

# **CHAPTER-III**

**Synthesis and performance evaluation  
of Vegetable oil polymer as a  
multifunctional lube oil additive**

### 3.2.1. Introduction

Engine oil is basically a combination of base oil and additives. Additives are chemical compounds necessary to provide performance beyond what base oils alone are able to offer. Base oils can be considered as a carrier for the additive. Many Different oil manufacturers can employ the same base stock for each formulation and can elect different additives for each specific request. Nearly all commercial motor oils contain additives, whether the oils are synthetic or petroleum based. Oil additives play a vital role for the proper lubrication and prolonged use of engine oil in modern internal combustion engines. Without many of these, the oil would become contaminated, break down, leak out, or not properly protect engine parts at all operating temperatures.

There are many additives are used as PPDs<sup>1, 2</sup> and VMs.<sup>3-5</sup> Most of the present day additives are synthetic acrylate<sup>6-8</sup> based, but because of potent toxicity<sup>9,10</sup> environment prevent them to become a noble additives.

Vegetable oil lubricants provide a renewable source of environmentally friendly<sup>11-16</sup> lubricants, relating to the lubricant's ability to biodegrade into harmless products. Now a days there has been an increased concern in enhancing the use of biodegradable plant oils in lubricants, mostly by environmental as well as health and safety issues, emerging due to changes in economic and supply factors.

India has a great potential of producing edible and non edible tree borne oils, which remain untapped and can be used as potential source for vegetable oil based lubricants with an objective of ecological compatibility in addition to technical performance. The ample availability and the relatively low cost make plant oils an industrially attractive raw material for the lubricant industry.

Concerning this background the present work is to synthesis of homopolymer of palm oil (PO) and copolymers of palm oil with decyl acrylate (DA) followed by characterization of them (by thermogravimetric, gel permeation chromatography [GPC], and spectral analysis) and evaluation of their biodegradability, shear stability, additive performance (as PPDs, VMs) in lubricating oil by standard ASTM methods.

### **3.2.2. Experiments**

#### **3.2.2.1. Materials**

Toluene, hydroquinone, and H<sub>2</sub>SO<sub>4</sub> were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (GC Purity 99%) and Decyl alcohol were purchased from Sisco Research Laboratories Pvt. Ltd. Hexane was obtained from S D Fine Chem. Ltd. Palm 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<sub>3</sub>-MeOH before use. Specifications of the chemicals are showed in **Table 3.6**. Two different base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata, India, and their physical properties are mentioned in **Table 3.7**.

#### **3.2.2.2. Preparation of palm oil polymer**

Homopolymer of Palm oil (PO, named as P-1) was synthesised by polymerisation reaction following the same procedure as mentioned in Chapter II of Part I, Page No. 28.

#### **3.2.2.3. Preparation of DA (Decyl acrylate) ester**

Decyl acrylate was prepared from acrylic acid and decyl alcohol by esterification reaction.<sup>7</sup> The purification of ester and polymerisation was carried out by following the method<sup>7</sup> reported earlier (Chapter-II of Part-1, Page No. 48).

#### **3.2.2.4. Preparation of copolymers**

The copolymer of Palm oil + DA was prepared by using different concentrations of DA (10%, 20%, and 30% [w/w]) with palm oil, P-2, P-3 and P-4 respectively. The polymerization was carried out following the method<sup>17</sup> as mentioned earlier (Chapter-II of Part-1 Page No. 48).

#### **3.2.3. Measurements**

##### **3.2.3.1. 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. Here CDCl<sub>3</sub> was used as solvent and tetramethylsilane (TMS) was used as reference material.

##### **3.2.3.2. Thermogravetric test**

The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of 10 K min<sup>-1</sup>.

##### **3.2.3.3. Molecular weight determination by GPC**

The number average and weight average molecular weights (M<sub>w</sub> and M<sub>n</sub>) and polydispersity 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.<sup>17</sup> The results are tabulated in **Table 3.8**.

##### **3.2.3.4. 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).

##### **3.2.3.5. 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.

#### **3.2.3.6. 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 calculation the viscosity index of each polymer solution was determined.

#### **3.2.3.7. Shear stability determination**

Shear stability was determined of various concentrated solution of homopolymer of palm oil and it's copolymer with DA and tests were conducted as per ASTM D-3945 method.

