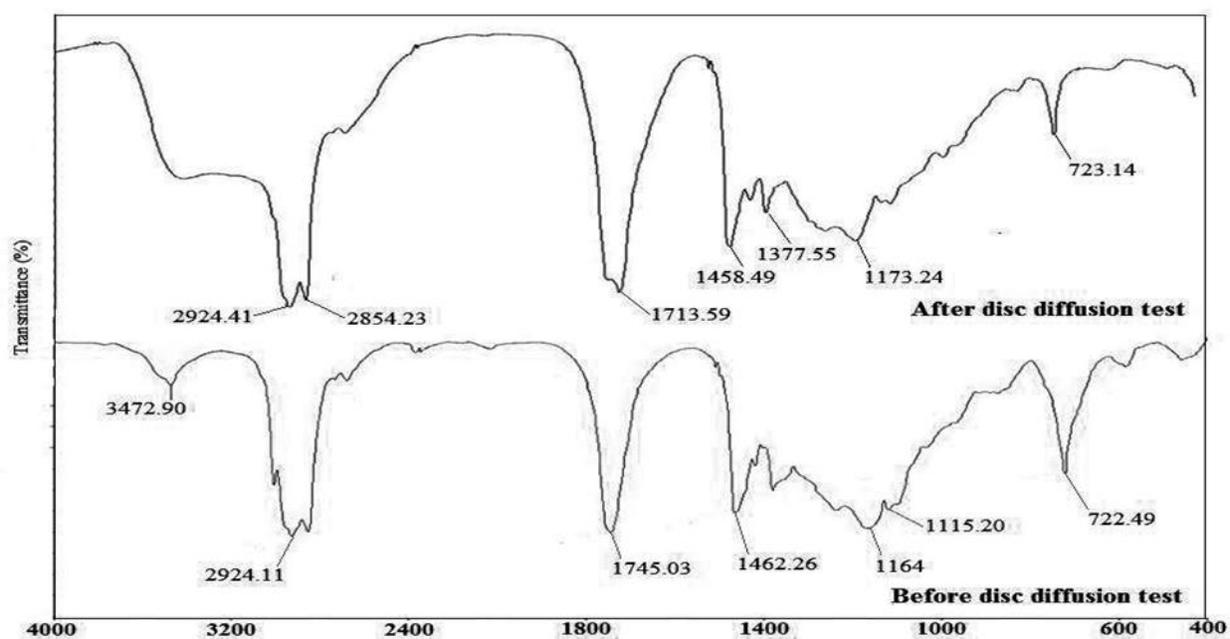


Figure 3.12. Comparative FT-IR spectra of Rice bran oil homopolymer (P-0) before and after disc diffusion test

