Chapter III

A Greener Lubricant Formulation using Rapeseed Oil Based Eco-Friendly Lube Oil Additives

2.3.1 Introduction

The origin of base oil is usually petroleum and it is a complex mixture of aromatic, paraffinic, and naphthenic hydrocarbons and its main function is to lubricate the engine components. For the smooth functioning of a modern engine, it is essential to add additives to the base oil. Lubricants i.e. the suitable formulated product of lube oil and additives are generally liquids or semiliquids and are used for the longevity and better performances of automotive engines. The main functions of a lubricant are to keep moving parts apart, protect against wear, reduce friction, transfer heat, prevent rust and corrosion, as antioxidants, detergents/dispersants, etc. Although, the petroleum-based lubricating oil exhibit satisfactory performance but they are not environmentally friendly. Because they are eco-toxicity and non-biodegradability. Therefore, currently, strict regulations are being imposed in various countries on lube oil-based lubricants and their non-biodegradable toxic wastes materials [1]. This increasing environmental awareness made the researchers search for some new, environmentally benign, multifunctional additives. In this regard, easily available vegetable oils have been considered as a potential substance. Moreover, they show excellent antiwear properties [2], enhanced extreme pressure (EP) additive performance, exhibited high viscosity index [3] and low volatility [4]. There are lots of research papers where chemically modified vegetable oils have been used as additives for base oil or base stocks in the formulation of bio-lubricant [5]. Rapeseed oil (RO) is very interesting for its richness of mono-unsaturated fatty acids, and its low content of saturated fatty acids in comparison to other edible oils. Rapeseed oil is also used in blends with other vegetable oils (sunflower, soybean, corn, etc.) to increase the fatty acid profile of the vegetable oils. It has huge applications in the field of nutritional and health claims. Apart from its above utilities, its unique composition and proven thermal stability over

the other edible vegetable oils, points towards the additive properties of its suitably prepared polymers. However, research articles regarding the application of RO as a green multifunctional lube oil additive are not yet reported. Therefore, in this work, we have synthesized homopolymer of RO (HRO) and the copolymer of it with styrene in different percentage ratios to get thermally stable, cost-effective as well as eco-friendly multifunctional lubricant additives. The Performance evaluation like viscosity index improver, pour point depressant and antiwear of the prepared polymeric additives was carried out according to the respective ASTM method.

2.3.2 Experimental Section

2.3.2.1 Materials

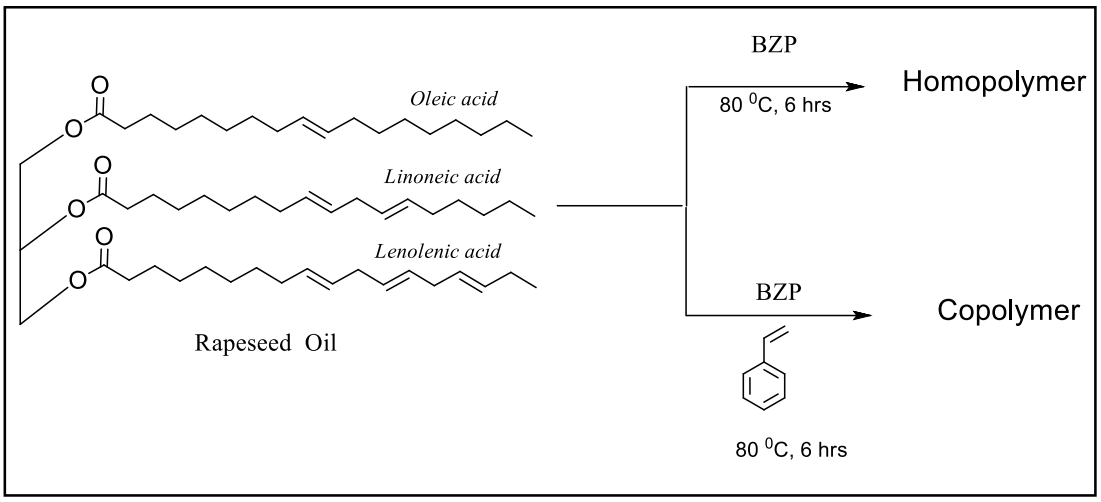
Rapeseed oil (about 90% unsaturation) was collected from a local grocer's shop. Toluene was obtained from Merck Specialties Pvt. Ltd., (India). Benzoyl peroxide (LOBA Chemie, India) was used after recrystallization from a chloroform-methanol mixture. Styrene (GC 99.8%, Thomas Baker Chemicals Pvt. Ltd., India). The mineral base oil (SN150) was collected from IOCL, Dhakuria, West Bengal, India. The physical properties of the rapeseed oil and base oil are shown in **Table 2.3.1**. Fungal specimens were collected from the Department of Microbiology, North Bengal University, West Bengal, India for determining the biodegradability of the polymers.

2.3.2.2 Synthesis of the Polymers

The copolymers were prepared by taking the monomers, RO, and styrene at different ratios (**Table 2.3.2**) in presence of BZP initiator by free radical polymerization method using toluene as solvent. The polymerization was done in a three-necked round bottom flask on a magnetic stirrer. A thermometer, condenser, and an inlet for nitrogen were in the three necks. In the flask, a definite amount of rapeseed oil and styrene was heated to 80^0C and maintained for 20 minutes. Initiator BZP (0.5% w/w, with respect to the

total monomer) was then added and refluxed for 6 hours. The detailed procedure was followed from our previous publication [3].

Scheme 2.3.1 Reactions for the preparation of homopolymer of rapeseed oil and copolymer with styrene



2.3.3 Measurements

2.3.3.1 Spectroscopic Measurements

NMR spectra were determined on Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl3 and tetramethylsilane (TMS) were used as a solvent and as reference material respectively. IR spectra were determined on a Shimadzu FT-IR 8300 spectrometer using 0.1mm potassium bromide cells at room temperature within the wavenumber range of 400 to 4000 cm^{-1}.