#### **3.2.3.8. 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 alternate*, *Colletotrichum gloeosporioides* and *Curvularia eragrostidis* following the method as reported earlier<sup>18</sup> taking homopolymer of decyl acrylate (HDA) as reference and (b) by the soil burial degradation test<sup>19</sup> of polymer sample films as per ISO 846:1997 as per the earlier literature report.<sup>18-20</sup>

### **3.2.4. Results and discussion**

#### **3.2.4.1. Spectroscopic data**

The IR absorption of the homopolymers of palm oil (PO) (**Figure 3.15**) in the region 1741.78  $\text{cm}^{-1}$  showed the presence of ester carbonyl groups. Peaks at 2921.18, 2852.21  $\text{cm}^{-1}$  for C–H stretching and 1456.83-1375.72  $\text{cm}^{-1}$  are due to C–O stretching vibration. The absorption bands at 975.11, 722.82  $\text{cm}^{-1}$  were due to the bending vibration of C–H bonds of  $-\text{CH}_3$  and  $-\text{CH}_2$

groups. The absence of peaks in the range of 1600-1700  $\text{cm}^{-1}$  for olefinic bonds indicates the formation of homopolymer. In its  $^1\text{H}$  NMR spectra (**Figure 3.16**) the polymer showed a broad singlet of  $-\text{OCH}_2$  protons ranging between 4.11 and 4.32 ppm along with the  $-\text{CH}_3$  protons ranging between 0.85 and 0.89 ppm together with  $-\text{CH}_2$  protons ranging between (1.25 and 1.62) ppm. Absence of  $\text{sp}^2$  hydrogen in its  $^1\text{H}$  NMR between 4.5 - 6 ppm proves the formation of polymer. In its  $^{13}\text{C}$  NMR spectra (**Figure 3.17**) peak at 173.98 ppm was due to the carbonyl carbon of ester and the absence of  $\text{sp}^2$  carbon peak in the range of 130-150 ppm proves the formation of polymer.

FT-IR spectra of palm oil + DA (**Figure 3.18**) exhibited broad absorption at 1744.03  $\text{cm}^{-1}$  due to ester CO stretching vibration along with other peaks at 1456.2, 1275.72  $\text{cm}^{-1}$  (C-O stretching vibration). Peak at 984.94, 810.09, 722.34  $\text{cm}^{-1}$  was appeared due to C-H bending along with other peaks at 2925.64  $\text{cm}^{-1}$  for stretching vibration of C-H bond. In its  $^1\text{H}$  NMR spectra (**Figure 3.19**) the polymer showed a broad singlet of  $-\text{OCH}_2$  protons ranging between 4.09 and 4.28 ppm along with the  $-\text{CH}_3$  protons ranging between 0.86 and 0.90 ppm together with  $-\text{CH}_2$  protons ranging between (1.23 and 1.60) ppm. The formation of the copolymer was further supported by the absence of  $\text{sp}^2$  hydrogen in its  $^1\text{H}$  and  $\text{sp}^2$  carbon in  $^{13}\text{C}$  NMR spectrum (**Figure 20**), respectively.

#### 3.2.4.2. Thermogravimetric analysis

Plot of TGA data in Figure 3.21 presents a comparison between the thermal stability of homopolymer of palm oil and its copolymers with DA. The analysis discloses that copolymers are more stable than that of homopolymer and thermal stability increases with increasing concentration of DA in the feed which are in concordance with their molecular weight data (**Table 3.8**).

### **3.2.4.3. 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 3.9**, 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 copolymer than that of homopolymer.

### **3.2.4.4. Photomicrographic analysis**

The photo micrographs of lube oil (BO2) with and without different additives are shown in **Figure 3.22(a–e)**. **Figure 3.22a**, 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 3.22(b–e)**] 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.

### **3.2.4.5. Performance evaluation of the prepared polymers as VMs**

The VI values in two base oils (measured in five different concentrations) tabulated in **Table 3.9** indicates that in both the base oils the values for homopolymer are lower than that of copolymer and the VI value increases with increasing DA 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 for both homopolymer and copolymer. The reason may be that although the viscosity of the lube oil gets decreased at higher temperature, the polymer molecules may effectively compensated 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 provide a higher VI compared to a low concentrated polymer solution.

#### **3.2.4.6. Shear stability analysis**

Kinematic viscosity (KV) data (**Table 3.10**) and PSSI and PVL values (**Table 3.11**) indicate less shear stability of copolymer than homopolymer. It also denotes increase of PSSI values with increase in concentration of all above mentioned polymers in base oil which signify the gradual loss in shear stability. The prediction is the direct reflection of the molecular weight values of the polymers as shown in **Table 3.8**. Higher molecular weight of the polymer results in greater hydrodynamic volume and thus susceptible to break down under shear.

