



## Greener additives for lube oil: Synthesis and evaluation of rice bran oil based copolymers as potential lube oil additives

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During the last few years, the lubricant industry has given special attention towards the application of vegetable oil based additives for lube oil due to their biocompatibility and enhanced additive performances compared to conventional additives. In this article, the author reported the preparation of homopolymer of rice bran oil (RBO) and copolymers with decylacrylate and alpha pinene at different percentage ratios in the presence of azobisisobutyronitrile (AIBN) as initiator. Characterization of the polymers was recorded by spectral technique (FT-IR and NMR spectroscopy). Gel permeation chromatography method (GPC) was used to determine the average molecular weight of the prepared polymers. Thermo gravimetric analysis (TGA) method was used to study the thermal stability of the prepared polymers at high temperature. Standard ASTM methods was 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). Biodegradability of all the polymers was tested by disc diffusion method and soil burial method.

Keywords: Homopolymer, copolymer, viscosity index, pour point, biodegradability.

### Introduction

Lubricating oil additives are the substances which when added to the oil, they can improve the properties already present or add some new properties<sup>1</sup>. The most important properties of lubricants are viscosity index improver (VII) pour point depressant (PPD), antiwear, extreme pressure, antioxidant, dispersant etc. Lube oil additives synthesized from vegetable oils are more environmentally benign due to their biodegradable property and low-toxicity<sup>2</sup>. Moreover, they exhibit high viscosity index (VI), low pour point and good antiwear property. Therefore, more focus has been laid on the research of lube oil additives from vegetable oils.

Rice bran oil contains high percentage of unsaturated triglycerides and can be used as monomer in the free radical polymerization<sup>3</sup>.

There are many research papers based on rice bran oil in the field of food<sup>4</sup>, pharmaceutical<sup>5</sup>, cosmetics<sup>6</sup>, industries etc. However, reports regarding the application of acrylate

and alpha pinene copolymers of rice bran oil as multifunctional additive for lubricant are very scanty.

In the present work, we have prepared the homopolymer of rice bran oil and different copolymers with decyl acrylate and alpha pinene to achieve potential greener lubricant additives. The performance of the additives in two types of base oil were evaluated as viscosity index improver (VII) and pour point depressant (PPD) according to respective standard ASTM methods.

### Experimental

*Synthesis of the polymers:* The homo polymer of RBO was synthesized by free radical polymerization method taking the monomers of RBO in presence of AIBN initiator. The polymerization was carried out in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. The monomer was heated to 90°C in presence of toluene as solvent.

Initiator AIBN (0.5% w/w, with respect to the total monomer) was then added and continuously heated for 5 h keeping the temperature constant at 90°C. After the completion of reaction, the product was poured into methanol with continuous stirring, filtered off and dried. The three copolymers of RBO with decyl acrylate (DA) and another three copolymers of RBO with alpha pinene at different percentage ratio were also prepared in the similar procedure.

**Spectroscopic measurements:** Bruker Avance 300 MHz FT-NMR spectrometer was used to record the NMR spectra by using CDCl<sub>3</sub> as solvent. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range of 400 to 4000 cm<sup>-1</sup>.

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

**Thermo gravimetric analysis (TGA):** TGA data was recorded on Shimadzu TGA-50 system, at a heating rate of 10°C/min.

### Performance evaluation

**Evaluation of viscosity index:** Viscosity index (VI) is an important parameter which determines the change of viscosity of the lubricant at high temperature. Higher value of VI indicates the small change in viscosity at high temperature. It was calculated according to ASTM D 2270-10. 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 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:** Biodegradability test was carried out by two methods – (i) Disc diffusion (DD) method and (ii) Soil burial test (SBT) method.

**Disc diffusion method:** The biodegradability test was car-

ried out for the prepared polymers against *Calletotricheme camellia* (CC), *Fussarium equisetiae* (FE), *Alternaria alternata* (AA), *Colletrichum gleosproides* (CG) and *Curvularia eragrostidies* (CE) pathogens. A suitable amount of potato extract, dextrose and agar powder were mixed to prepare culture media strain. All the experiments were completed in petridishes and were kept incubator at 37°C for 90 days after addition of about 1 g of the polymer sample. The fungal growth was confirmed by a change of yellow to blackish colour. After 90 days, the polymer samples were recovered from the fungal media by chloroform, purified and dried. The dried samples were weighed.