2.3.3.2 Molecular Weight Determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by the GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at room temperature at a flow rate of 1mL/min.

2.3.3.3 Thermo Gravimetric Analysis (TGA)

TGA data were measured on the Shimadzu TGA-50 system, at a heating rate of 10^0 C / min.

2.3.3.4 Evaluation of Viscosity Index

Viscosity index (VI) was calculated according to ASTM D 2270-10. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40^0C and 100^0C. The effect of additive concentration on VI was investigated by using different concentrations ranging from 1% - 5% (w/w).

2.3.3.5 Evaluation of Pour Point

The ASTM D 97-09 method was used to determine the pour point of the additive blended lube oil using the cloud and pour point tester model WIL-471 (India).

2.3.3.6 Evaluation of Anti Wear Performance

The anti-wear performance of the additive doped lube oil in terms of wear scar diameter (WSD) was determined by Four-ball wear test apparatus (FBWT) using the ASTM D 4172-94 method. In this experiment, 392 N (40 Kg) load at 75^0 C for 60 min was applied to measure the wear scar diameter. The rotating speed and diameter of the ball were1200 rpm and 12.7 mm respectively.

2.3.3.7 Biodegradability Test

Vegetable oil-based additives are inherently biodegradable compared to synthetic additives. In the present investigation, biodegradability was tested by (a) the soil burial degradation test, and (b) the disc diffusion method against fungal pathogens [6].

2.3.3.8 Disc Diffusion (DD) Method

In this method, the biodegradability of the prepared additives was tested using four different fungal pathogens, (viz. *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternate* (AA) and *Colletotrichum gloeosporioides* (CG)) in an incubator (Sigma Scientific Instruments Pvt. Ltd., India) and the culture media for the fungal strain was prepared by mixing potato extract, agar powder, and dextrose, in a 10:1:1 proportion by weight. 1.0 g of each of the polymeric vegetable oil-based additives were placed in Petri dishes with 2 g of the culture media and incubated at 40^0C for 30 days with the different fungal pathogens. The change of colour from

yellow to blackish confirmed fungal growth. After 30 days, the additive samples were collected from the fungal media and washed with chloroform, purified, and dried. Finally, the weight loss for each of the samples was calculated.

2.3.3.9 Soil Burial Degradation Test (SBD Test)

In this method, the microorganisms attack the surface of the polymer film [7]. 1.0 g of each of the polymeric additive was taken to prepare the polymer films. The films so obtained were then buried in the soil (containing the microorganisms) in an incubator. The soil was placed in a tray, the relative humidity was maintained to 50−60% with the help of a humidity chamber and the temperature was set at 30^0C. The soil used in this investigation was taken from the campus of the North Bengal University (West Bengal, India) and have pH 7.3 and moisture content of 25%. The buried polymer films were collected at regular intervals of 15 days up to 3 months. After the biodegradation test, recovered films were washed with $CHCl_3$, filtered with the help of Whatman grade 41 filtration paper, and dried in a vacuum oven at 53^0C. The recovered polymer so obtained was purified by precipitation of their hexane solution by methanol and dried in a vacuum oven at 53^0C to constant weight. The test was carried as per ISO 846:1997 [8], [9]. The extent of degradation of the polymeric additives in the tests was determined by measuring the percent of weight loss (PWL) of the samples. The PWL was determined by the equation,

$$PWL = [(M0 - M1)/M0] \times 100 \qquad \text{Eq.(1)}$$

Where M0 is the initial mass and M1 is the remaining mass after the test and subsequent drying until constant weight. The degradation of the polymeric additives was also established by observing the shift in the IR absorption frequency of the ester carbonyls after the biodegradability test.

2.3.4 Result and Discussion

2.3.4.1 Spectroscopic Data Analysis

The spectroscopic data of all the prepared polymers were analyzed to confirm the predicted structure of the additives. In the case of a copolymer, the characteristic IR absorption peak at 1743cm^{-1} was for the ester carbonyl group of the rapeseed oil part along with other peaks in the range 2857cm-1 to 2931 cm^{-1}. The peaks at 810 cm^{-1}, 756 cm^{-1}, 724 cm^{-1}, and 695 cm^{-1} were assigned to the phenyl group of styrene. A peak at around 3000 cm^{-1} was due to the stretching of C-H bond of the aromatic ring (**Figure 2.3.1**). In the ^{1}H NMR, the methyl protons appear in the range of 0.87 - 0.89 ppm, the methylene protons in the range of 1.28 - 1.62 ppm and the methine protons appeared in the range of 2.03 - 2.29 ppm for the alkyl chains. A peak at 4.08 ppm indicates the protons of –OCH_2 group. The peaks in the range of 4.10 - 4.14 ppm indicate the protons of –$COOCH_2$ group of rapeseed oil. A broad peak in the range of 6.80 - 7.64 ppm indicates the protons of the aromatic ring of styrene (**Figure 2.3.2**). In the ^{13}C NMR of the copolymer, the peaks in the range of 14.14 - 41.03 ppm were due to carbons of all CH_3 and CH_2 groups. The peaks at 58.13 ppm indicate the methine carbons of –CH- of –COCH group. The peaks in the range of 60 - 62.08 ppm represent the carbons of –OCH_2 groups. The -CH_2 carbons of –$OCOCH_2$– group of rapeseed oil showed peaks in the range of 64.61– 68.99 ppm. The aromatic carbons appear in the range of 127.93 -130.88 ppm. The peaks in the range of 165.65 - 173.00 ppm confirm the carbons of ester carbonyl groups (**Figure 2.3.3**). In the case of the homopolymer of rapeseed oil, the IR absorption band at 1741 cm-1 (**Figure 2.3.4**) showed the presence of the ester carbonyl group. In the ^{1}H NMR spectra of the homopolymer of rapeseed oil (**Figure 2.3.5**), the peaks in the range of 4.12- 4.33 ppm indicate the protons of –$COOCH_2$ group of rapeseed oil, the methyl protons appear in the range of 0.86 - 0.90

ppm, the methylene protons in the range of 1.26 - 1.62 ppm and the methine protons appeared in the range of 2.29 - 2.34 ppm for the alkyl chains (**Figure 2.3.6**). In the ^{13}C NMR spectra of the homopolymer of rapeseed oil, the ester carbonyl group appears at 173.98ppm, the carbons of $–OOCH_2$ group appears at 62.07 - 68.91 ppm (**Figure 2.3.7**).