#### **3.2.4.7. Analysis of biodegradability test results**

Biodegradability test results (**Table 3.12**) with both set of copolymers showed significant biodegradability against the fungal pathogens, *Colletotrichum camelliae* and *Alternaria alternata*, the result is better for the palm oil + DDA copolymer. Soil burial test results also indicated similar extent of biodegradability. Change in molecular weight also supported the biodegradable nature of the polymers (**Table 3.8**). It was further confirmed by the shift of IR frequency of the ester carbonyl after the test is over (**Figure 3.23 and 3.24**). HDA does not show any weight loss under identical experimental conditions and thus confirmed its non-biodegradable nature.

#### **3.2.5. Conclusions**

1. The palm oil + DA copolymers are thermally more stable than homopolymer of palm oil. Again thermal stability increases with increasing concentration of DA in the copolymers. But, shear stability of homopolymer of palm oil is more than that of its DA copolymer and shear stability decreases with increasing concentration of DA in the copolymers.

2. Performance evaluation of the additives indicates that the palm oil + DA copolymer act as better PPD and viscosity modifiers compared to the palm oil homopolymer.
3. Study also reveals that although the homopolymer of palm oil is considerably biodegradable but it gains poor thermal stability and average performance as a PPD and VM. On the other hand copolymer of palm oil with DA 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.

### **3.2.6. References**

References are given in Bibliography under Chapter-III of Part-III (Page No.208-210).

**Table 3.6. 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 <sub>2</sub> SO <sub>4</sub>	Merck Specialities Pvt. Ltd.	-
Acrylic acid	SRL Pvt. Ltd.	0.990
Decanol	S. D. Fine-Chem Ltd.	0.980
Hexane	S. D. Fine-Chem Ltd.	0.995
Methanol	Thomas Baker Pvt. Ltd.	0.980
Benzoyl peroxide	LOBA chemicals	0.980
Palm oil	Local Market	-

**Table 3.7. Base oil properties.**

Properties	Base oils	
	BO1	BO2
Density at 313 K, Kg.m <sup>-3</sup>	839.98	940.03
Viscosity at 313 K, in cst	6.808	22.953
Viscosity at 373 K, in cst	1.792	3.927
Cloud point, °C	-5	-8
Pour point, °C	-3	-6
Viscosity index	80	85

**Table 3.8. The weight average and number average molecular weights (M<sub>w</sub> and M<sub>n</sub>) and polydispersity of the polymers before and after biodegradability test.**

Polymer samples	Before biodegradability test			After biodegradability test		
	M <sub>n</sub>	M <sub>w</sub>	PDI	M <sub>n</sub>	M <sub>w</sub>	PDI
P-1(10:0)	10352	14547	1.40	8321	12536	1.50
P-2(9:1)	17503	24323	1.38	14865	21895	1.47
P-3(8:2)	22953	30523	1.32	18712	28247	1.50

P-4(7:3) 34362 42264 1.22 30231 39135 1.29

P-1 (homopolymer of PO), P-2 to P-4 (PO: DA) w/w,  $M_n$  = number average molecular weight;  $M_w$  = weight average molecular weight; PDI = poly dispersity index.

**Table 3.9. Pour point (in °C) and VI values of polymers in different concentration.**

Property/base oil/(PP/VI)	Conc., %	Sample			
		P-1	P-2	P-3	P-4
PP/BO1(-3)	1	-3	-6	-9	-12
	2	-6	-9	-12	-15
	3	-9	-12	-12	-15
PP/BO2/(-6)	1	-6	-9	-12	-12
	2	-9	-12	-15	-18
	3	-12	-12	-18	-18
VI/BO1(80)	1	87	92	95	99
	2	92	96	101	105
	3	97	101	110	115
	4	101	105	118	122
	5	106	110	121	129
VI/BO2(85)	1	93	96	100	102
	2	99	105	108	113
	3	106	109	115	120
	4	110	115	124	127
	5	114	120	131	138

BO = base oil; PP = pour point; VI = viscosity index.