**SBT method:** 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 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 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.

### Results and discussion

**Spectroscopic analysis:** The homopolymer of RBO (P-0) showed IR absorption band for the ester carbonyl group at 1732.5 cm<sup>-1</sup>. The peaks at 2852.4 cm<sup>-1</sup> and 2924.2 cm<sup>-1</sup> are the stretching vibration of CH<sub>3</sub>-CH<sub>2</sub>- group. In the <sup>1</sup>H NMR spectra of homopolymer, the peaks in the range of 4.02–4.22 ppm indicate the protons of -COOCH<sub>2</sub> group. In the <sup>13</sup>C NMR spectra of homopolymer, the peaks in the range of 170.95–176.41 ppm indicate the carbons of ester carbonyl group. The carbons of -OCH<sub>2</sub> group appear in the range 64.10–68.86 ppm. The IR spectra of three copolymers (P-1 to P-3) are almost similar. The absorption band at 1734.08 cm<sup>-1</sup> is due to ester carbonyl group. In the <sup>1</sup>H NMR spectra, peaks at 3.607–3.656 ppm indicate the protons of -OCH<sub>2</sub> of decyl acrylate moiety. The peaks in the range of 3.988–4.156 ppm indicate the protons of -COOCH<sub>2</sub> group of RBO. No peaks in the range of 5–6 ppm indicate that polymerization was carried out successfully. In the <sup>13</sup>C NMR spectra, peaks ranging from 168.31–172.63 ppm confirm the presence of

carbons of ester groups. There is no any peak in the range of 120–150 ppm and it indicates that polymerization was carried out successfully. The IR spectra of three copolymers (P-4 to P-6) are almost similar. The absorption band at 1736.02  $\text{cm}^{-1}$  is due to ester carbonyl group of RBO moiety. The absence of any peak in the range of 4–6 ppm in  $^1\text{H}$  NMR and 120–150 ppm in  $^{13}\text{C}$  NMR spectrum indicated the formation of copolymer of RBO with  $\alpha$ -pinene.

**Molecular weight data analysis:** The experimental value of 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 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.

**Table 1.** The weight average and number average molecular weights ( $M_w$  and  $M_n$ ) and polydispersity index 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: 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.

**Analysis of TGA data:** From the experimental TGA values of the seven polymers, it was observed that homopolymer of RBO (P-0) is thermally less stable than the prepared copolymers. This indicates that when DA or  $\alpha$ -pinene moiety is introduced in the backbone of RBO oil, the thermal stability increases. Two major decompositions have been observed at 160°C and 330°C with 23% and 85% weight

loss respectively in 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 homo polymer of RBO (P-0).

**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. 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 temperature, expansion of additive molecules takes place and as a result, the size of micelle increases. This increased in micelle size prevent the reduction of the viscosity of the lubricant composition. It is also observed that with increasing concentration of the lubricant composition, the VI values increases. It may be due to increase of total volume of polymer micelle and hence improves the VI property<sup>2</sup>. It was found that VI value increases by incorporation of DA and  $\alpha$ -pinene moiety in the backbone of homopolymer of RBO. This may be due to higher molecular weight and higher crosslink density of the copolymers<sup>7</sup>. 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.

**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 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<sup>8,9</sup>. Among the seven polymers, P-3 showed best performance as PPD than the others in both types of base oil.

**Analysis of biodegradability test results:** Biodegradability test results obtained by using the disk diffusion and soil burial test method are presented in Table 3. All the polymers showed

**Table 2.** Pour point (°C) and VI values of lubricant 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
	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.

significant biodegradability against the pathogens *Calleotricheme camellia* and *Alterneria alternata* only. The mass loss after biodegradation of the prepared polymers was further confirmed by shifting of IR frequency of the ester carbonyl along with other shifted peaks and determining the GPC molecular weight after biodegradation shown in Table

**Table 3.** Results of biodegradability test by the disc diffusion method and soil burial test method

Sample	Weight loss in disc diffusion method (in g)					Weight loss in soil burial test (in 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	0.35	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 = *Calleotricheme camellia*; FE = *Fussarium equisetae*; AA = *Alterneria alternata*; CG = *Colletrichum gleosporoides*; CE = *Curvularia eragrostidies*.

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.

### 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. 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  $\alpha$ -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.

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