2.3.4.2 Molecular Weight Data Analysis

The experimental values of number average molecular weights (Mn) and weight average molecular weights (Mw) of the prepared polymers (P-1 to P-5) are given in **Table 2.3.3.** From the experimental data, it is seen that among the five polymers, P-5 has the highest molecular weight. Moreover, it is also observed that with increasing the percentage of styrene in the backbone of rapeseed oil, the molecular weight increases. Therefore, the percentage of styrene has a significant role during polymerization.

2.3.4.3 Analysis of TGA Data

The TGA values of the five polymers are given in **Table 2.3.2.** From the table, it is clear that the thermal degradation of polymer P-1 is higher than the other polymers which signifies that P-1 is thermally less stable. The thermal degradation of polymers P-3, P-4, and P-5 are almost similar. In the case of polymer P- 1, major decomposition starts at 160^0C with about 30% weight loss. For polymers P-3, P-4, and P-5, major decomposition starts approximately at 268^0C with 18% weight loss. Due to the copolymerization of rapeseed oil with styrene, the thermal stability increases. Therefore, copolymerization with styrene has significant importance to improve thermal stability.

2.3.4.4 Analysis of Viscosity Index Values

VI was calculated at different concentrations ranging from 1% to 5% (w/w) to the base oil. The experimental values of VI are given in **Table 2.3.4**. From the table, it is found that VI values increase with increasing the concentration of polymers in the base oil. The viscosity of lubricating oil decreases with increasing temperature but the expansion of polymer molecules takes place with increasing temperature and due to this, the size of the micelle increases. This increased in micelle size interfere with the reduction of the viscosity of the lubricant [10]. Moreover, increasing the concentration of polymer in lubricating oil leads to an increase in the total volume of polymer micelle in lube oil and improves the VI property [11]. It has been observed that the VI value increases by the incorporation of styrene in the backbone of the homopolymer of rapeseed oil. This may be due to the higher crosslink density of the copolymers. The copolymer P-5 has the highest effect on VI increments followed by P-4, P-3, P-2, and P-1. The higher values VI in the case of P-5 containing the maximum percentage of styrene in the feed, are due to greater volume of the solvated additive molecule i.e. micelle compared to others which may be associated with its higher average molecular weights and lower PDI value.

2.3.4.5 Analysis of Pour Point Values

The pour point of the lubricants prepared by blending the polymers at different concentration levels ranging from 1%−5% (w/w) are shown in **Table 2.3.5**. All the polymers are effective as PPD and the efficiency as pour point increases with increasing the concentration of polymers up to a certain limit (4% concentration). This indicates that at this concentration, the polymer interacts with the paraffinic wax of base oil effectively and decreases the size of crystals of the paraffinic wax [12]. Among the prepared five polymers, P-4 showed better performance as PPD.

2.3.4.6 Analysis of Anti-wear Properties

The tribological properties of the lubricant compositions were determined by measuring WSD through FBWT apparatus applying 392 N load and values are given in **Table 2.3.6**. The antiwear performance of the lube oil is significantly improved when the polymers are blended with it and is reflected in the lower WSD values of the lubricant compositions. The copolymers showed better results compared to the homopolymer. The polymer P-5 at 5% concentration showed the highest reduction in WSD values compared to the other polymers. This indicates that the film formed by the lubricant between the two moving metal surfaces is very strong. It may be due to higher molecular weight and hence higher number of polar side chains of the ester carbonyl groups and hydroxyl groups present in rapeseed oil [13], [14]. The contribution of the higher percentage of styrene in the polymer feed has also played a significant role in it with its aromatic ring structure.

2.3.4.7 Analysis of Biodegradability Test

Biodegradability test results (**Table 2.3.7**) with the homo (P-1) and copolymers (P-2 to P-5) showed significant biodegradability against the fungal pathogens, *Calletotricheme camellia*, and *Alterneria alternata*, though the result is, as expected, better for the homopolymer of rapeseed oil. A close observation of the test results showed considerable biodegradation for all the samples. The analysis of the SBD tests indicated that the degradation of the polymeric additives increased continuously with the increasing number of days. Further, both the homo and copolymer showed significant weight losses against the fungal pathogens, especially against *Alternaria alternate* (AA), in the DD test. Moreover, as expected for zero styrene content and owing to the presence of the natural monomer unit, the HRO (P-1) showed the highest biodegradability among all the additives in both of the tests. The FT- IR peaks of the

polymer P-1 showed a shift in the peak positions and a considerable decrease in peak height and intensity after the DD test. The biodegradable nature of the prepared polymers was confirmed by the shift of IR peak and the decrease in the IR peak intensities of the polymers before and after the biodegradation tests and also with the PWL of the polymers [14].

2.3.5 Conclusion

From the above study, it was found that the copolymer of rapeseed oil with styrene showed excellent multifunctional performance for base oil. As a viscosity index improver, pour point depressant, and antiwear additive, the copolymers are found more effective than the homopolymer. In addition, the presence of rapeseed oil in the additive composition introduces excellent biodegradability too, in the additive. The average molecular weight and thermal stability of the copolymers increase with the increase in the percentage of styrene. Therefore, the above study is definitely a potential approach to formulate a greener lubricant composition with excellent multifunctional additive properties for lube oil.

2.3.6 Reference

References are given in *BIBLIOGRAPHY* under “Chapter II of Part III” (Page No.147-148).