**Table 3.10. Kinematic Viscosity Values of the Additives Doped in Base Oil**

Conc. (%)	KV (at 373K)								
	Base oil	before shear				after shear			
		P-1	P-2	P-3	P-4	P-1	P-2	P-3	P-4
0%	BO1	1.79	1.79	1.79	1.79	1.79	1.79	1.79	1.79
	BO2	3.92	3.92	3.92	3.92	3.92	3.92	3.92	3.92
1%	BO1	2.00	2.05	2.08	2.10	1.97	2.01	2.03	2.04
	BO2	4.07	4.11	4.17	4.21	4.05	4.08	4.13	4.15
2%	BO1	2.05	2.09	2.13	2.16	2.01	2.04	2.06	2.08
	BO2	4.15	4.25	4.31	4.41	4.11	4.19	4.23	4.30
3%	BO1	2.10	2.13	2.21	2.27	2.04	2.06	2.11	2.15
	BO2	4.27	4.33	4.46	4.57	4.20	4.25	4.33	4.41
4%	BO1	2.15	2.17	2.29	2.34	2.07	2.08	2.16	2.17
	BO2	4.35	4.46	4.68	4.76	4.26	4.33	4.48	4.51
5%	BO1	2.21	2.21	2.33	2.39	2.11	2.11	2.17	2.20
	BO2	4.45	4.57	4.88	5.12	4.33	4.42	4.60	4.75

**Table 3.11. PVL and PSSI Values of the Additives Doped in Base Oil**

Conc. (%)	PVL					PSSI			
	Base oil	P-1	P-2	P-3	P-4	P-1	P-2	P-3	P-4
1%	BO1	1.44	1.99	2.29	2.8	13.7	15.6	16.2	18.7
	BO2	0.49	0.6	0.95	1.2	13.4	15.1	16.3	18.5
2%	BO1	1.94	2.34	3.19	4.01	15.2	16.3	20.1	23.0
	BO2	0.81	1.26	1.82	2.53	15.1	16.5	20.2	23.0
3%	BO1	2.17	3.19	4.56	5.23	18.6	20.0	24.1	24.7
	BO2	1.52	1.91	2.93	3.47	18.8	20.3	24.4	24.4
4%	BO1	3.7	4.05	5.49	6.99	21.8	23.2	25.0	29.7
	BO2	2.11	2.77	4.14	5.16	21.4	23.1	25.6	29.3
5%	BO1	4.2	4.64	6.88	7.97	22.1	24.1	29.5	31.6
	BO2	2.62	3.38	5.85	7.31	22.1	23.9	29.7	31.2

**Table 3.12. 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-1	0.38	0	0.57	0	0	0.37
P-2	0.35	0	0.49	0	0	0.31
P-3	0.26	0	0.46	0	0	0.25
P-4	0.24	0	0.39	0	0	0.22
HDA	0	0	0	0	0	0