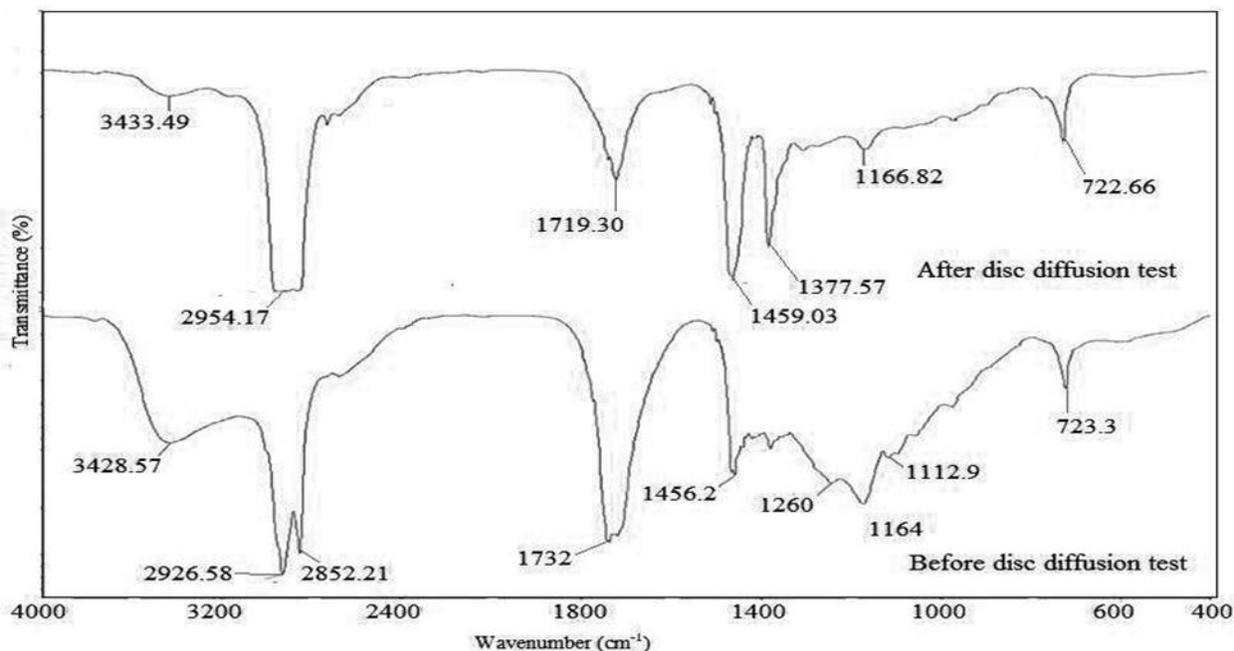


Figure 3.13. Comparative FT-IR spectra of Rice bran oil + DDA copolymer (P-2) before and after disc diffusion test

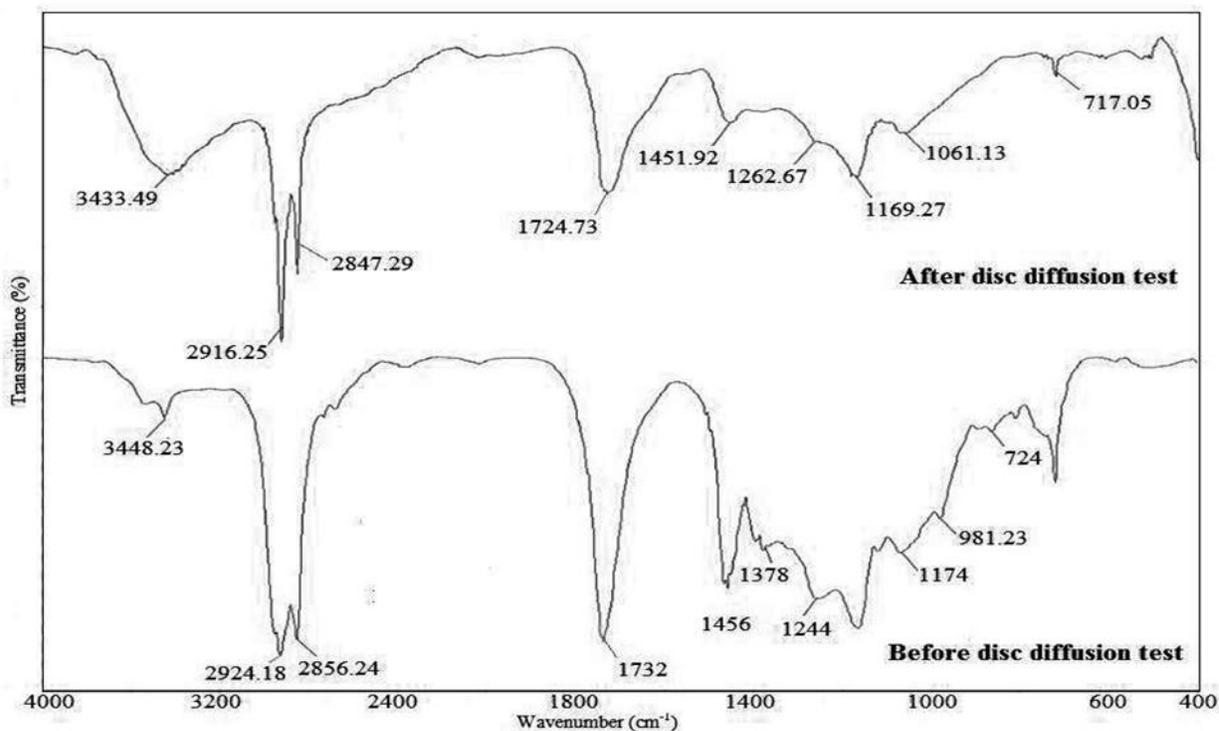


Figure 3.14. Comparative FT-IR spectra of Rice bran oil + styrene copolymer (P-5) before and after disc diffusion test