2.3.7 Tables and Figures

Table 2.3.1: Properties of Rapeseed oil and Base oil

Rapeseed Oil		*Base Oil*	
Properties	*Values*	*Properties*	*Values*
Saponification index (mg/g)	167-74	Density at 313K, $Kg.m^{-3}$	868.03
Iodine index 9mg/g)	97-100	Viscosity at 313K	20.31x10
Refractive index at 50 ^{0}C	1.462	Viscosity at 373K	3.25x10
Density (g/mi)	0.916	Viscosity index	85
Saturated fatty acid (%)	7.36	Pour point (^{0}C)	-6
Monounsaturated fatty acid (%)	63.27	Cloud point (^{0}C)	-8
Polyunsaturated fatty acid (%)	28.14	-	-
Oleic acid(g)	61.744	-	-
Linoleic acid ω-6 (g)	19.005	-	-
α-Linoleic acid ω-3 (g)	9.137	-	-

Table 2.3.2: Percentage composition and TGA values of the prepared polymers

Polymer Code	*% Composition of monomer (w/w) in the feed*		*TGA values*	
	RO	Sty	Decom. Temp.	PWL
P-1	100	0	160/320	28/78
P-2	98	2	210/355	24/85
P-3	96	4	266/382	17/80
P-4	94	6	268/382	19/81
P-5	92	8	268/384	18/79

RO=Rapeseed Oil, Sty= Styrene, Decom. Temp.= Decomposition temperature, PWL= Parcentage Weight Loss,

Table 2.3.3: Molecular weight of the prepared polymers

Polymer Code	Average molecular weight (before biodegradation)			Average molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P-1	8328	11522	1.31	4132	4645	1.26
P-2	18657	26536	1.34	14211	21427	1.44
P-3	19497	29166	1.43	15512	24876	1.59
P-4	22671	33612	1.88	16536	29271	1.73
P-5	29654	38644	1.29	22320	29664	1.34

Table 2.3.4: Viscosity index (VI) values of polymer blended base oil

Polymer Code	VI of polymer blended base oil at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	85	89	95	104	112	118
P-2	85	94	98	112	115	128
P-3	85	96	104	114	123	131
P-4	85	101	106	116	124	133
P-5	85	103.5	111	125	135	145

Table 2.3.5: Pour point values of polymer blended base oil and its graphical representation

Polymer Code	*Pour point (^{0} C) base oil at different concentrations (w/w)*					
	0%	*1%*	*2%*	*3%*	*4%*	*5%*
P-1	-6	-9	-12	-12	-15	-16
P-2	-6	-10	-12	-16	-18	-16
P-3	-6	-10	-12	-16	-20	-18
P-4	-6	-12	-15	-18	-22	-24
P-5	-6	-10	-15	-18	-18	-22

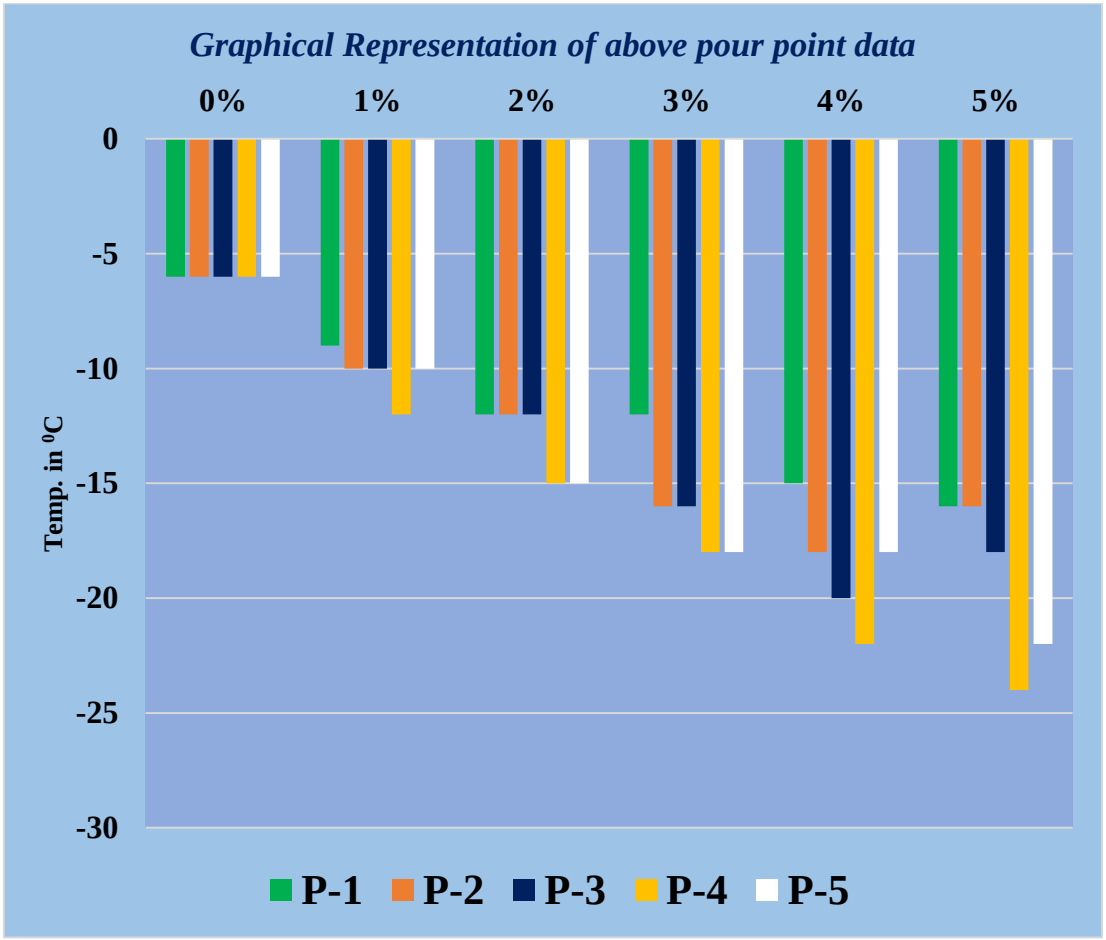


Table 2.3.6: Anti-wear property in terms of wear scar diameter (WSD in mm) values of different lubricant compositions and its graphical representation