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

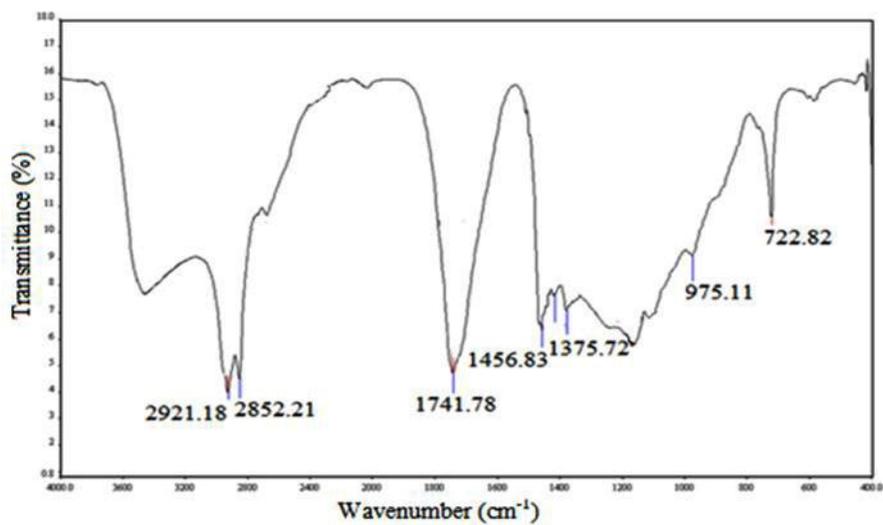


Figure 3.15. FT-IR spectra of Palm oil polymer

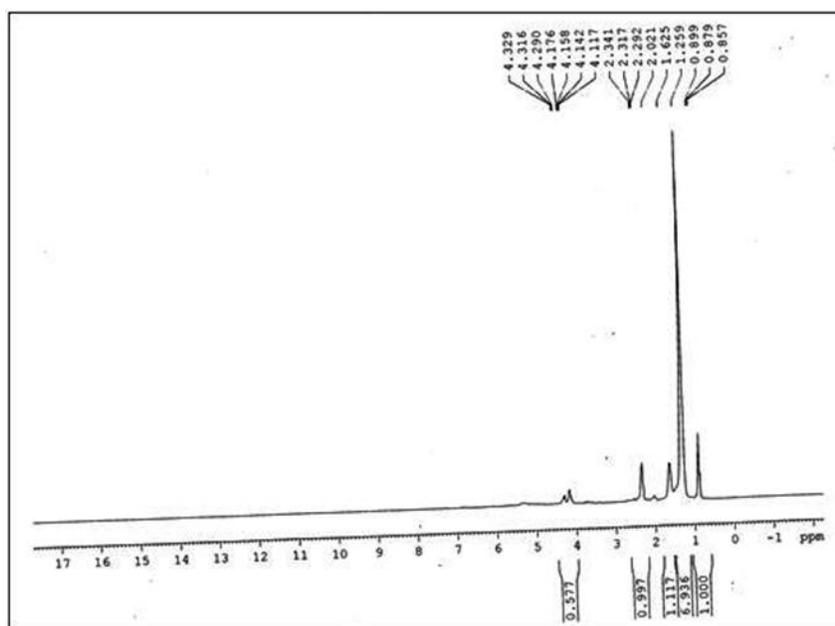


Figure 3.16. <sup>1</sup>H- NMR spectra of palm oil polymer

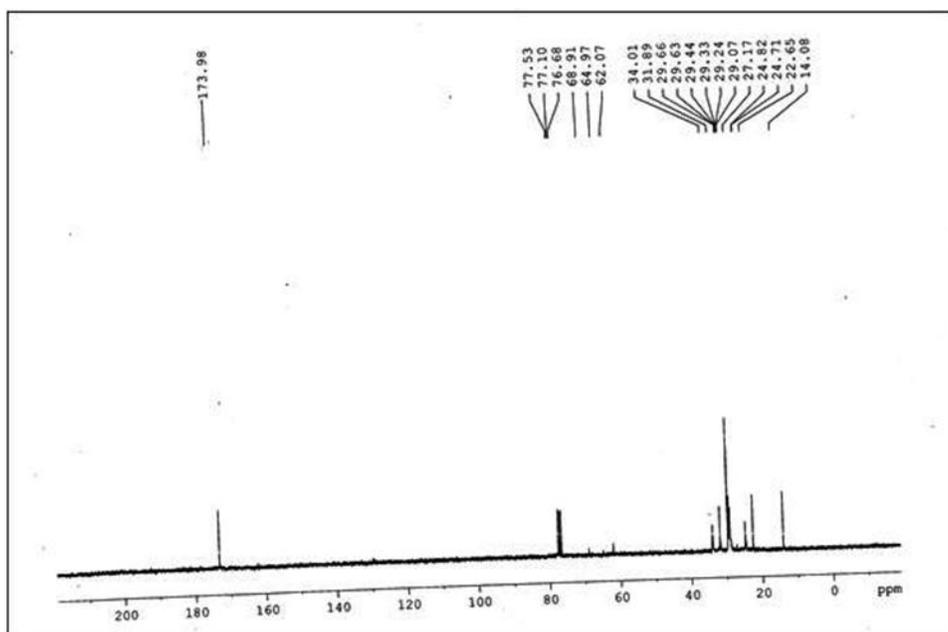