Polymer code	*WSD of lubricant (in mm) at different polymer concentration (w/w)*					
	0%	1%	2%	3%	4%	5%
P-1	1.116	1.067	1.044	1.025	1.007	0.964
P-2	1.116	1.065	1.037	1.023	1.003	0.957
P-3	1.116	1.06	1.028	1.018	0.992	0.955
P-4	1.116	1.052	1.022	1.002	0.958	0.931
P-5	1.116	1.031	1.013	0.992	0.943	0.911

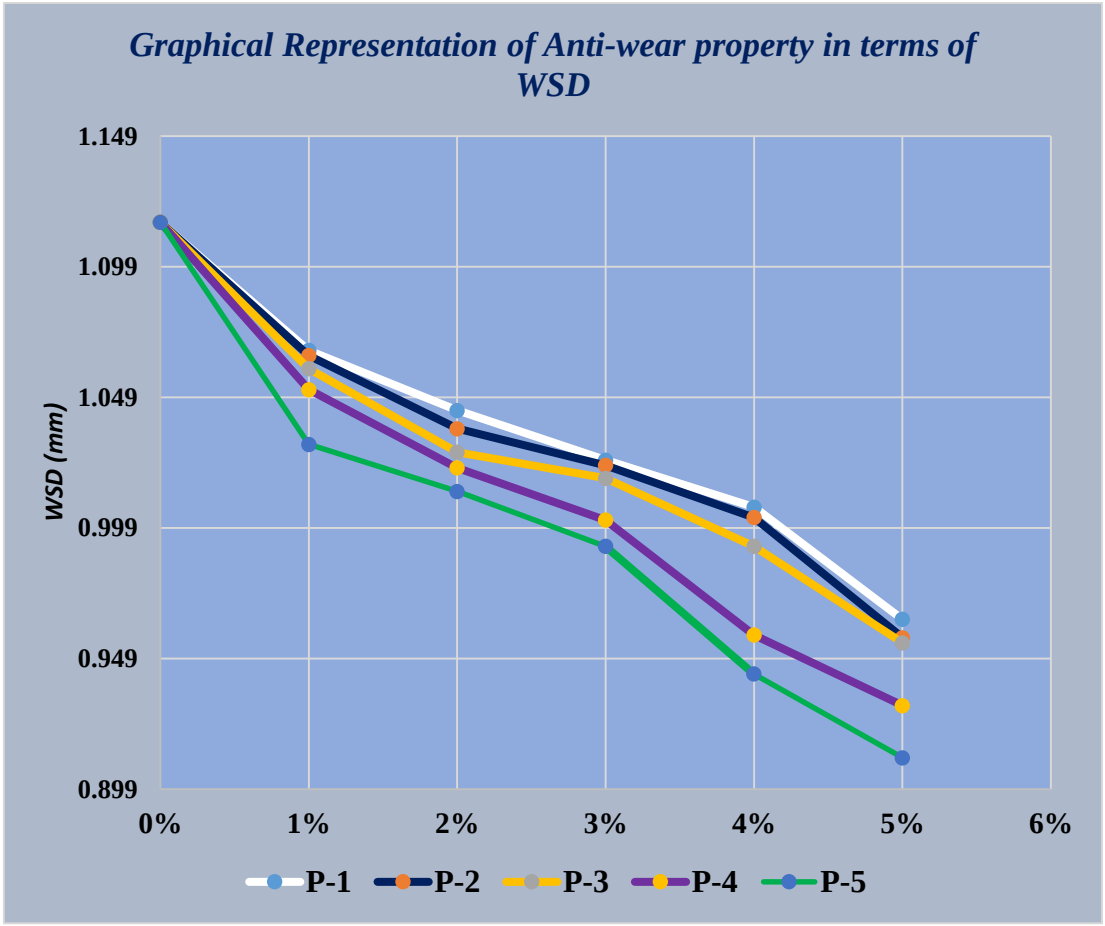


Table 2.3.7: Result of biodegradability test by the disc diffusion method and soil burial degradation

Sample	*Weight loss in disc diffusion method (g) [Pathogens used]*					*Weight loss in soil burial degradation*
	[CC]	[FE]	[AA]	[CG]	[CE]	*(g)*
P-1	0.45	0	0.62	0	0	0.47
P-2	0.38	0	0.54	0	0	0.35
P-3	0.3	0	0.48	0	0	0.3
P-4	0.26	0	0.39	0	0	0.25
P-5	0.22	0	0.35	0	0	0.19
CC=Calletotricheme camellia, FE= Fussarium equisitae, AA=Alterneria alternata, CG=Colletrichum gleosproides, CE=Curvularia eragrostidies						