Figure 3.17.  $^{13}\text{C}$ - NMR spectra of palm oil polymer

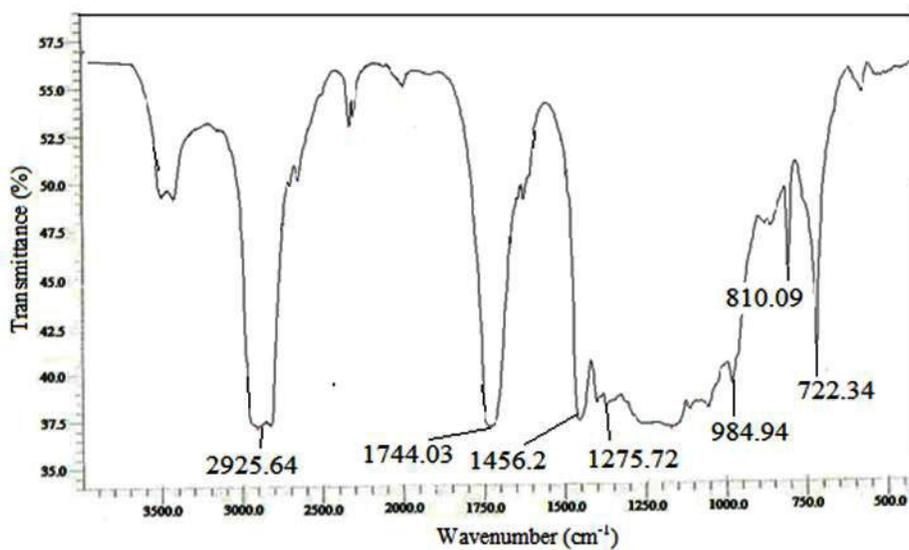


Figure 3.18. FT-IR spectra of Palm oil + DA copolymer (P-3)

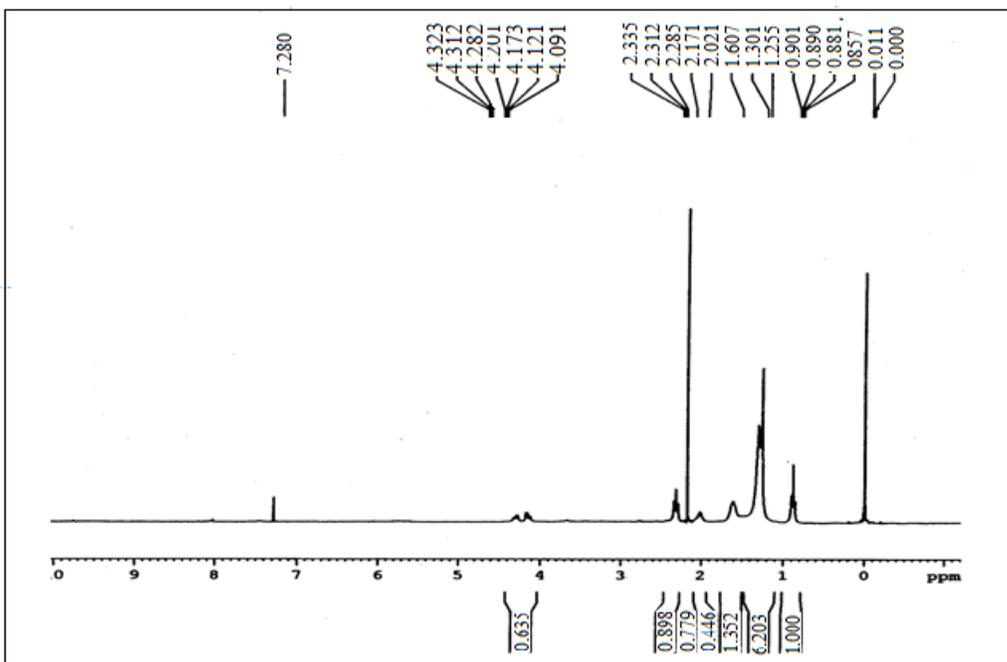


Figure 3.19. <sup>1</sup>H NMR spectra of Palm oil + DA copolymer (P-3)

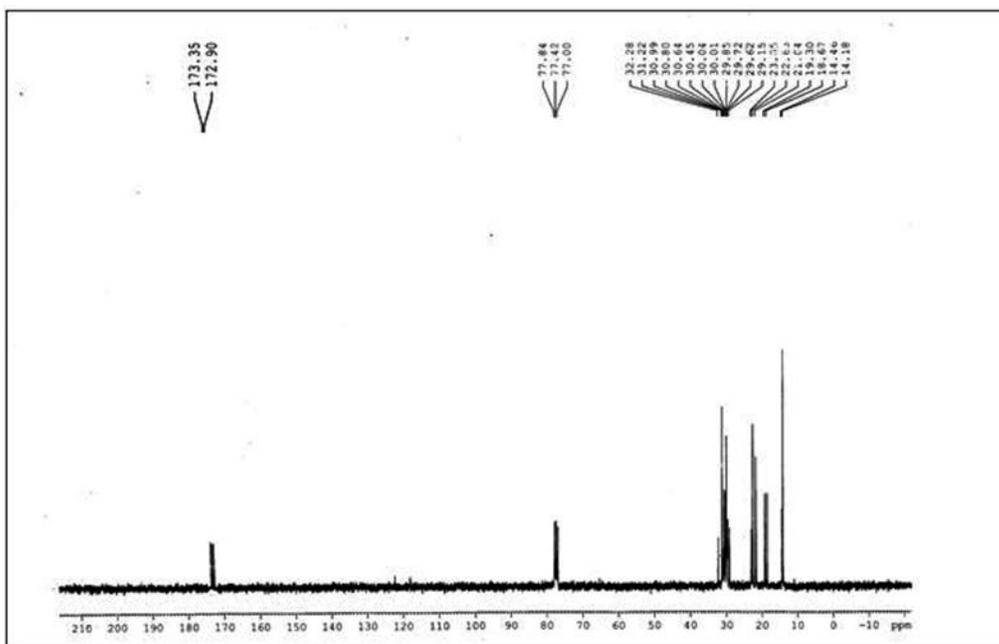
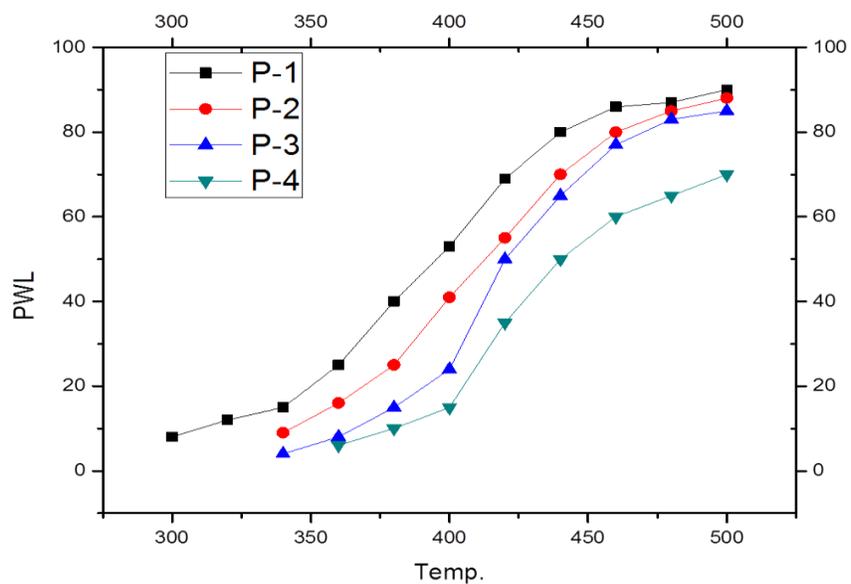


Figure 3.20. <sup>13</sup>C- NMR spectra of Palm oil + DA copolymer (P-3)



**Figure 3.21. Plot of PWL (Percent Weight Loss) vs Temperature (in K)**



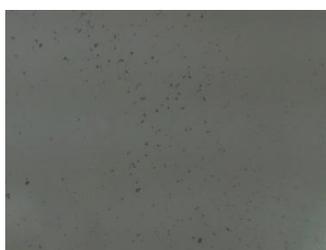
2(a)  
Base oil (BO2)



2(b)  
P-1 (3%)



2(c)  
P-2 (3%)



2(d)  
P-3 (3%)



2(e)  
P-4 (3%)