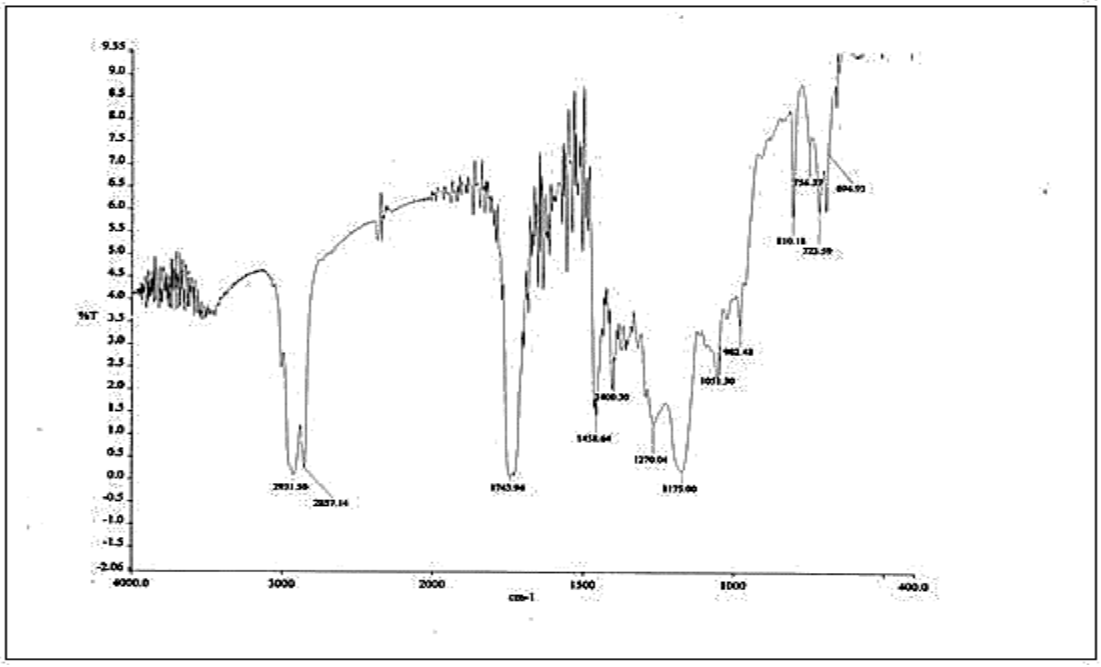


Figure 2.3.1: A representative FT-IR spectra of the rapeseed oil – styrene copolymer

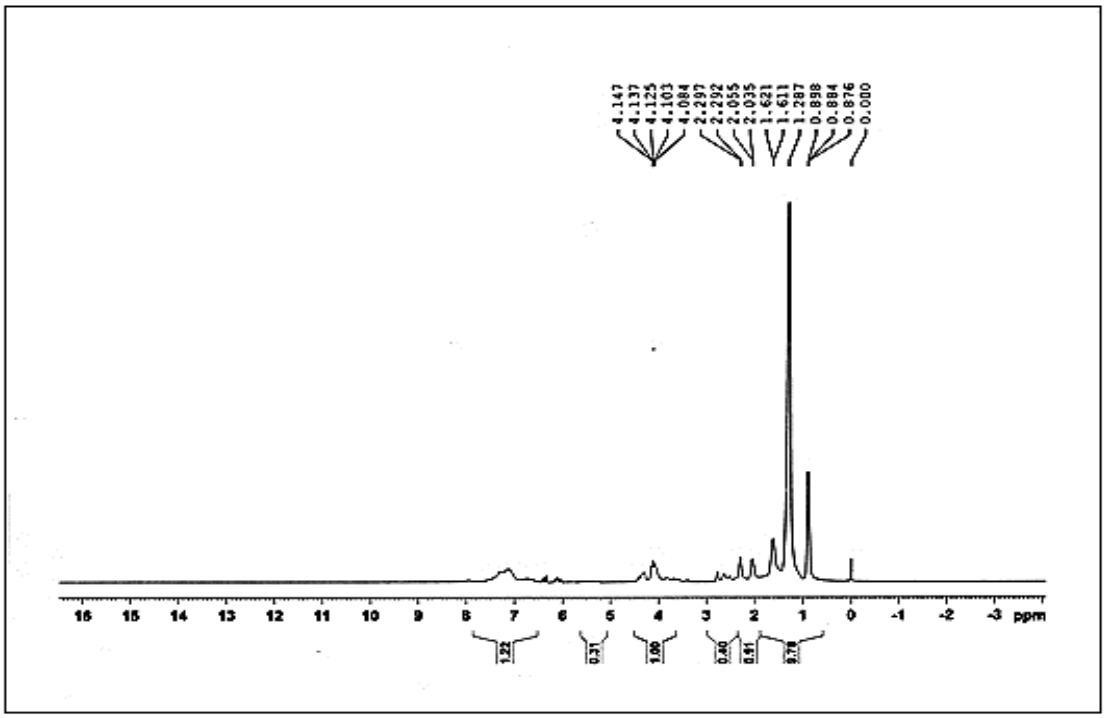


Figure 2.3.2: A representative ^{1}H NMR spectra of rapeseed oil – styrene copolymer

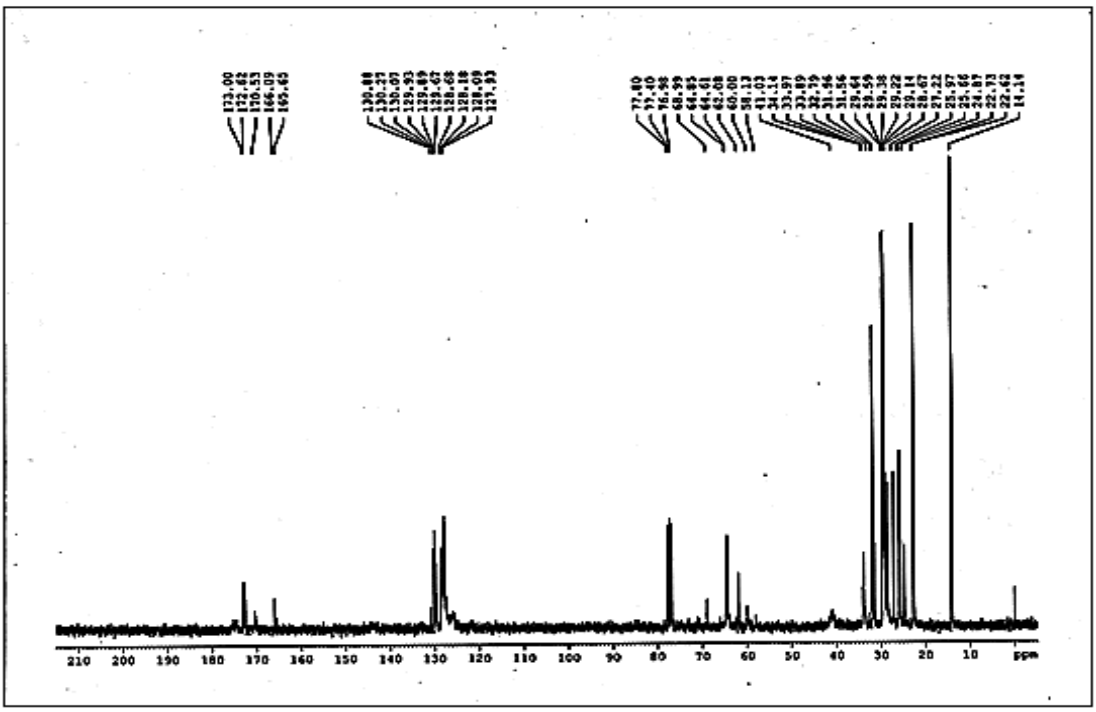


Figure 2.3.3: A representative ^{13}C NMR spectra of rapeseed oil- styrene copolymer

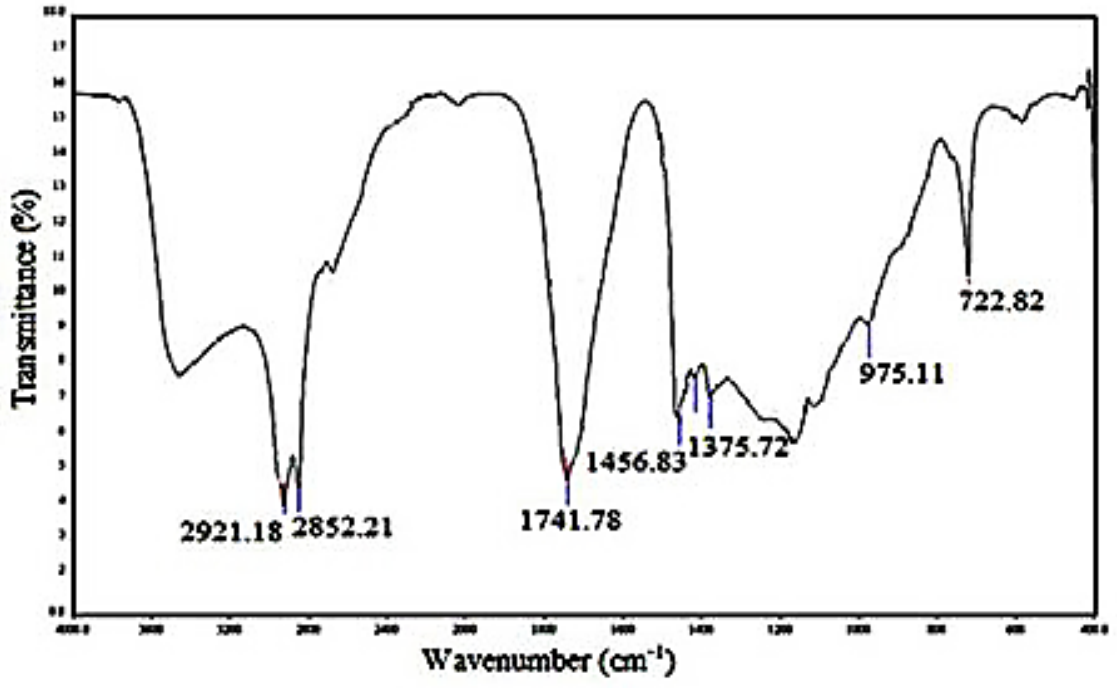


Figure 2.3.4: FT-IR spectra of the homo polymer of rapeseed oil

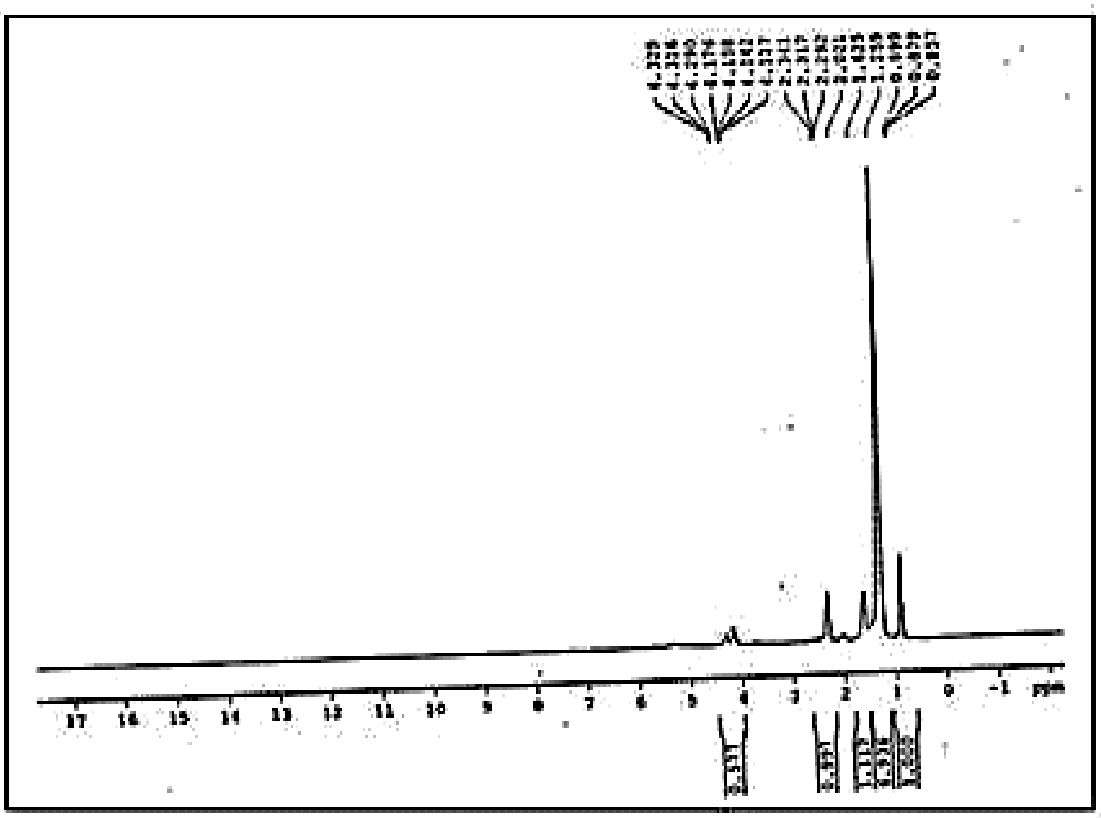


Figure 2.3.5: ^{1}H NMR spectra of homo polymer of rapeseed oil