**Figure 3.22(a-e). Plot of Photomicrographic images of base oil and additive (P-1, P-2, P-3, P-4) doped base oil**

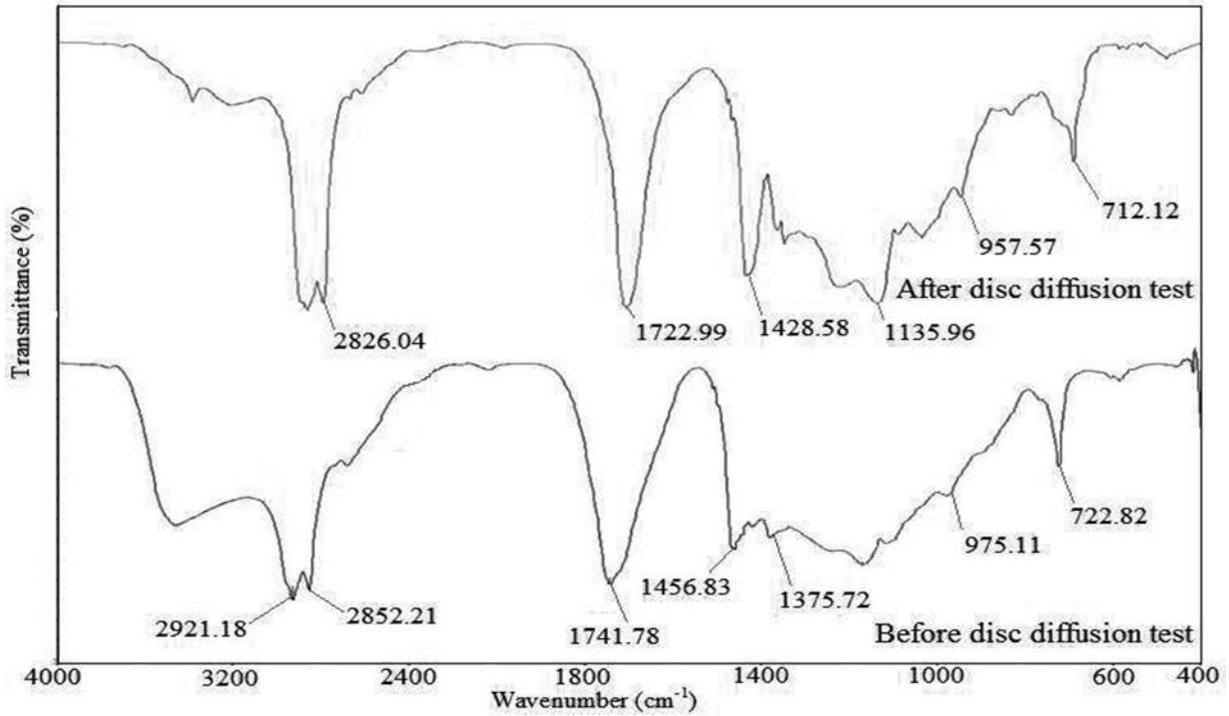


Figure 3.23. Comparative FT-IR spectra of Palm oil homopolymer (P-1) before and after disc diffusion test

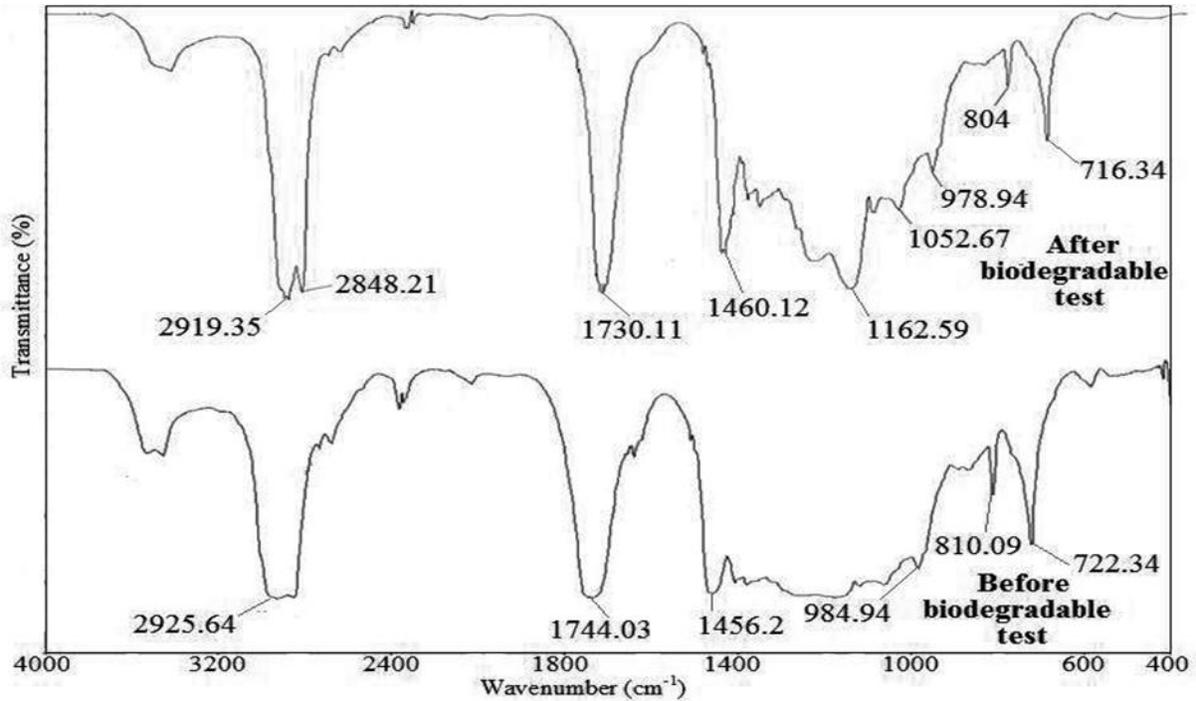


Figure 3.24. Comparative FT-IR spectra of Palm oil+DA copolymer (P-3) before and after disc diffusion test