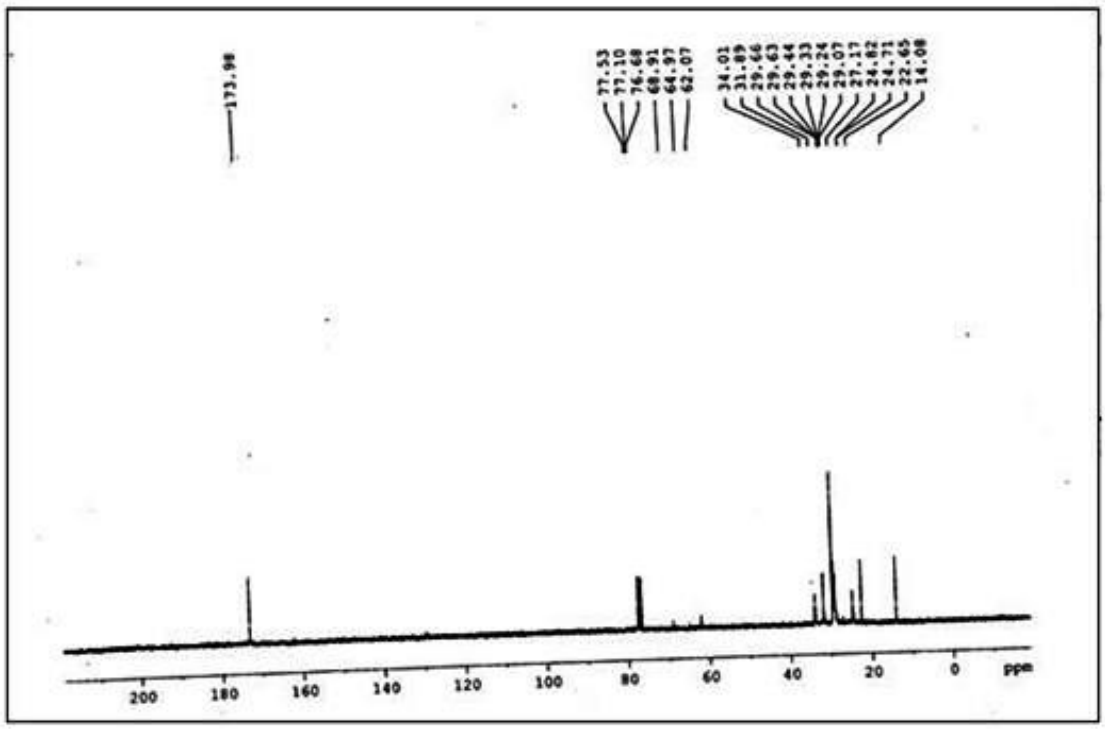


Figure 2.3.6: ^{13}C spectra of homo polymer of rapeseed oil

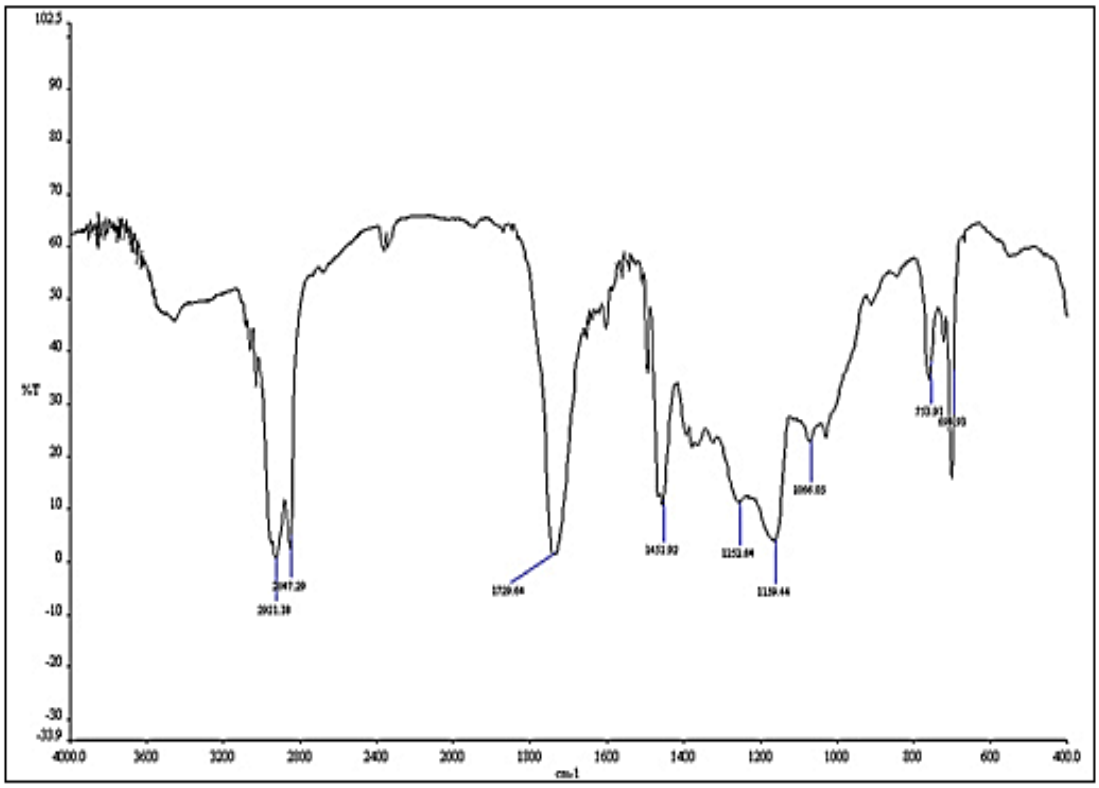


Figure 2.3.7: A representative FT-IR spectra of the copolymer after biodegradability test